Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 45
ISSUE 2
April
2011

The preparation of aramid fibres in silicone based composite materials

L.A. Dobrzański [a], A.J. Nowak [a,*], A. Pusz [b], M. Górniak [a]
[a] Division of Materials Processing Technology, Management and Computer Techniquesin Materials Science, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
[b] Division of Metal and Polymer Materials Processing, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
* Corresponding author: E-mail address: agnieszka.j.nowak@polsl.pl

Received 26.02.2011; published in revised form 01.04.2011

Materials

ABSTRACT

Purpose: The evaluation of modified aramid fibres – Kevlar – as reinforcement in silicon materials used in medicine.
Design/methodology/approach: Samples of laminated material based on modified aramid fibres and medical silicone were made by a method of manual formation of laminates that is impregnation of reinforcement with matrix to hardening silicone process using hardening methods connected with heat. Created material was observed on Scanning Electron Microscopy manufactured by Zeiss.
Findings: The results show that the modification of aramid fibres has a positive influence on adhesion of silicon material to aramid fibres and strengthening of tested samples.
Research limitations/implications: Carried out investigations show that the problem with modification of aramid fibres is very important in having proper percentage of intensifier in developed material used for medical purposes.
Originality/value: Taking the specific properties of material into account it seems that modification of aramid fibres would be useful in medicine. However, application of aramid fibres as reinforcing phase of polymer medical materials requires many additional investigations which are already planned and will soon be done in Institute of Engineering Materials and Biomaterials at Silesian University of Technology.
Keywords: Composites; Engineering polymers; Aramid fibres; Silicone; Biomaterials

Reference to this paper should be given in the following way:
L.A. Dobrzański, A.J. Nowak, A. Pusz, M. Górniak, The preparation of aramid fibres in silicone based composite materials, Journal of Achievements in Materials and Manufacturing Engineering 45/2 (2011) 125-131.

1. Introduction

Composite materials are the most promising and developing group of engineering materials. They are widely applied in scientific and research works. Nowadays, properties of basic groups of engineering materials in many cases are too limited to meet the technology, industry and medicine needs. The realization of technological objectives defined by present-day engineers is impossible without parallel development of advanced materials like composite materials colloquially referred as composites. Those materials potentially could be widely applied in medicine where the big stress is put on modern engineering materials with specific properties which are possible to make only by connecting various components [1-4, 10, 13-16, 19-24].

Silicones and fibres are playing an important role among wide range of polymers applied in medicine. Silicone materials were worked out as a result of researches of plastic that satisfy much more higher and specific requirements which were not fulfil by well-known and widely used materials by the time. Developed medical silicones, contrary to technical ones, are produced from substrate of very special chemical grade. It guarantees the lack of substances that can undergo biochemical reactions, which lead to inflammatory condition, irritations, allergy or cell mutation. For this reason medical silicones are applied for implants and silicone scar sheets. There are only a very few substances with such a high compatibility as medical silicones. That fact makes them very attractive material. Unfortunately, silicones are characterized by pour mechanical properties. Attempts of their modification are extremely important. One of the experimental method of reinforcement is introducing the phase in the form of rigid and strength continuous synthetic fibres. In practice, there are important such factors as: volume percentage of introduced fibres, their adhesion to the matrix, as well as biocompatibility of resulting composite material. The most modern high-resistant plastic fibres are aramid fibres. Those fibres were produced for the first time in 1972 by DuPont. They are made by condensation reaction in solution of terephtalic acid chloride and para-phenylenediamine (PPD). Fibres, produced by this method, are characterized by high degree of order, it means, the presence of rigid chain of particles that are parallel to the roll axis of the fibre devoid of tangling. Strength parameters for those fibres are high and are as follows: for axial tension of the order of 3300 MPa, stiffness E= 1.25 · 105 MPa and the density equal to 1.44 is quite low. Aramid fibres are practically neutral for surface defects and are stable up to 300°C. For these reasons, application of aramid fibres in modern engineering is very frequent and common; nevertheless, they are not so often and commonly applied in medicine materials. Despite of its very good mechanical properties, low density and low elongation, they are rarely used in medical branch, unlike the polyethylene, glass or carbon fibres, which are characterised by worse properties. However, last scientific reports with optimistic results of investigations of aramid fibres biocompatibility and their subsequent prognoses positively influence on increase in interest of applying them in widely understood medicine [4-9, 11-12, 17-22].

