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The elimination of micropores and surface defects in aramid-silicon laminated materials with special properties

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Properties

ABSTRACT

Purpose: Development of the manufacturing technology of aramid-silicon laminated material and define of the micro-cavities amount during production of the laminates and identification of their influence on product properties with assumed medical implantation.

Design/methodology/approach: Aramid-silicon laminated material was made by method of manual formation of laminates, that is impregnation of reinforcement with matrix, to hardening silicone process using hardening methods connected with hot. Created material was observed on Olimpus HIGLIGHT 2000 optical microscope with magnification 40x.

Findings: The results show that the preliminary manufacturing technology of aramid-silicon laminated materials allows to create a material with specific and special properties. Aramid-silicone laminate could be used in medicine for example as gullet prosthesis.

Research limitations/implications: Carried out investigations show the problem with cautioning and ageing which are very important in having proper percentage of intensifier in developed material.

Originality/value: Taking into account the material specific properties one can suppose that the aramid-silicon laminated material would be useful in medicine. Aramid silicone laminate could be attractive alternative for composite material used in medical and others purposes.

Keywords: Composites; Engineering polymers; Biomaterials; Technological devices and equipment; Aramid; Silicone; Application

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1. Introduction

For many years, composite materials based on a polymer matrix, are being widely used in Poland and in worldwide technology, too. Its advantage is good constructional propriety such as low specific gravity, easiness to form finished product, also large-size products, variety of processing techniques and great possibility of diversify proprieties due to used components and technique of processing. In the beginning composites were based on thermosetting polymers mainly polyester and epoxy resins reinforced with glass fibers (E type). But in last ten years development of composites based on thermosetting polymers reinforced with carbon, graphite, aramid, special polyethylene and organic natural fibers has increased. Now the evolution possibilities of the discussed group of materials allow searching more and more responsible and new fields of use [1-5].

Laminate, also called the polymer fiber composites, possess very good mechanical properties with its low mass density, and gives many possibilities of structure design. Therefore they are willingly used by constructors, and their participation in different specialties is constantly developed and increased [6-8].

Engineering materials are used in medicine and in our case polymer composite in future will be used to make gullet's prosthesis. It comes with fulfillment of many directives. The most important condition which has to be fulfill is the best possible bio-biocompatibility also called indifference or physiological naturalness. Biomedical polymers or biopolymers which as well as products of their decomposition in the organism (and products used to its modification) are non toxic, not causing the inflammatory state or other immunological reaction and change the composition of body fluids, also don't have the mutagenic and concentric abilities [9-12].

In that case, the choice of composite components was controlled by following factors, that is:
Aramid cloth was choose because of its mechanical properties, thermal resistance, good chemical resistance, large coefficient of elasticity, low flammability and very good strength to density ratio. Additionally factor that convinced to choose that material was research on the degree of biocompatibility aramid fibers with live tissue. Research was made in Medical Academy in Wroclaw [15]. The proposes of that research was to affirm that aramid fibers cause minimal oxide reaction and don't cause local and systemic stimulation of cytokine after inflammation IL-1 i IL-6. It was ascertained also that this material can be used to increase mechanical resistance of medical materials or use as individual biomedical material resistant to high mechanical loads [9-13].

Medical silicone was also chosen because of its advantageous viscosity (139 cSt) for technological process. It has diametrical influence to process the composite - makes easy to moisten. Additionally medical silicones are doubtless one of few substances of such a high biocompatibility, which have also effects on their desirability. Proof of that is use of silicones to implant and as an anti-scar dressing. The result is that both components can create biomedical indifferent material [14-16].

As it was told before, during making the laminate often takes place generation micro cavities (gas inclusions) in the resin layer. Presence of these defects can affect in different ways outcome properties of material. Possibilities of appearance such as defects has great meaning in establishing process of design suitable material for specific product, keeping in mind expected conditions of use and environment. If hostile environment and operating conditions product will be considered, there has to be paid special attention to that if those kinds of defects are generated during the production process and in what amount they appear in main product [23-26].

