

Anna Murárová,
Silvia Podobeková,
*Zuzana Murárová

Structuralisation and Functionalisation of a Fibre Surface by Modifying the Fibre Material

Slovak University of Technology,
Faculty of Chemical and Food Technology,
Radlinského 9, 812 37 Bratislava, Slovak Republic
E-mail: anna.murarowa@stuba.sk

*Comenius University, Medical Faculty,
Špitálska 24, 813 72 Bratislava, Slovak Republic

Abstract

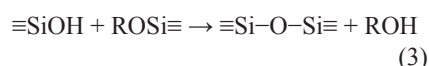
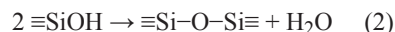
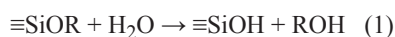
Fibres are used in various fields of social life. Several functional properties are required from them according to the purpose of use. Due to their chemical composition and macromorphological structure, functional properties of fibre materials mutually differ and thus limit their general use. The materials on the fibre surface represent a great challenge to increase their functionality. The modification of fibre surfaces by various physical and chemical procedures deliberately changes some functional properties of the surfaces and thus increases the possibilities of wider usage of fibres. In our research work, the surfaces of fibres were functionalised mainly by pigments and sol-gel, focusing on the wetting ability as well as electrical and thermal properties. Plasma processing and pigmentation causes faster wettability of fibre materials, whereas sol-gel modification causes a slower wettability compared to the original unmodified surface. A significant decrease in volume and surface resistivity of the samples by surface pigmentation was also indicated.

Key words: fibre material, functionalisation, surface, wetting ability, electrical resistivity, thermal conductivity.

Introduction

The surface materials of textile exhibit great potential for their structuralisation and functionalisation. There are many procedures for the structuralisation and functionalisation of fibre surfaces, and their selection depends on the purpose of the change. The functionalisation of the fibre surface material assumes that the material maintains its original properties. The functionalisation of fibre surface material depends on and is directly affected by surfaces structuralisation. We used plasma and laser modifications under various conditions for the structuralisation of the textile materials, which brought about important changes to the surface layers. Some procedures required combined methods to foster the effect of structuralisation. We created a more open structure in order to obtain the resulting chemical effects on the surfaces of the fibres, which was achieved by cold plasma radiation. Further surface modification of the irradiated textile materials we obtained by applying an inorganic-organic nano-sol containing SiO₂, which created hybrid inorganic-organic compositions on the polymer surface. Such compositions create transparent, solid and elastic surface layers with an added value [1 - 5].

The structuralisation of textile materials based on the polymer sol of SiO₂ represents a physico-chemical nano modification of the surface. The most used material is alcoxid Si(OR)₄. Hydrolysis and polycondensation react in a water environment according to the following equations (1 - 3):



Depending on the conditions of the reaction, an inorganic-organic polymer is created with linear branches or colloid elements. At a certain number and size of the polymer elements in relation to the colloid elements, the free movement inside the liquid is restricted. A network of appropriate elements is created, and the sol changes into a gel.

Low water content ($\text{H}_2\text{O}/\text{Si}(\text{OR})_4 \leq 4$), low temperature and the presence of an acid-based catalyst create perfect conditions for linear polymerisation. On the other hand, high water content ($\text{H}_2\text{O}/\text{Si}(\text{OR})_4 \gg 4$), higher temperature and alkali catalyst result in the creation of colloid SiO₂ elements [2 - 4].

Functionalisation of the fibre surface material is a deliberate physical or chemical modification of the surface in order to obtain qualitatively new properties. Nanotechnologies using various physical and chemical procedures meet such criteria [6 - 8].