On the basis of carried out own investigations, there were noticed the delimitation of fibrous composite materials based on silicone and aramid fibres during mechanical tests. Therefore, authors decided to do further researches allowing for the preparation of aramid fibres which improves its adhesion to silicone matrix. For this purpose there were chosen several adhesion promoters, and only two of them were used for preliminary investigations: P3 and FW as well as ultrasounds. Limitation of group of adhesion promoters that are tested is caused by high price of matrix material – medical silicone. At the beginning, researches were realized using inexpensive silicone alternative not applied in medicine.

2. Material

Investigations were conducted on aramid fibre – Kevlar from DuPont (USA). The material for examinations was delivered in the form of fabric with basis weight equal to 61 g/m^2 manufactured by Havel Company PL SP Z O.O. and one by one selected fibres (Table 1. and Fig. 1.) were used. As adhesion promoters FW and P3 were used Substances for fibres modification available in the market. Upon performance of preliminary studies following preparations have been selected: FW and P3. In order to determine active substances in mentioned preparations, the analyses with the aim of superconducting high-resolution nuclear magnetic resonance spectrometer (NMR) have been done. 1H NMR spectra were recorded at 300 MHz (Varian Unity Inova plus) in solution of deuterated chloroform ($CDCl_3$) for FW and deuterated methanol (CD_3OD) for P3. (Fig. 2 and Fig. 3).

NMR spectrum of FW: in obtained spectrum (Fig. 2) the peak at δ=4.9 ppm corresponding to water and two intensive peaks at δ=0.09 and δ=0.19 ppm with less intensive peak at δ=0.12 ppm corresponding to methyl groups in methyl oxasilane system are dominant. Moreover, spectrum shows very little intensive (altogether below 2% of total intensity of the spectrum), broaden signals at δ=1.6, δ=2.1 and δ=4.0 ppm corresponding to polymeric stabilizing agent of emulsion (emulsifier with surfactant properties). Taking into consideration only peaks coming from water and methyl oxasilane groups, estimated composition of emulsion is 74% of water and 26% w/w of silicone. As regards three different peaks of methyl groups: the share of linear form of poly(methyl oxasilane) is 57% (peak at δ=0.09), less intensive peak (7%, δ=0.12) probably corresponds to the end groups, whereas peak at δ=0.19 ppm (share 36%) is connected with other form of oxasilane, may be cyclic ones.

NMR spectrum of P3: the spectrum presented in the Figure 3 shows very intensive peak of methyl oxosilane at at δ=0.04 ppm and accompanying much less intensive peak (about 2% in relation to the main one) at δ=0.13 ppm. Additionally, in the range from δ=5.33 to δ=6.10 ppm, there is seen a number of multiplets with little intensity. Its shift and shape suggests the presence of vinyl group (CH_2=CH-). From intensity of vinyl protons to methyl oxosilane ones peaks ratio follows, that silicone is functionalized with vinyl groups capable of polymerization in ratio one vinyl group per thirty three dimethyloxosilane ones, what corresponds to 1.1 % weight content of vinyl groups in silicone.

Table 1.
Technical information about aramid fabric manufactured by Havel Composites PL. SP. Z O.O

KIND OF FABRICS	TECHNICAL INFORMATION					
	Basic weight [g/m^2]	Thickness fabric [mm]	Matrix	Plot	Mass density fabric [g/m^3]	Mass density linear [Tex]
FABRIC 61	61	0.12	Aramid 49 T 965 21,5	Aramid 49 T 965 21,5	1.45	22
Type of plait for all kind of fabrics: linen						

a) b)