Appearance those defects informs us about that the drying process individual layers of laminate probably was not completed in result the material still contains vestigial amount of diluents used in that substance and cause negative influence on laminate proprieties.

Formation of micro cavities in laminates can be treated as a natural process, particularly if we consider existent in nature porous structure such as bones or Balsa tree. Now we can divide the gas inclusions:

- micro cavities, diameter < 0.1 [mm]
- cavities, diameter 0.1 – 1.0 [mm]
- macro cavities, diameter > 1.0 [mm]

Number of micro cavities in polymer laminates depends on many factors mainly on parameters of production, e.g. surface tension, viscosity of matrix (resin) and wet-ability of fiber [16,19-22]. Often the appearance and growth of micro-cavities during the processing, main role perform the type of intensification – its form (fiber, mate or cloth).

The aim of the following paper is developing a technology of composite production: elastic aramid-silocone laminate and define of the micro-cavities amount during production of the laminates and their influence on product properties with assumed medical implantation.

2. Material

The chosen material used for the elastic aramide-silicone laminate production as:

• Aramid fabric manufactured by Havel Composites PL. SP. Z O.O.: CCC120 with basic weight 36 g/m^2, 61 g/m^2 and 173 g/m^2; technical date are shown in Table 1 and Fig. 1,

• Medical silicone that consists of 50% silicone and co dissolving ingredients: mineral spirits and isopropanol (iPA) with concentration 70% and 30%, Chemical and physical properties of medical silicon are shown in Table 2.

Aramid fabric was used because of its strength properties, heat resistance, chemical resistance, high elasticity modulus, low flammability and good ratio of strength to density. Another factor was recently led researches of degree of biocompatibility aramid fibers with living tissue that have been mentioned in [13-22].

Medical silicone, that is available on the market has been chosen basically for its low adhesiveness, that has essential impact on composite production - it simplifies soaking procedure, eliminates additional dilute of resin. An important role has biocompatibility of discussed substance that influence the ability of creation bioneutral.

Dow Corning MDX4-4159, 50% Medical Grade Dispersion is 50% silicone in a co-solvent system of 70% Stoddard Solvent (mineral spirits) and 30% isopropanol (iPA). The silicone is an amine functional polymer that also incorporates reactive methoxy- groups and has the following structure look at Fig. 2.

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

KIND OF FABRICS / TECHNICAL INFORMATION	FABRIC 36	FABRIC 61	FABRIC 173
Basic weight [g/m^2]	36	61	170
Thickness fabric [mm]	0.10	0.12	0.16
Matrix	Aramid 49 T 965 21,5	Aramid 49 T 965 21,5	Aramid 1210 dtex type 2200
Plot	Aramid 49 T 965 21,5	Aramid 49 T 965 21,5	Aramid 1210 dtex type 2200
Mass density fabric [g/m^3]	1.45	1.45	-
Mass density linear [Tex]	22	22	-
Type of plait for all kind of fabrics: linen			

