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DYNAMICS OF LIQUID PENETRATION INTO FIBROUS MATERIALS

AUTOREFERÁT DISERTAČNÍ PRÁCE

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1. Předmět a cíl práce - *The goal of the work*

The thesis have brought a way to the recognition or clarification of some legalities from the branch of dynamics of liquid penetration into porous materials, its simulation by means of Auto models and its application on a “journey” to the solution of the factual problem with the production of composite materials reinforced with electrospun nanofibre layers. Thus the complete text is divided into three parts.

The first part is focused on introduction of dynamics of liquid penetration into porous materials. Theoretical part dealt with basic terms and legalities of wetting. There are described model of cylindrical capillary and model of radial capillary as model systems for better understanding of drops penetration into complex porous or even textile structures. There is also part devoted to the enhancement of liquid penetration into porous materials with the intention of ultrasound usage. Experimental part should bring a design of a simple and an effective method for studying the dynamics of liquid penetration into fibre materials and its testing for a scale of nonwovens with different geometrical parameters (change of fibre volume fraction, change of orientation of fibres, change of fibre diameter…).

The second part of the thesis shortly describes basic terms and legalities of automodels and Monte Carlo methods, examples of automodels usage for simulation of wetting phenomenon. Testing and evaluation of a possibility to use the simulation models for the observation of wetting dynamics follows the theoretical part as an introduction of thesis author the simulation study.

The last part is devoted to nanofiber-reinforced composites. There are described composite nanofibers and nanocomposites reinforced by carbon nanotubes and electrospun nanofibers. Experimental part involves the description of a concrete solution for composite materials reinforced with electrospun nanofibre webs. The manufacturing process requires special approach because the electrospun nanofibre web brings several untraditional complications, which are necessary to solve. The entrance to the world of “nano” dimensions brings great challenges (problems), but evidently also several advantages in results. The thesis does not focus on testing and applied research in the branch of electrospun nanofibre reinforced composites. The work wants to show that it is possible to apply all theoretical knowledge, experimental and simulation skills for concrete examples.

2. Přehled současného stavu problematiky - *State of the art*

2.1. Wetting Processes

Pivotal work, which has motivated the author of the thesis, is an article [1] from an outstanding French “workshop” that deals with drop suction into porous membranes. The group of researchers, lead by Brochard-Wyart, is the leader in Europe in the field of wetting physics. It was necessary to describe the model situations as the model of cylindrical capillary (Lucas-Washburn equation) and the model of radial capillary (Marmur equations; as it is described in [1, 2]) and their theoretical background at first in the thesis. The knowledge of a drop shape is critical for a description of a drop’s behavior during its penetration into porous materials. There is a huge difference between the so-called spherical drops and cake drops or puddles. Thus it was necessary to mention where the difference lies and what are the basic parameters of these drop types.

Wetting of porous media describes the properties of very rough surfaces. The tree-dimensional nature of roughness raises the phenomena of liquid penetration and impregnation by liquid [3]. The dewetting processes on flat, smooth surfaces are relatively clear (see for example article [4]), although inertial regimes still raise some questions. But if the surface is porous, the situation is very different. A drop placed on a porous medium does not merely spread on the surface but also penetrates into the depth of the material, thereby modifying its wetting properties. A liquid film deposited on a porous substrate recedes via two separate mechanisms: suction and dewetting. Suction through the pores is opposite to spreading. The previously mentioned two models (model of cylindrical capillaries and model of radial capillary) are the most often used ones for dynamics of liquid penetration into porous materials. Attention, in the thesis, is focused mainly on the applicability of the radial model, because the cylindrical capillary model is very wide spread and there are an inexhaustible amount of articles related to the wetting of porous materials and their description by means of cylindrical capillaries model in the technical literature available. The greatest attention was devoted to the wicking phenomenon. Besides considerations about the process of liquid penetration into porous materials, it was also necessary to mention phenomena and mechanisms, which can influence the dynamics of liquid penetration into porous materials. This influence of the wetting process leads either to the acceleration or deceleration of wetting. Less known but apparently very effective method how to improve the dynamics of liquid penetration into porous materials is the usage of ultrasound treatment, which is shortly described in the thesis too.

2.2. Simulation

This part of the work is devoted to auto-model simulations. The models are based on so called modified Ising models and Monte Carlo method. Ising model is one of the auto-models for the modeling of real physical systems. These models are used mainly for simulation of wetting phenomena here. Ising model originally described a behavior of a group of elementary magnets with respect to external magnetic field value [5, 6]. Other applications of Ising model are in ecology, chemistry, cybernetics and modeling of images and textures. The models described and used in the thesis are strictly oriented towards computer simulations of selected transport wetting phenomena in connection with porous solid structure as model structure of radial capillary, cylindrical capillary and nonwoven-like structures.

Simulation's principles, potentialities and limits are described in the thesis. There are also notes about usage of this kind of simulations in relation to wetting dynamics. These computer models, their historical progress, basic principles, complete statistical-physical explanation and of course simulation examples are detailed in the monograph [7], written by Lukáš and Košťáková. Other particular information from detailed literature review and simulations outgoing from the same basics can found in thesis [8] and of course in several publications of the real "discoverer" of these computer simulations based on automodels (or modified Ising models) for the textiles and fibrous materials wetting description [9-13].