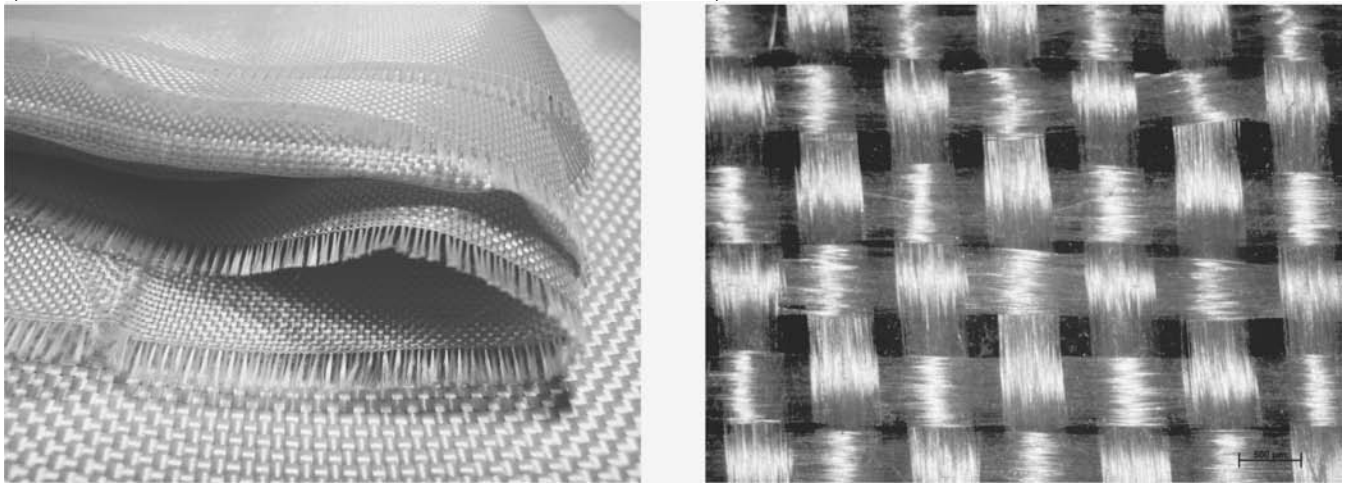

Fig. 1. Aramid fabric with basic weight 61 g/m^2; a) FUJI 6500 Digital Camera; b) figure was observed on the light microscope MEF4A type Leica with a magnification 25x

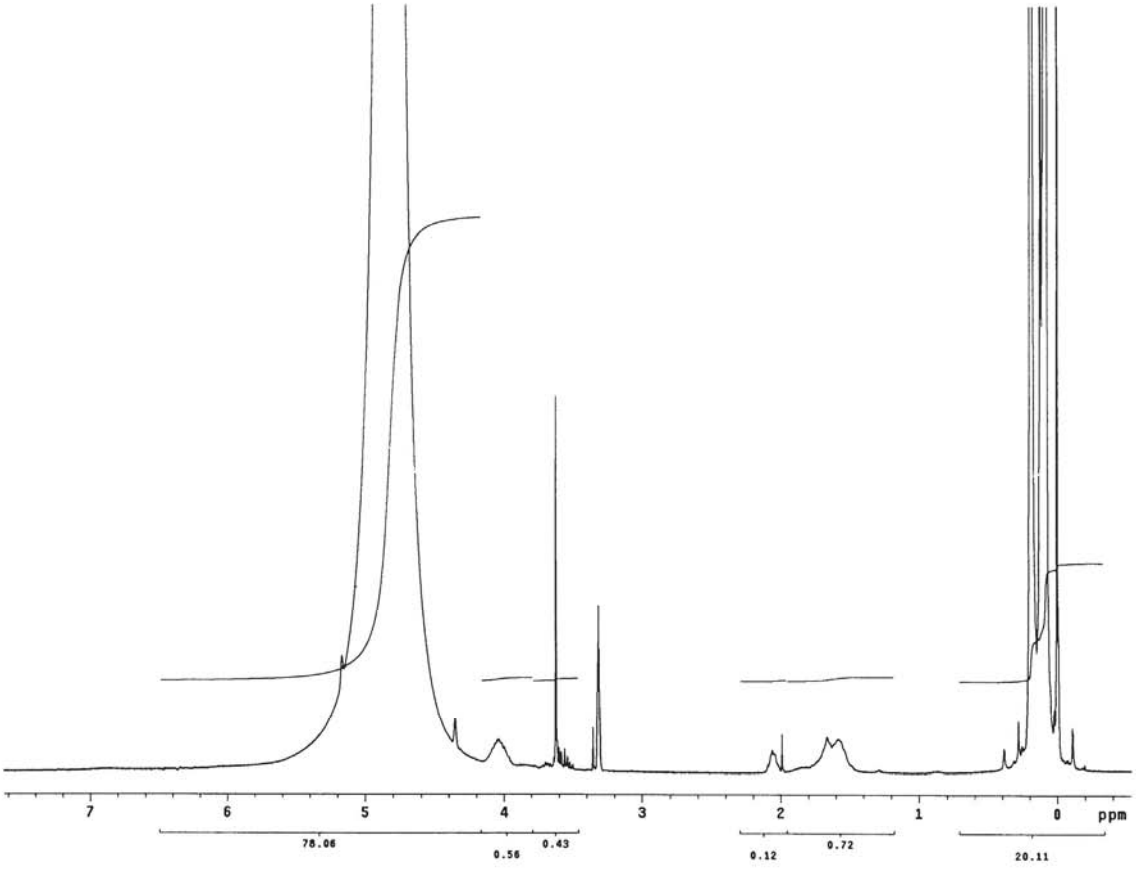

Fig. 2. NMR spectrum of FW made on UNITY/*INOVA* 300 MHz (Varian)