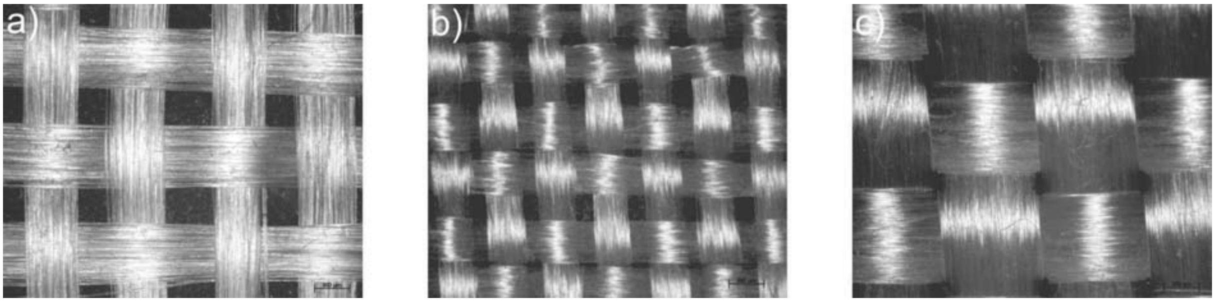

Fig. 1. Aramid fabric with basic weight a) 36g/m^2; b) 61 g/m^2; c) 173g/m^2 figure was observed on the light microscope MEF4A type Leica with a magnification 25x

Table. 2.
Chemical and physical properties of medical silicone MDX4-4159 manufactured by COW CORNING

CHEMICAL AND PHYSICAL PROPERTIES	
Boiling point/range [ºC]	>82
Flash point [ºC]	13.3 (Pensky-Martens Closed Cup)
Specific Gravity [g/cm^3]	0.865
Viscosity [cSt]	160 at 25°C
Appearance**:** Form/Liquid; Colour/Straw; Odour/Solvent	

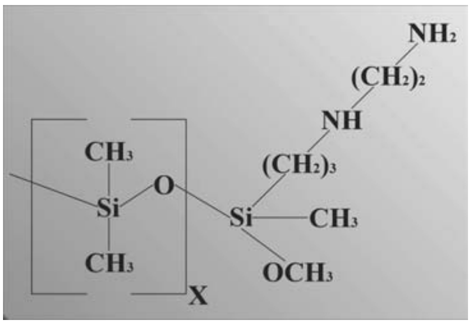

Fig. 2. The scheme of the structure of silicone Dow Corning MDX4-4159, 50% Medical Grade Dispersion

3. Lamiate forming

The preparation of samples:

Samples has been created by method of manual formation of laminates, that is impregnation of reinforcement with matrix. This method has been chosen because it is simple and low cost production. Forming process of laminate was prepared in room temperature under normal pressure.

Combination of both ingredients in laminate is a melting fibers of the fabric into hardened matrix (silicone), what provides discomposed material. One can see clear surface between components - micro built of is heterogeneities [3].

Investigations executed in the present paper were divided on two parts. In first part it was occupied the optimization of parameters (time, temperature, the humidity of air in the chamber) the process of the production of the laminate. Second part concentrates on the getting rid of the superficial defects of the ready material it mean: blisters and superficial little holes.

I PART

In this part preliminary investigations were divided on two stages. First consisted of execution of the tests of hardening silicone in the higher temperature than recommended by the manufacturer (this was controlled in short time periods). However, it was on the other side the humidity of the air in the chamber which influence on the hardening speed chosen silicone was examinated.

Stage

The preparation of samples:

Aramid fabric was manufactured by Havel Composites PL. SP. Z O.O.: CCC120. On the beginning, samples has been taken from aramid fabric with basic weight 36, 61 and 173g/m^2 the 5x5 cm (Fig. 3). Samples has been absorbed with silicone (Table 3).

Samples has been placed in heat chamber WTB BINDER 7200 (Fig. 4) for 24h in the temperature 100 ºC, and for next 24h in temperature 110 ºC and then for 4h in temperature 200 ºC. After 52 h in the heat chamber the sample were staged for cooling.

The samples of pure silicone were also prepared with the different mass - with the diverse thickness in the final effect (Fig. 6) (Table 4). These samples were also placed in heat chamber WTB BINDER 7200 .