2.3. Fiber Reinforced Composites

A utilization of nanofiber materials as a component of composite materials is introduced in the part of the thesis. The part is devoted to the best-known nanofibers (carbon nanofibers, carbon nanotubes and polymer electrospun nanofibers) and their combinations in composites. These fibers – not visible to the naked eye – cannot be produced by classical textile manufacturing methods. Nanofiber materials have generally a plenty of interesting properties that influence the characteristics of other materials, if these fibrous nanomaterials are added as their component. The literature review in the thesis introduces three types of nanocomposite materials including nanofibers: composite nanofibers; composite reinforced by carbon nanofibers and nanotubes and composite reinforced by electrospun nanofibers. Only a few papers deal with the manufacturing of composite materials reinforced by polymer nanofibers produced by electrospinning, and the most important publications written by research groups dealing with a possibility to use electrospun nanofiber materials as composite reinforcement are reviewed below. It is necessary to refer to the first review devoted to this type of composites written by Huang et al. [14].

3. Použité metody - *Used methods*

3.1. Wetting Processes

The testing method used in the experimental part associated with wetting processes is called *drop test*. The method was designed by author of the thesis exactly for studying the dynamics of drop penetration into porous materials, namely nonwovens. The test has following consecutive phases: preparation of nonwoven samples and liquid or solutions, preparation of a set up (a computer connected with a digital camera) for recording the drop's suction into the porous material, cutting of the recorded video with software to obtain a photo time sequence (VirtualDub), usage of an image analysis software (LUCIA G, Matlab) for the determination of important data such as volumes of drops, shapes of drops and contact angles. Every video recording has had its own calibration by means of a scale. Individual pictures were treated by image analysis. The drop volume could be estimated as a volume of a spere cap. Then *sphere cap volume* can be calculated from height *h* and width *w* of the cap.

However the above-mentioned calculation of drop volume can be inaccurate, when the shape of the drop is not spherical. Due to these cases it was necessary to design and use a second method, referred to as *"method of pixel calculation"*, which is also based on the usage of image analysis and software Matlab as is described below.

Firstly, individual color pictures have been separated from the video recording of a drop's penetration at a defined time interval. The length scale calibration to a number of pixels has been noted. Every color picture was transferred to a binary form. The transformation was done by means of image analysis (software LUCIA G) using the threshold function. Thresholding of a picture is based on finding a threshold value. In case of a gray-scaled picture, the value represents one number of two hundred and fifty-six numbers in the gray scale (from 0 to 255). For a fully colored picture, the color threshold consists of three numbers that represents the so-called RGB values – values of red, green and blue colors. After the selection of the threshold value, the pixels of the complete picture are checked. If the color parameters of a pixel (value of gray scale or RGB) are below the threshold mark, they will be substituted by zero – black color. If the color parameters of a pixel are above the threshold mark, they will be substituted by two hundred and fifty five – white color. The resultant picture has been saved as a bitmap (*.bmp). The binary picture was transported to software Matlab as a matrix of numbers 0 and 1. Then the software counted the pixels. Finally the total number of white pixels was calculated for every row of drop profile projection. The number presents the diameter of a cylinder of height $v=1$ *pixel*, assuming that drop is rotationally symmetric. All these discs (cylinders) were summed. After the calibration that defines how many length units are in one pixel in the real picture, the volume of drop was estimated. For better understanding see ***Fig.A*** in the picture attachment.

The original method for evaluation of a drop penetration experiment was designed and tested specially for this type of studies. It was firstly introduced in [15]. The main advantage of the method is that all errors caused by drops of different shape from the spherical cap are eliminated.

3.2. Simulation

Automodels (modified Ising model), Monte Carlo method and Kawasaki kinetis for long distance exchanges were used for simulations described in the chapter of the thesis. The simulation programs are written in program language C++ in software Borland C++ and Turbo C.

Simulation starts with a creating of three-dimensional simulation box, which is composed from finite number of elementary cubic cells. These cells are assigned with indexes according Cartesian system of coordinates. A lattice variable (so called Ising parameter), which represents different physical meaning of cell's content or more precisely different medium (liquid, gas, solid material), is assigned to each cell. A model of “liquid-fibrous material” is in initial configuration that mimics the real system at the beginning of liquid penetration into fibrous system. The system is in initial configuration energetically unstable. Thus over time a liquid transport into the fibrous system happened with the aim of finding an equilibrium state with the lowest total energy or more precisely with the aim of finding the most probable configuration (if the statistical temperature τ is not zero, then the equilibrium state is not the state with the lowest energy; concept of thermal contact between the system and reservoir). The system is heading towards equilibrium probability distribution of states/configurations. Configuration exchanges, therefore the transport of liquid, are achieved through changes of the positions of liquid cells with the gas containing cells. If evaporation is not considered, then the liquid retains its volume. It means there is constant number of cells liquid. Selecting and later moving are the cells from the liquid-gas interface only, what ensures that cells containing the liquid are not separated from each other.