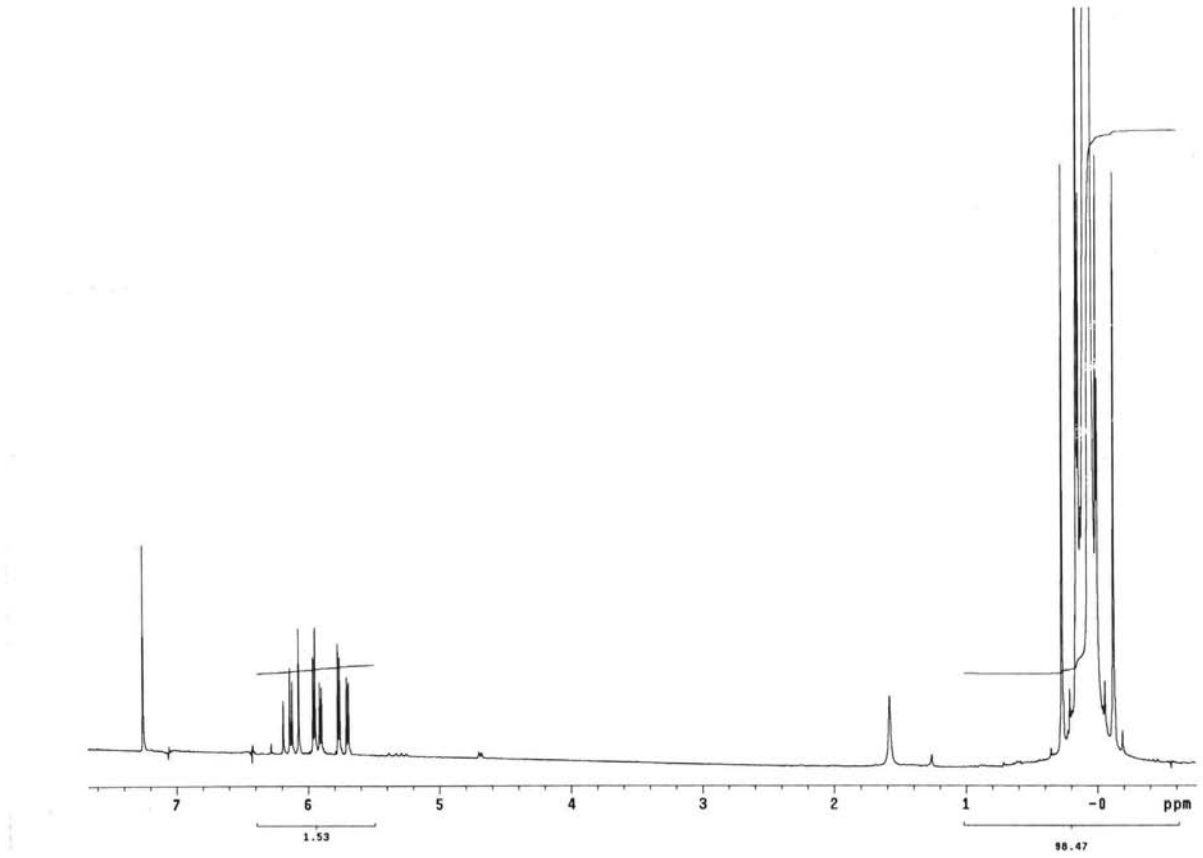

Fig. 3. NMR spectrum of P3 made on UNITY/*INOVA* 300 MHz (Varian)

3. Laminate forming

In order to aramid fibres preparation, fragments of fabric of size 10×100 mm have been cut out. Prepared pieces of fabric have been divided on five groups in ten pieces of each type. First group have not been subjected to any kind of preparation before medical silicone saturation, next two groups have been subjected to ultrasounds in distilled water in 20°C for 1.5 h and 3 h respectively. This process was conducted in ultrasound generator. Then, fragments of aramid fabric were carefully dried and prepared for key part of medical silicone saturation. Last two groups of fabrics were properly prepared and were coated with selected adhesion promoters, one for each group.

All prepared fragments were placed in previously chosen package of forms and subsequently saturated with medical silicone and placed in laboratory drier KC 100/200 in temperature of 70°C for 14 days. After the samples were cross-linked, they were put out from the forms and carefully measured.