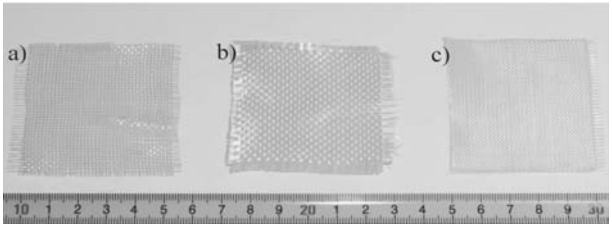

Fig. 3. The survey of prepared samples taken from aramid fabric with basic weight a) 36g/m^2; b) 61 g/m^2; c) 173g/m^2

Table 3.
The data for samples - the laminate

BASIC DATA	KIND OF THE FABRIC		
	A1	A2	A3
Quantity of silikonu [ml]	0.25	0.30	0.40
Time [h]	52	52	52
Temperature [ºC]	100/24h; 110/24h; 200/4h		

Table 4.
The data for samples - pure silicone

BASIC DATA	SAMPLE NUMBER					
	1	2	3	4	5	6
Quantity of silikonu [ml]	0.05	0.10	0.15	0.20	0.40	0.60
Time [h]	52	52	52	52	52	52
Temperature [ºC]	100/24h; 110/24h; 200/4h					

Table 5.
The data for samples - the laminate

BASIC DATA	KIND OF THE FABRIC		
	A1'	A2'	A3'
Quantity of silikonu [ml]	0.10	0.15	0.20
Time [h]	336	336	336
Temperature [ºC]	80		

Table 6.
The data for samples - pure silicone

BASIC DATA	SAMPLE NUMBER					
	1'*	2'*	3'*	4'	5'	6'
Quantity of silikonu [ml]	0.20	0.40	0.60	0.20	0.40	0.60
Time [h]	312	336	336	312	336	336
Temperature [ºC]	80					
1* - 0.05ml; 2* - 0.08ml; 3* - 0.08ml of H_2O						

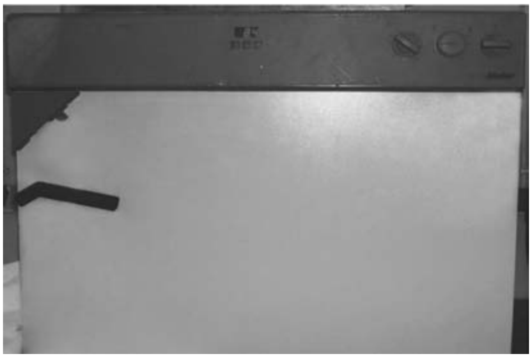

Fig. 4. The heat chamber WTB BINDER 7200

Fig. 5. The samples of pure silicone before hardening

Stage

The preparation of samples:

Aramid fabric manufactured by Havel Composites PL. SP. Z O.O.: CCC120. On the beginning from aramid fabric with basic weight 36, 61 and 173g/m^2 the 5x5 cm samples has been taken. Samples has been absorbed with silicone (Table 5).

Samples has been placed in heat chamber WTB BINDER 7200 for the time in the temperature 80 º C. After max 336h in the heat chamber the sample were staged for cooling..

The samples of pure silicone were also prepared with the different mass - with the diverse thickness in the final effect (Table 6). Firstly it has to wait 2h then in the peaceful temperature to let in the case of the laminate on exact the penetrations of fibres through silicon and in the case of pure silicon on exact mixing water with silicon. These samples were also placed in heat chamber WTB BINDER 7200.

In both cases to enlarge humidity in chamber, and make easier to remove the solvent from silicon. That has why water was added to the mixture.

Daily since samples was placed in drying chamber, samples surface has been visual checked for completed hardening in outer parts. Almost fourteen days later material was ready – aramid silicone laminate had specific properties and diversified surface roughness.

II PART

This part of the work was concentrated on the elimination of the superficial defects of the laminate in the figure of blisters and formation of superficial little holes during solvent vaporizing from applied silicon. The future use of this laminate in medicine is connected with appearance of this kind of defects. The holes in the materials determines the presence of the solvent in, at least one of the layers of laminate and this makes impossible its use as gullet prosthesis. This is the reason for necessity of elimination of blisters and superficial little holes during technological process of the production of the laminate materials.