A liquid movement is caused by exchanges of cells, which contain liquid and gas, in the 3D lattice. The simulation runs in repeating steps and a structure of one step (which is called in this type of simulation Monte Carlo Step – MCS) consists of following operations:

1) A random chose of two different cells (one containing liquid and the last containing gas) from liquid-gas interface.
2) Total energy of the system is calculated according equation

$$H = \sum_{i=1}^{N} E_i = C_g \sum_{i=1}^{N} z_i + \sum_{i=1}^{N} \sum_{j=1;i\neq j}^{N_j} C_{ij} \ ,$$

where H is total energzy-Hamiltonian; E_i are elementary energies; C_g is gravitational constant and C_{ij} represent exchange energies between cell *i* and cells *j* in the neighborhood of *i*-cell.

3) Positions of cells are exchanged
4) Total energy of the system is calculated again
5) Difference between total system energy before and after cells exchange is calculated
6) If the energy after the exchange is lower than the energy before exchange, cells will stay in their new positions and the next step starts. However, if the energy after the exchange is greater than the energy before the exchange, the decision-making process is more complicated. Firstly, there is necessary to decide about the size of temperature in the Ising model. If the temperature is zero, and if the energy after the exchange is higher than the energy before exchange, cells will return to their initial positions and the simulation continues from the first step. If the temperature is different from zero, there is necessary to calculate so called transition probability using Boltzman law. If the calculated probability is higher than randomly generating number from interval (0; 1), the exchange is accepted. However if the calculated probability is lower than the randomly generating number, the exchange is not accepted and cells are returned to their initial positions. The program goes again to the initial point of the simulation.

The next MCS starts the same process from another randomly chosen pair of cells. The simulation process is finished when the system achieves the equilibrium state. The energy of the system in equilibrium varies around a constant and minimal value. The simulation is also stopped when the number of MCS initially written to the particular simulation program is reacted. Graphical outputs from such computer simulation are introduced in ***Fig. B*** in the picture attachment.

3.3. Fiber reinforced composites

The real experiments devoted to production of composite materials with electrospun nanofibrous reinforcement can be divided into several parts according to the production method of samples: a) composite material produced by Hand Lay-up method without ultrasound impregnation enhancement; b) composite material produced by Hand Lay-up method with ultrasound impregnation enhancement; c) composite material produced by Hand

Lay-up method with ultrasound impregnation enhancement and nanofiber plasma treatment; d) composite material produced by Hand Lay-up method with ultrasound impregnation with change of nanofibers polymer material; e) composite materials produced by Hand Lay-up method with ultrasound impregnation with different types of matrixes. The apparent interlaminar shear strength was determined by the short-beam method for fiber reinforced plastic composites according to international standard ISO 14130:1997(E).

The Hand Lay-up fabrication method, described in [16], was used for producing all samples. The initial experiment dealt with production of composite material reinforced by electrospun nanofibers. To obtain better impregnation of nanofiber materials and to remove the air bubbles that were trapped inside the wetted material we decided to use ultrasound. The decision was based on the knowledge that the application of ultrasound enhances the sorption of highly viscous impregnants [17]. Redundant resin or binder was drained using a woven fabric after the nanofiber layer was impregnated. Then ultrasonic treatment was used again to obtain better uniformity of resin distribution and to remove air bubbles from the inner structure of the impregnated nanofiber samples. The curing of resin and binder was performed under normal conditions, at ambient temperature. Just an exsiccator was used for the reduction of humidity during curing.

4. Přehled dosažených výsledků - *Review of results*

The presented thesis goes from the basic theoretical descriptions of liquid behavior in contact with solid capillary, through their experimental verifying with textile material as solid porous systems, through introduction of computer simulations studying equilibrium states and wetting process dynamics, to the particular example of the previous knowledge usage for the special composite material production.

The review on wetting brings not only generally known models but also nontraditional solutions of Lucas-Washburn equation and except the cylindrical capillary model also model of the radial capillary. In addition, it is also devoted to the specific drops penetration into porous materials and ultrasound enhancement of liquid penetration. Wetting experiments are based on the experimental procedure with new, more accurate principle – the method of pixel calculation. These experiments dealing mainly with drops penetration into nonwoven materials show except expected also several interesting new results:

i) Dynamics of drop penetration into nonwovens depends significantly on nonwovens volume fraction. The main result is that drops penetration into bulky nonwovens does not follow Lucas-Washburn equation. See ***Fig. C*** in the picture attachment.

ii) The third suction regime is described here, compared with publications [1, 2], where only two suction regimes are presented. The radial capillary model introduced only two suction regimes. Although according drops observation during their penetration into nonwovens, there exists clearly the third regime in initial phase of penetration. See ***Fig. D***.

iii) Usage of ultrasound as an enhancement of liquid penetration is efficient only for high viscous liquids as epoxy resin. The drop penetration dynamics with usage of ultrasound does not follow Lucas-Washburn equation.