4. Research

In the investigations, silicone samples based on medical silicone reinforced with aramid fabric were used. Dimensions of the aramid fabric pieces were as follows: 10 mm in width, 100 mm in length and 0.3 mm in thickness. Preparation of aramide fabric consisted in subjection of aramid fabric to ultrasounds or coating with adhesion promoters. Width, length and thickness of obtained cast profile were equal to 5 mm. Manufactured samples, 10 for each investigated groups, had been placed in distilled water in room temperature until strength tests were done. Directly prior to strength tests, dimensions of the samples were checked with the use of electrical slide caliper. Cast profiles without reinforcement were control samples group. Strength tests were carried out at room temperature on the testing machine ZWIC/ROELL (Fig. 4). The speed of holder displacement were 20 mm/min (during bending), spacing of samples 60 mm and preload 0.1 MPa. Finally, 50 tests of three point bending were done and obtained results were analyzed statistically. To determine the effectiveness of carried out preparative treatments of aramid fibres surface, observations on scanning electron microscope by ZEISS were done. The samples of aramide fibres not subjected to any kind of preparation as well as samples coated with adhesion promoters before and after saturation with silicone were observed.

5. Results

On the pictures taken from Scanning Electron Microscope Zeiss, clean unmodified aramid fibres, characterized with smooth,

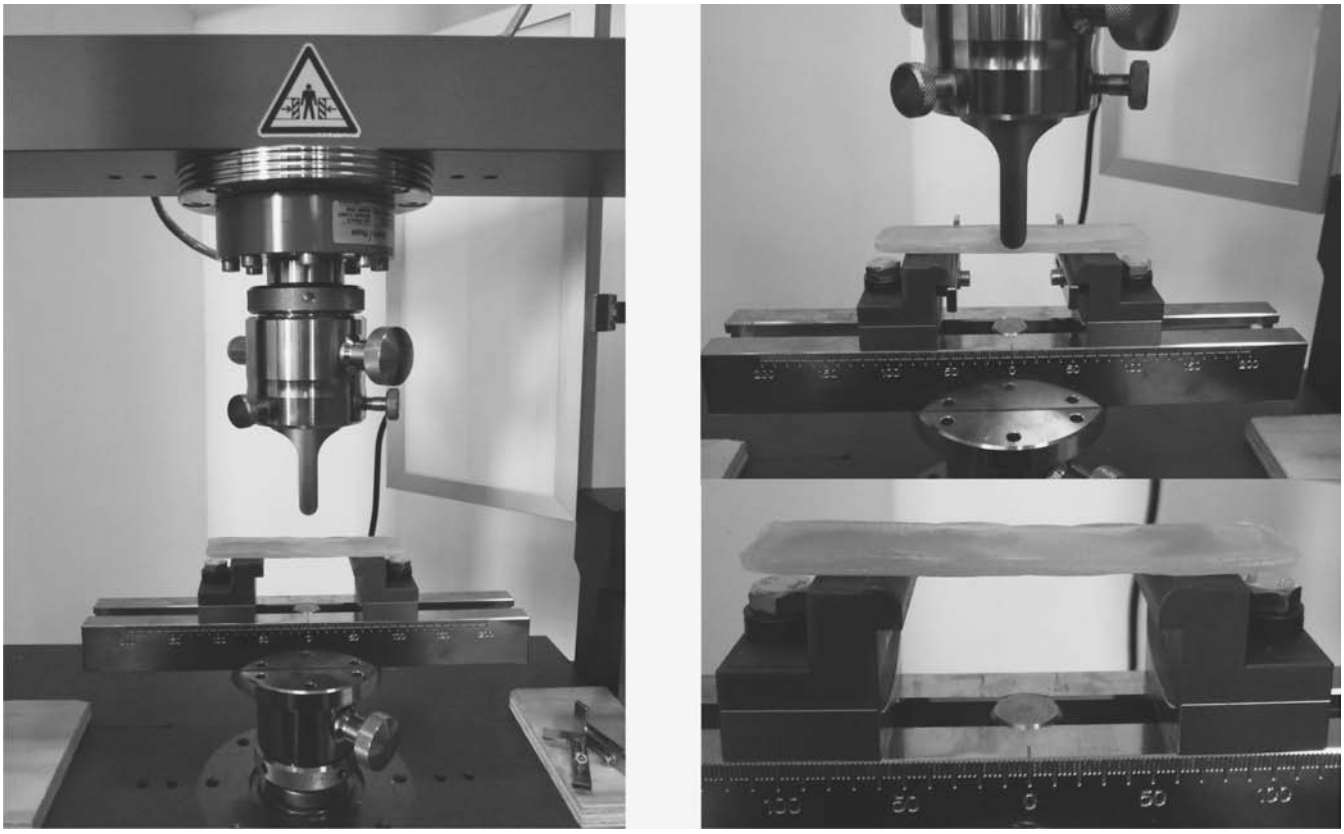

Fig. 4. Fixing the sample in the testing machine ZWIC/ROELL

continuous structures are observed (Fig. 5). When the ultrasounds are used, slight roughness appears resulting from heat effect caused by ultrasounds (Fig. 6a). Time of ultrasounds activation does not significantly influence on fibres surface (Fig. 6b). Surface of aramid fibres after modification with adhesion promoters is presented in the Figures 7a and 7b. Application of adhesion promoters influence on macroscopic features of fibres surface making it more rigid and too hard, especially application of FW.