The problem described above concedes decide to usage of the vacuum chamber with to prevent the formation of blisters and superficial defects. That is whey the samples must be prepared follows: Aramid fabric manufactured by Havel Composites PL. SP. Z O.O.: CCC120. On the beginning from aramid fabric with basic weight 36, 61 and 173g/m^2 the 5x5 cm samples has been taken. Samples have been absorbed with silicone (Fig.6.)(Table7). Three samples were executed without the part of the aramid fabric (Fig. 7)(Table 8.)

In both cases in preparation samples of silicon composite and pure silicon the watcher was added to the mixture enlarge the humidity in the chamber, and make easier the removal of the solvent from silicon. In next stage the sample were left in ambient temperature for 4 hours to allow the precise penetration aramid fibers with silicon in the case of laminate and good mixing the water with silicone in the case of pure silicone. Then, both kind of samples, were placed in heating chamber HERAEUS INSTRUMENTS - VACUTHERM (Kelvtron:t) (Fig. 8) in temperature adjusted to 85 ºC. The samples were in the stove until the moment of hardening the silicone. The samples were placed in drying chamber and checked visually for completion of hardening in outer parts every day.

Almost fourteen days later the material was ready to oft the chamber - aramid silicone laminate with specific properties and diversified surface roughness was made.

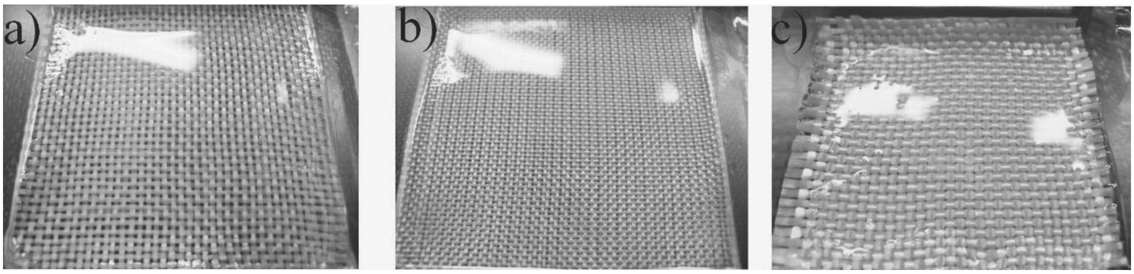

Fig. 6. The survey of sample after one absorbing process, sample made base on aramid fabric with basic weighta) 36 g/m^2, b) 61 g/m^2, c) 173 g/m^2

Table 7.
The data for samples - the laminate

BASIC DATA	KIND OF THE FABRIC					
	A1’’		A2’’		A3’’	
Quantity of silikonu [ml]	0.20	0.50	0.30	0.75	0.35	1.00
Time [h]	168	336	168	336	168	336
Temperature [ºC]	85					

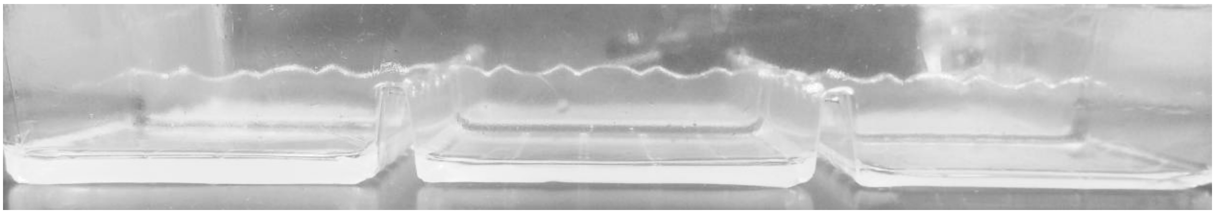

Fig. 7. The samples of pure silicone before hardening

Table 8.
The data for samples - pure silicone

BASIC DATA	SAMPLE NUMBER		
	1’’	2’’	3’’
Quantity of silikonu [ml]	0.25	0.50	0.75
Time [h]	120	144	168
Temperature [ºC]	85		