The second part, devoted to computer simulation of wetting phenomena based on Auto models and Monte Carlo method, brings these very interesting results:

i) The exact thermodynamical temperature determination according to statistical temperature input to this type of simulation is found there and exactly agrees with Sčukin theory [18]. This is very important for all these simulation results explanation and their comparison with real wetting processes. As the author of the thesis knows, it was not published in literature yet. The knowing of the thermodynamical temperature appropriate to the simulation is very important with regards to its final interpretation. The method is based on the finding of the critical temperature. The graphical documentation is in ***Fig. E***.

ii) The computer simulations describe easy possibility how to show and study liquid body inside the fibrous material after a drop penetration (see ***Fig. F***), what is not possible in real experiments.

iii) Special situations, when liquid with contact angle 180°, are studied by these computer simulations too. The situations are not easy to use in real wetting experiments. The computer simulation shows there is possibility when such liquid cannot escape from fibrous material.

iv) Dynamics of capillary wetting processes is described, as the thesis author knows, for the first time in the thesis. Real proofs that the computer simulation (both liquid wicking into cylindrical capillary – see ***Fig. G*** and drop penetration into the radial capillary) is able to simulate some wetting process of porous material are presented here. Unfortunately there cannot be done any clearly explanation why in some cases it works and in other the simulation does not work according theoretical presumptions. There is necessary to continue in this study deeply.

Novel (new, untraditional) composite material, combination classical fiber reinforcement and electrospun nanofibers, manufacturing and testing is described into the last part of the thesis, to complement previous two parts of the work. The three-point test showed good results from testing composites with polyacrylonitrile nanofibers as secondary reinforcement of fiber reinforced composite material. A more obvious result is the increase of flexural stress when using polyacrylonitrile electrospun layers previously impregnated with resin by means of ultrasound (growth is 21% in comparison with composite blind samples; see ***Fig. H***). Another important but predictable fact is that the higher fiber content in the final composite material can be reached with the lower matrix viscosity.

5. Zhodnocení výsledků a nových poznatků - *Conclusions*

The thesis introduces the untraditional method for studying of drop penetration with its advantages and disadvantages in the part devoted to wetting. The method is able to detail study process of drop penetration and to recognize even small changes during the penetration. According the studying several new findings was recognized as for example the situations, where drop penetration dynamic does not follow Lucas-Washburn equations were found there.

Beside the equilibrium observed computer simulation, also dynamic process were studied in the second part of the thesis. Liquid wicking into cylindrical capillary and droplet penetration into radial capillary was simulated at different conditions. The most of presented influences agrees with theoretical prediction. Although some limits, where simulation did not agree with predictions, were shown and discussed there too.

Many authors, for example in [12, 27, 28], wrote that the computer simulation (Ising model with Kawasaki kinetics) can be used to study the dynamics of systems, although the method is based on the principle of equilibrium thermodynamics. But there exist only a few articles, which really bring a proof, that the Ising model with Kawasaki kinetics is available to simulate also dynamic processes. Among these publications belongs [27] from Manna, Herrmann and Landau and [28] from Lukas et. al. The first work is devoted to the study of the height of the center of mass of the drop on a wall as a function of time (Monte Carlo exchanges). The second work [28] introduced the simulation model for correct Rayleigh instability prediction finding, which has dynamic nature. Thus the main benefit of the simulation part of the thesis is showing of other proofs, that the Ising model with Kawasaki kinetics can simulate also dynamic processes as liquid penetration into fibrous or porous materials is.

The composite production method described in the third part of the thesis is one of the easiest, but the nontraditional reinforcement brings new facts to the process. The very important conclusion is that it is necessary to help the highly viscous matrix to impregnate the electrospun nanofibrous reinforcement. One possibility which was described in this thesis and has really good results is the application of ultrasound enhancement. The usage of ultrasound helps impregnation and also the removal of air bubbles from all the volume of the forming composite material.

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8. Summary – *Abstrakt*

Tato disertační práce se věnuje problematice dynamiky průniku kapalin do vlákenných materiálů a to experimentálně, pomocí počítačových simulací a v konkrétní aplikaci výroby kompozitních materiálů. Práce je rozdělena do tří hlavních částí.

První část je zaměřena na dynamiku průniku kapalin do porézních materiálů obecně. Teoretická část obsahuje základní termíny a zákonitosti smáčení. Jsou zde popsány modely válcovité kapiláry a model radiální kapiláry jako dva základní modelové systémy pro lepší porozumění komplexnímu procesu pronikání kapek do porézních vlákenných i nevlákenných struktur. Je zde také část věnovaná možnostem podpory pronikání kapalin do porézních materiálů a to účinkem ultrazvuku. Experimentální část představuje nejprve navrženou jednoduchou a efektivní metodu pro studium dynamiky průniku kapek zejména do vlákenných materiálů s relativně velmi hrubým povrchem. Tato metoda je pak využívána k testování dynamiky průniku kapek do různých druhů netkaných textilií s ohledem na: (i) změny jejich geometrických parametrů (zaplnění, orientace vláken, průměr vláken); (ii) změny viskozity kapalin použitých ke smáčení a (iii) využití ultrazvuku k podpoření dynamiky průniku kapek do netkaných textilií.