The highest mean strength determined in 3-point bending test (that is 44.87 MPa) have been recorded for samples reinforced with aramid fabric after modification with ultrasounds. Results obtained for samples containing aramid fabric coated with adhesion promoter FW slightly differ from those modified with ultrasounds. The worst results have been obtained for samples coated with Substances P3, which have appeared to be even worse than results for control samples reinforced with unmodified fabric (Table 2). This phenomenon can be related with modification of aramid fabric by manufacturer, the composition of modifier is unknown and it can affect the quality of connection between fibres and matrix after applied preparation.

Determined differences between investigated the samples belonging to control group and the samples reinforced with aramid fibre modified with ultrasounds (1.5 h) or P3 to turn out to be statistically significant (significance calculated in t-student test is respectively 0.0314 and 0.1507). Whereas differences between control samples and samples subjected to ultrasounds (3 h) and FW are statistically significant. There has been obtained significance equal to 0.0055 for ultrasounds (3 h) and 0.0057 for FW respectively. In carried out t-student test it has been assumed $p<0.05$ and 9 degree of freedom.

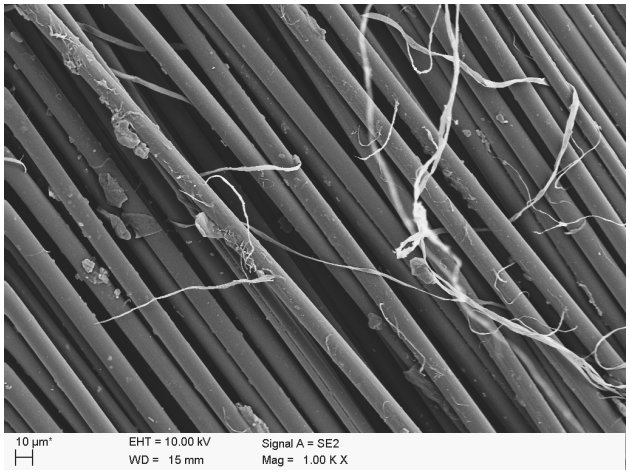

Fig. 5. Aramid fibres without preparation before coating of silicon

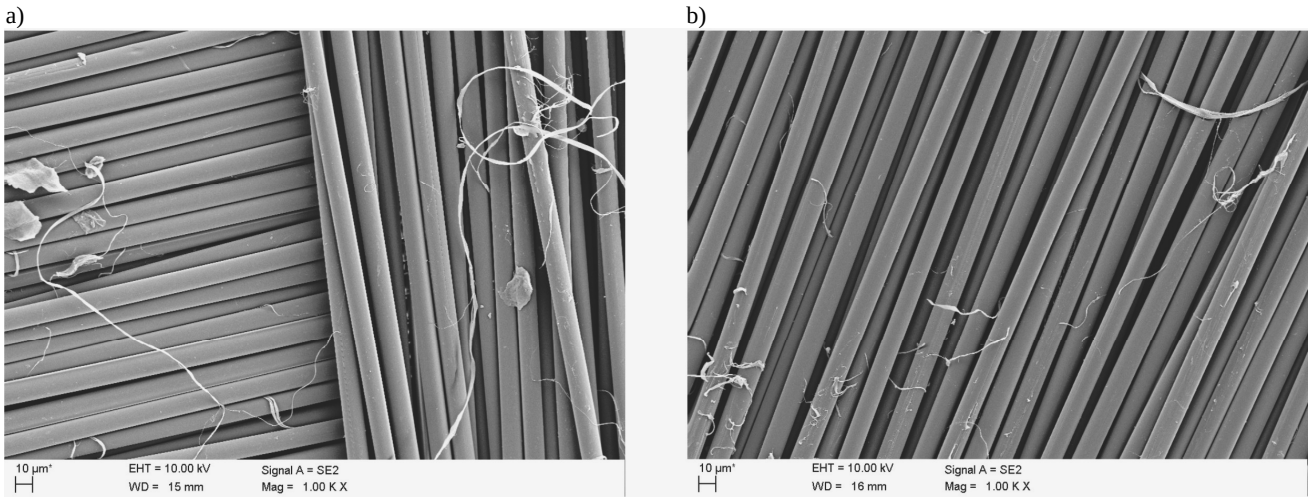

Fig. 6. Aramid fibres after ultrasound preparation before coating with silicone: a) 1.5 h; b) 3 h