Fig. 8. The heat vacuum chamber: Heraeus Instruments - Vacutherm (Kelvtron:t)

4. Research

Visual observation was made on Olimpus HIGLIGHT 2000 optical microscope with magnification 0.67- 4x (Figs. 9-12.). Samples has been properly prepare to be pure additionally visual observation of samples has been made to identify possible surface defect like:

- ripple marks,
- surface holes,
- vesicles made by bad silicone adhesion,
- cracks
- uncovered impregnated hardening[3]

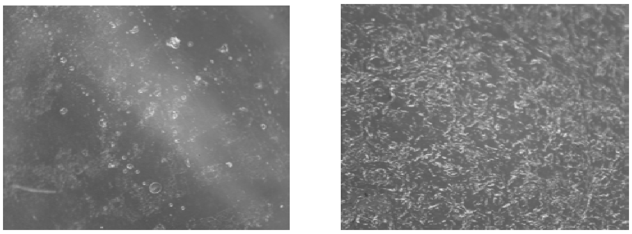

Fig. 9. Surface of samples made based of pure silicone 40x. Left side - top surface of samples, right side - contact with base bottom surface

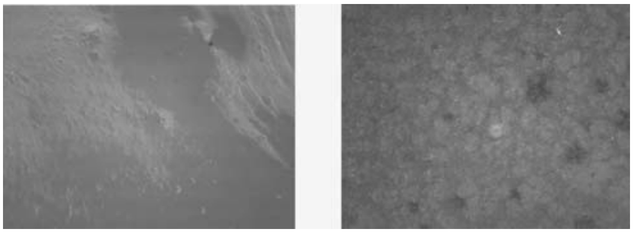

Fig. 10. Surface of samples made based of pure silicone (the vacuum chamber) 40x. Left side - top surface of samples, right side - contact with base bottom surface

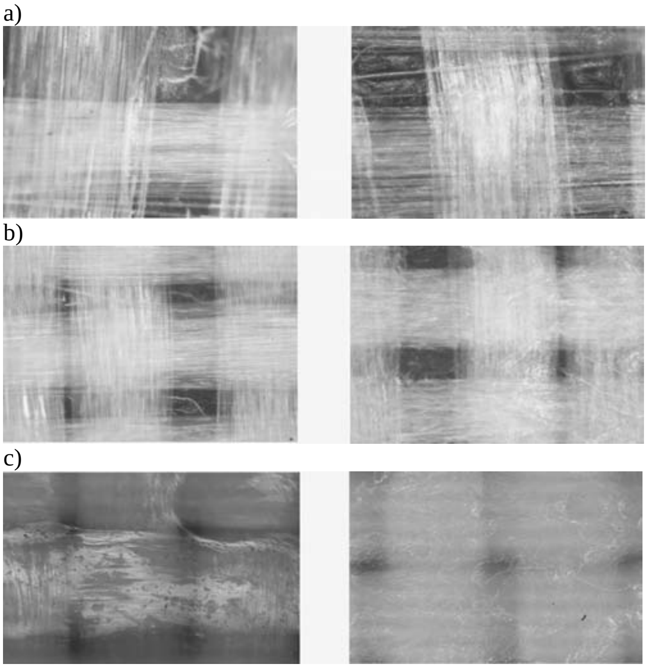

Fig. 11. Surface of samples made based on aramid fabric with basic weight a) 36 g/ m^2, b) 61 g/m^2 , c) 173 g/m^2; 40x. Left side - top surface of samples, right side - contact with base bottom surface