Druhá část stručně představuje Isingův model, metodu Monte Carlo, Kawasakiho kinetiku a další termíny a zákonitosti nutné k uvedení do problematiky počítačových simulací procesů smáčení. Vlastní počítačové simulace a jejich vyhodnocení jsou součástí experimentů v této části práce. Tyto počítačové simulace jsou zaměřeny jak na procesy vedoucí k rovnováze (k čemuž jsou prioritně tyto simulace určeny) tak zejména na odhalení možnosti jejich využití v simulacích dynamických jevů – sledování dynamiky průniku kapalin do porézních materiálů. Tyto simulace jsou samozřejmě porovnávány zejména s teoretickými poznatky z první části práce.

Výroba a testování kompozitních materiálů s nanovlákennou výztuží je tématem poslední, třetí části předkládané disertační práce. V teoretické části jsou představena kompozitní nanovlákna, kompozity vyztužené uhlíkovými nanovlákny či nanotrubicemi a kompozity vyztužené elektrostatickými nanovlákny. Právě elektrostatická nanovlákna jsou pak použita jako jediná či sekundární výztuž kompozitních materiálů v experimentech. Výrobní proces vyžadoval netradiční přístup a řešení několika nezvyklých problémů spojených se vstupem do „nano“ oblasti vlákenných materiálů. Výsledný kompozitní materiál je spojením znalostí ze studia teorie a zkušeností z experimentů i simulací procesů smáčení v konkrétním příkladu.

OBRAZOVÁ PŘÍLOHA - PICTURE ATTACHMENT

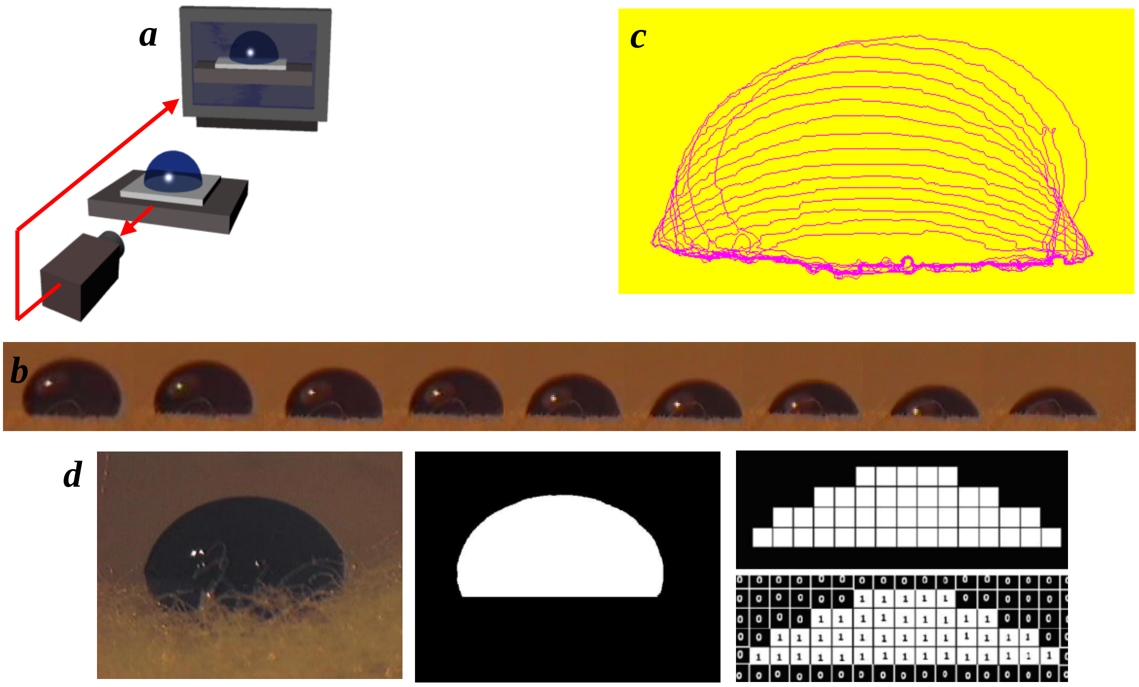


Figure A: *Scheme of an experiment configuration for spontaneous drop penetration (a). Example of drop penetration with time step 1 second - glycerin plus methyl violet, needle punched nonwoven (b). Example of a graphical output from image analysis of a drop's penetration into a nonwoven material. The change of drop's shape and contact angles is visible as a function of time (c). Explanation of "method of pixel calculation": real picture of a drop on porous surface; binary picture created from the picture above; and a scheme of a binary picture of a drop composed of pixels (d).*