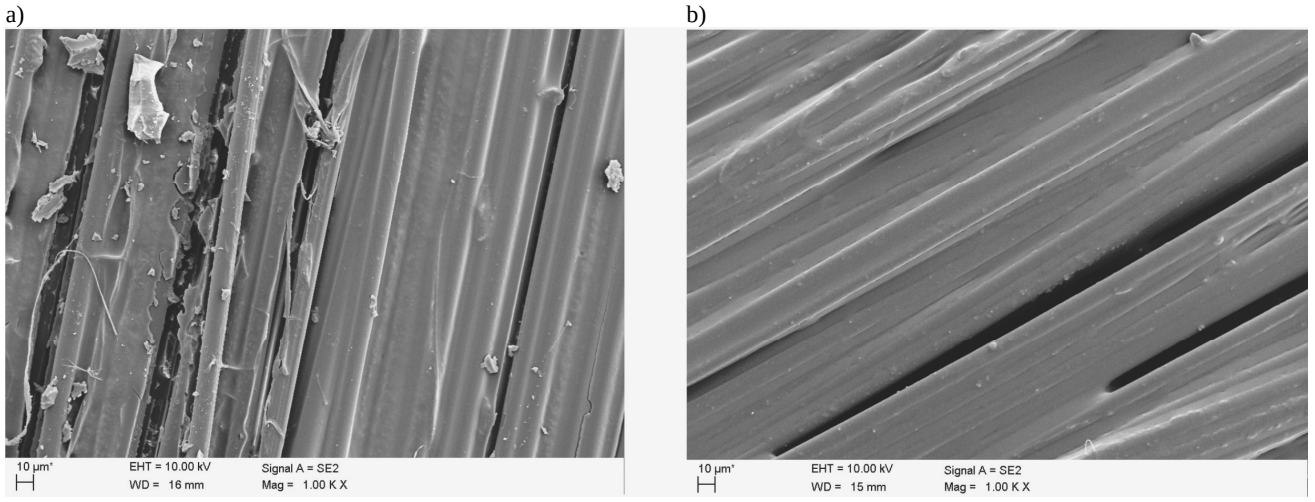

Fig. 7. Aramid fibres after ultrasound preparation before coating with silicone: a) FW; b) P3

Table 2.
Strength profiles in the three-point bending test [MPa]

No.	Control samples (the fibre without preparation)	Fibre samples after preparation of ultrasounds		Fibre samples after preparation of FW	Fibre samples after preparation of P3
		1.5 h	3 h		
1	39.1	42.2	37.9	33.4	23.1
2	21.5	34.9	48.7	43.1	24
3	32	29.4	43.9	52.6	30.6
4	44.1	51	39.3	48.2	27.8
5	30.2	38.7	40.4	42.3	32.6
6	28.6	40.2	47	36.8	29.4
7	35.4	36.1	52.2	45.4	31
8	31.8	46.4	49.1	39.7	25.8
9	34.2	39	53.5	47.2	29.1
10	26.3	43.5	45.3	34.9	32.3
Average	32.32	41.58	44.87	42.66	28.57
Standard deviation	6.41	7.38	4.89	6.50	3.34

6. Summary

Preparation of aramid fibres Kevlar have slightly influenced only on increased adhesion of medical silicon to fibres. Application of aramid fibres as reinforcement is very problematic, especially regarding thin elements with cross-section of few millimetres dimension, where disturbances of applied matrix caused by introduced fibre occurs resulting from bad connection on the silicone-fibre interface. For that reason, further investigations of Kevlar aramid fibres, that will enables activation of its surface to other compounds, are planned. Application of aramid fibres as reinforcement in polymeric materials designated for medicine requires many additional laborious researches of biocompatibility of used adhesion promoters.

In the light of carried out preliminary studies on applied additional preparation of aramid fibres that are reinforcement of medical composites, it is expected that application of additional adhesion promoters improves in a little degree on connection between reinforcing fibre and matrix (especially in the case of matrix with low stiffness) and extends the time of biological tests and thus incorporates the risk of additional irritating factors occurrence. Aramid fibre as a reinforcement in composite materials applied in medicine requires many additional and time-consuming studies before possible introduction to the medical market as biocompatible filling, what is the priority for the authors of this article at the moment.

Acknowledgements

Authors would like to thank Prof. A. Lampe from Medical University of Silesia in Katowice for cooperation.

This scientific work is financed within the framework of scientific financial resources as a research project N N507 422136 headed by Prof. L.A. Dobrzański.