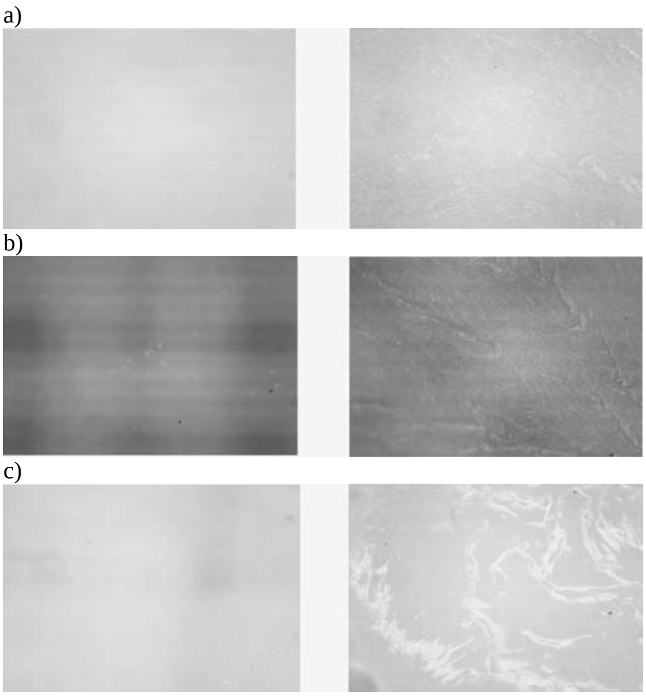

Fig. 12. Surface of samples made based on aramid fabric with basic weight a) 36 g/m^2, b) 61 g/m^2 , c) 173 g/m^2(the vacuum chamber); 40x. Left side – top surface of samples, right side – contact with base bottom surface

5. Results

The result of the research is shown in Figs. 9-12. It can be notice that obtained composite has various degree of fabric impregnation. Upper layer has been precisely impregnated with matrix and perfect surface has been obtained (very small roughness).

Samples made from pure silicone let to define the length of the time of hardening of this substance. Time of hardening is short for one layer but time this lengthens after then you putting on several layers and it is longer for several layers because of bigger probability of the occurrence of the superficial defects (Figs. 9, 10).

In the Figs. 11 a-c can be observed the perfect impregnated of aramid fabric with the thin and smooth layer silicone on the top surface of the sampels.

Bottom layer shows much more roughness in comparison to upper layer - this can be noticed in Figs. 11 a-c left side, the thinnest silicone layer was obtained in the sample with highest basic weight of reinforcing fabric (Figs. 11 a-c right side).

Microscope research enabled to identify surface holes on the surface of the regarded material, with are included on to surface defects (Figs. 11-12 left said). This defect shows that evaporate of solvent from silicone resin was not completed. After the heating of the samples in the vacuum chamber, the defects did not completely disappear but their number decreased (Fig. 12). Other surface effects were not identified.

6. Summarize

Based on investigation described in this article, it can be observed that there are a lot factors which should be improved, especially in manufacturing of aramid-silicone laminte, to obtain the final material without any surface defects (e.g. blisters or holes). To make possible using this material in medicine applications, it is necessary to eliminate the remains of the solvent. Moreover, the tests shows certifies that developed method of aramid-silicone laminate manufacturing process allow to produce engineer material with good elastic and plastic property. In addition, this material may be used as a modern biomedical material with good strength properties, plasticity, human tissue interlayer and high bio-compatibility, for example as gullet prosthesis.

The next advantage of these materials is its diversified surface roughness. Very smooth surface obtained on the one side facilitate easy glide and surface obtained on the other side facilitate stabilization in specified environment.

Other subject of the elaborate is technological process to produce material without surface defects such as blister, holes and solvent rests, as a result of researching a method of the manufacturing processing of the laminated material free of toxics chemical compounds for human and without material defects.

These two problems determines a possibility of using medical application of this composite, taking under consideration some special properties and a probability of usage it in the medicine, for instance, a good bio-compatible gullet prosthesis, which work with the human body environment.

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