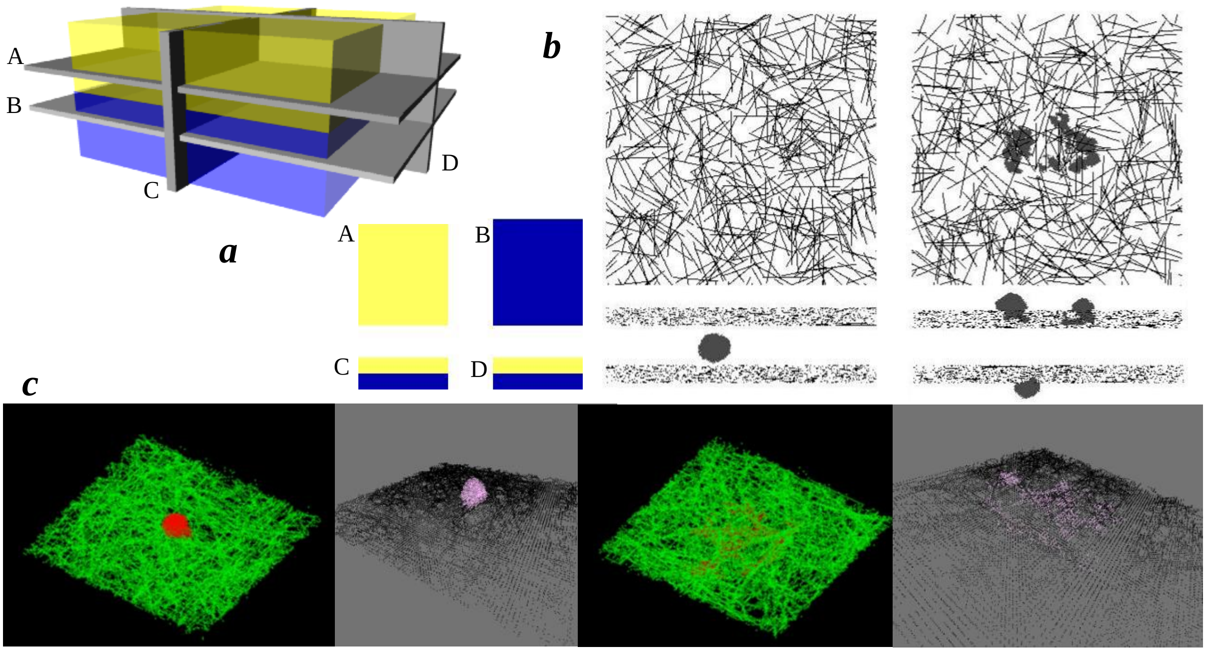


Figure B: *Four two-dimensional graphical outputs as cross-sections (A-D) on the right side from three-dimensional simulation model (a). Graphical output from simulation of a liquid droplet in contact with nonwoven material with random orientation of fibers with two different liquid-fiber surface characteristics (left side - extremely high contact angle; right side - lower contact angle (b). Three-dimensional graphical output from simulation representing droplet of liquid in contact with nonwoven material. The graphical outputs were presented in [15] (c).*

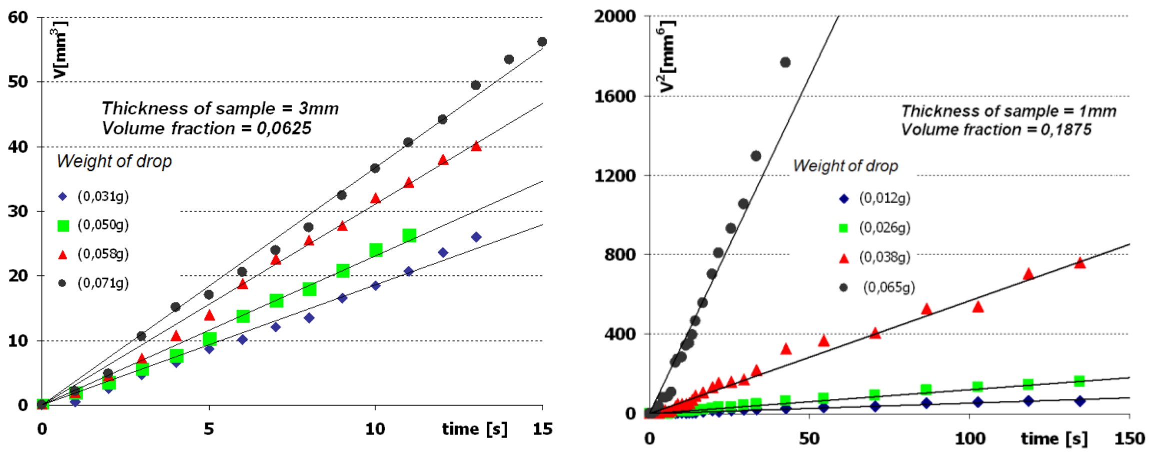


Figure C: *Linear dependence of penetrated drop volume on time for nonwovens with lower volume fraction (on the left side). Average regression coefficient is 0,9952. Dependence of the second power of penetrated drop volume V^2 on time for nonwovens with higher volume fraction is on the right side. Average regression coefficient is 0,9928.*