References

[1] M.A. Freilich, J.C. Meiers, J.P. Duncan, A.J. Goldberg, Fiber – Reinforced Composites In Clinical Dentistry, Quintessence Publishing Co, Inc., 1999.
[2] W. Królikowski, Plastics reinforced materials and reinforcing fibers, WNT, Warsaw, 1988 (in Polish).
[3] A. Krysztafkiewicz, The improve factors to the adhesion in the system of the filler - polymer, The Applied Chemistry 33 (1989) 438-446.
[4] L. Domka, A. Malicka, P. Łajdus, W. Hędzelek, The modification of aramid fibers as a filler for acrylic materials, Technical Magazine 6 (2006) 149-154.
[5] K. Imielińska, R. Wojtyra, Effect of water and impact on the mechanical behaviour of hybrid polymer composites for marine applications, Materials Engineering 6 (2003) 627-630.
[6] K. Imielińska, Effect of low velocity impact on compression strength of laminated polymer composites, Archives of Materials Science 1 (2004) 73-87.
[7] M. Kałuża, T. Bartosik, Strengthening the construction materials based on carbon, glass and aramid fibers, Building Materials 2 (2007) 36-38.
[8] E. Stodolak, M. Błażewicz, I. Rajzer, B. Czajkowska, Composite with carbon fibres: biological and mechanical study, Carbo 4 (2007) 187-190.
[9] D. Kwiatkowski, Estimation of dynamic properties of PA/PP blend filled with glass fibre, Composites 3 (2003) 322-324.
[10] R. Sobczak, Z. Nitkiewicz, J. Koszkul, Dynamic properties and structure of polypropylene composites reinforced glass fibre, Composites 4 (2004) 369-373.
[11] A. Szarek, P. Postawa, Composites PMMA - carbon fibre as an alternative to connection of endoprosthesis with bone, Composites 1 (2010) 46-51.
[12] N.T. Xiem, D. Kroisová, P. Louda, T.D. Hung, Z. Rozek, Effects of temperature and plasma treatment on mechanical properties of ceramic fibres, Journal of Achievements in Materials and Manufacturing Engineering 37/2 (2009) 526-531.
[13] M. Cieślik, D. Sabat, A. Cieślik-Bielecka, M. Adwent, G. Bajor, P. Kłapcińska, T. Cieślik, Comparative valuation of biological properties of pure and reinforced by carbon fibers P(LLA/GLA) co-polymer after implantation in rabbits mandible and soft tissues, Biomaterials Engineering 58-60 (2006) 54-57.
[14] H. Leda, Glass or carbon fibres in polymer matrix composites, Composites 3 (2003) 209-215.
[15] M. Guigon, M. Klinkin, The interface and interphase in carbon fibre-reinforced composites, Composites 25 (1994) 534-539.
[16] A. Wilczyński, The fiber polymer composites, WNT, Warsaw, 1996.
[17] K. Dobrucki, A method of designing of polymer composites for impact loading, Proceedings of the 10th Jubilee International Scientific Conference "Achievements in the Mechanical and Materials Engineering" AMME'2001, Gliwice - Sopot, 2001, 56-60.
[18] M. Rojek, J. Stabik, S. Sokol, Fatigue and ultrasonic testing of epoxy-glass composites, Journal of Achievements in Materials and Manufacturing Engineering 20 (2006) 183-186.
[19] L.A. Dobrzański, A. Pusz, A.J. Nowak, Aramid-silicon laminated materials with special properties – new perspective of its usage, Journal of Achievements in Materials and Manufacturing Engineering 28/1 (2008) 148-156.
[20] L.A. Dobrzański, A. Pusz, A.J. Nowak, M. Górniak, Constructional model of internal oesophageal prosthesis, Archives of Materials Science and Engineering 42/2 (2010) 69-76.
[21] L.A. Dobrzański, A. Pusz, A.J. Nowak, The effect of micropores on output properties of laminates materials with assumed medical implantation, Journal of Achievements in Materials and Manufacturing Engineering 37/2 (2009) 408-415.
[22] L.A. Dobrzański, A. Pusz, A.J. Nowak, The elimination of micropores and surface defect in aramid-silicon laminated materials with special properties, Journal of Achievements in Materials and Manufacturing Engineering 35/2 (2009) 121-128.
[23] M. Rojek, J. Stabik, Ł. Suchoń, Hard coal modified with silanes as polyamide filler, Journal of Achievements in Materials and Manufacturing Engineering 39/1 (2010) 43-51.
[24] L. Kroll, P. Kostka, M. Lepper, W. Hufenbach, Extended proof of fibre-reinforced laminates with holes, Journal of Achievements in Materials and Manufacturing Engineering 33/1 (2009) 41-46.