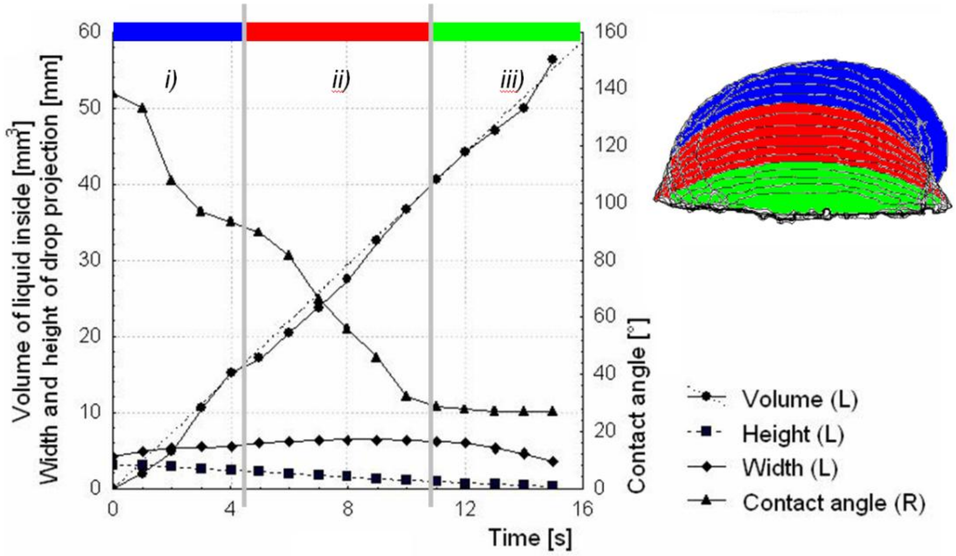


Figure D: *Example of the graphical recording of increasing the volume of liquid inside the nonwoven, the change of a height, a width and a contact angle of drop versus time and the image analysis for this drop presenting three different suction regimes. The weight of the drop was 0.07 g.*

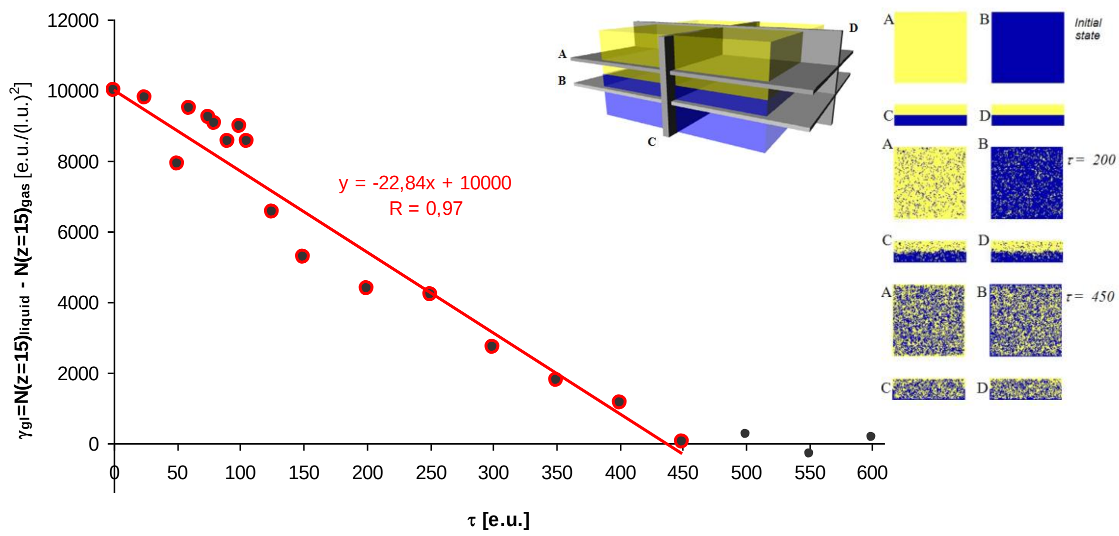


Figure E: *Graph of surface tension γ_{gl} calculated as the excess of Helmholz energy at gas-liquid interface from simulations with different τ (statistical temperature) values. The liquid level was in z=15. The total number of cells in one layer in the simulating box is 10 000. The red line is regression function for red signed data (from τ=0 to τ=450). The two-dimensional graphical outputs are presented on the right side: gas-yellow color; liquid-blue color.*

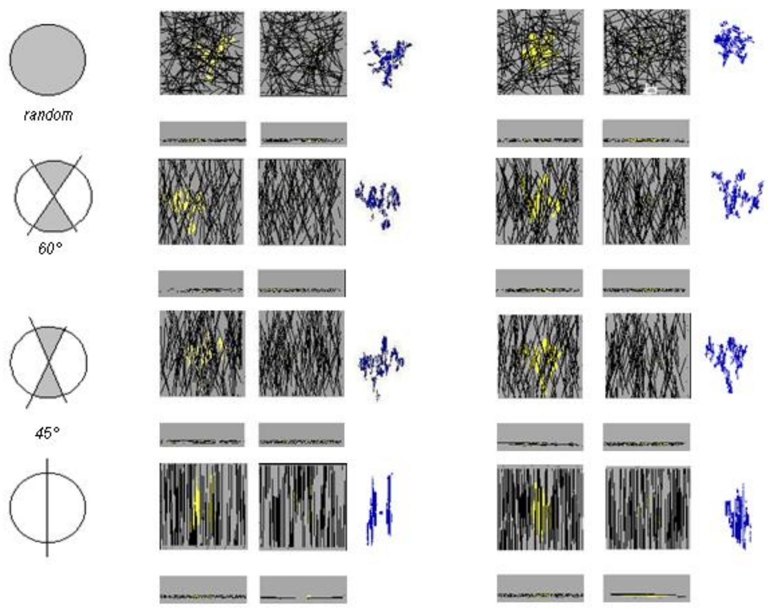


Figure F: *Two two-dimensional graphical outputs of the drop penetration into fibrous materials simulation for four various fiber orientations and contact angle θ=60°. Vertical and horizontal cross-sections of all systems and resultant liquid bodies from inside are depicted.*

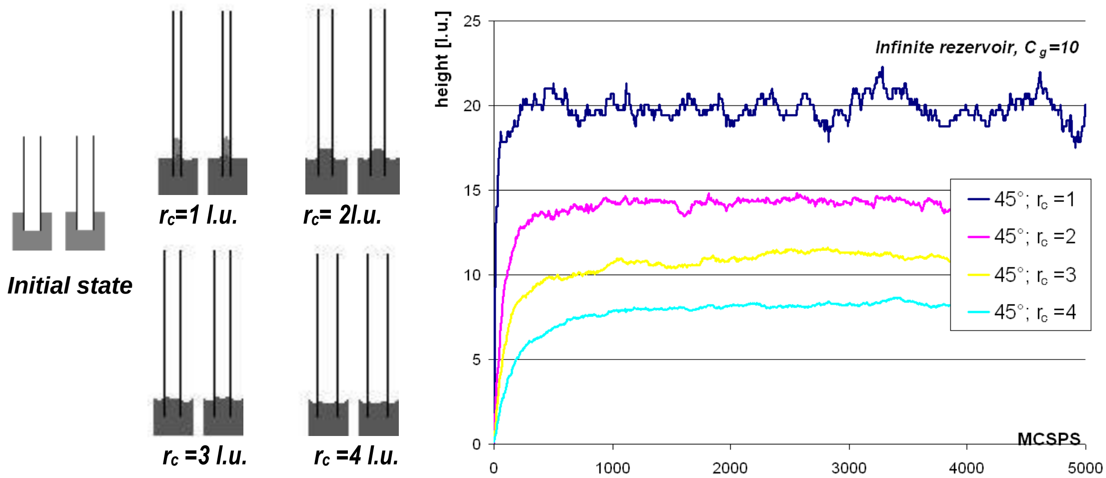
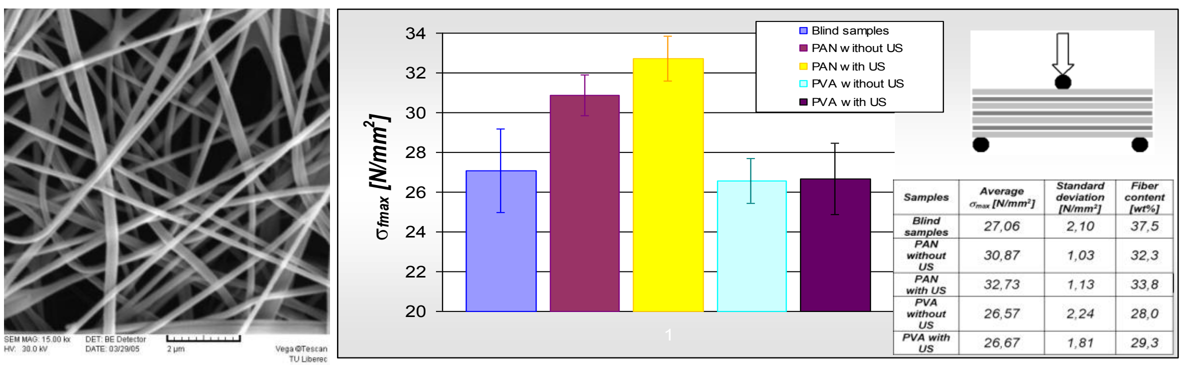


Figure G: *Example of the simulation graphical outputs and graph of height of liquid inside cylindrical capillary versus MCSPS. The simulation parameters were these: contact angle 45°; finite liquid reservoir, gravitation C_g = 10; MCSPS 5000; capillary radius is r_c; contact angle is 45°.*



Samples	Average σ_{max} [N/mm²]	Standard deviation [N/mm²]	Fiber content [wt%]
Blind samples	27,06	2,10	37,5
PAN without US	30,87	1,03	32,3
PAN with US	32,73	1,13	33,8
PVA without US	26,57	2,24	28,0
PVA with US	26,67	1,81	29,3

Figure H: *SEM figure of used PAN electrospun material and the final results from three-point tests of composites reinforced with both glass mats and nanofibrous layers in comparison with composites reinforced only with glass mats. Three point bending specimen (four layers of primary reinforcement and three layers of nanofibrous materials) and test system in principle with denoted direction of loading is shown in the upper right corner.*

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