This paper deals with the functionalisation of the surface fibre material of polyethyleneterephthalate (PET). Plasma in nitrogen atmosphere, laser energy effect, the sol-gel method, nano-pigment fixation on the surface and surface modification by pigmentation in combination with the sol-gel method were used to modify

the surfaces. The functionalisation of worm fibre materials carried out in our research was focused on such functional properties as electroconducting, thermal-conducting and wetting ability. The aim was to improve the surface properties of PET fibres.

Experimental

Structuralisation of the fibre surface material

1. Plasma surface modification of the PET textiles occurred at atmospheric pressure during a barrier corona discharge at a voltage of 10 kV, 5 kHz frequency, power of 30 W, and process energy of 4 J/cm². This process was carried out in an atmosphere of N₂ and air. Consequently, after plasma modification of the sol-gel was applied to the test samples.
2. Sol SiO₂ (Si(OEt)₄ + EtOH + HCl) was applied to the PET textile fabric by raising the substrate from the solution. A sol-gel film was created on the textile surface after the free alcohol evaporated and was thermally stabilized. Consequently, after plasma and sol-gel modification, the samples tested were irradiated by laser.
3. The source of laser light was a semi-conducting LDD 3.3 diode with an optic capacity of 25 mW and $\lambda = 690$ nm. The surface was activated for 10 minutes.
4. The samples tested were pigmented by Printex L-6 (carbon), Hombitec S-100 (TiO₂), Graphite (carbon black) and ALBO 615 (Al powder) nano-pigments with pigment content in

the pigmenting paste of 1, 3 and 5%. Apart from pigments, acrylic fixing reagent and wetting textile auxiliary means were used in the pigmenting paste.

- The samples tested were modified by nano-pigments according to point 4 and consequently by the sol-gel method according to point 2.

Test material

Reference samples of PET fabrics, according to ČSN standard 80 01 01 were used during the experiments.

Testing methods

Testing the contact angle of wetting

We applied a drop of water with a volume of 5 μl on the sample surface and measured the wetting contact angle. In order to measure the contact angle of wetting we used the See system method with a CCD camera and software for evaluating the real time of the actual drop profile count from the moment the drop was set on the fabric surface.

Testing the electrical volume and surface resistivity

The transport of electrical charge by the pigmented PET fabric surfaces was monitored by the flow method at a constant DC voltage with the use of a Keithley 617 Programmable Electrometer, and a TETTEX 2904/SA Guard Ring Capacitor. Next, the electrical volume and surface resistivities of the samples tested were determined. The current was measured after 1 minute of voltage connection. The values of volume and surface resistivity were calculated as the average of five measurements.

Testing of the thermal conductivity

The Alambeta device has an internal program related to a single layer mode, whose results should be considered conventional in comparative values. An



Figure 1. Change in time of the drop profile on the surface of the PET textile in 150 seconds.

Alambeta device was used to measure the thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$) of the test samples. The samples were conditioned at a temperature of 23 $^{\circ}\text{C}$ and a relative air humidity of 65%. The thermal conductivity was measured at a stabilised thermal flow through the PET fabric at an initial temperature of 33 $^{\circ}\text{C}$. The results measured are the averages of ten measurements executed.

Results and discussion

Assessing the contact angle of wetting

The samples tested should not be considered as homogenous multilayer objects. Figure 1 demonstrates the See system method used to evaluate the wettability of the structuralised surfaces of PET textiles with dependence on time, which determined the wetting contact angles.

Figure 2 shows the kinetics of the wetting of a plasma modified surface in a nitrogen atmosphere. The figure distinctively demonstrates that the wetting was considerably faster than that of an unmodified surface. The effect of plasma on wetting corresponds with the structural changes in the surface layer of the PET fibres caused by plasma. Plasma modification is the most effective method for the hydrophilisation of PET textile surface.

Sol-gel modification covered the structural changes on the sample's surface, caused by the plasma effect and displayed

the effect of sol-gel modification related to the kinetics of wetting in the opposite direction as compared with plasma modification alone. The contact angle of wetting is more than 90 $^{\circ}$ during an interval of up to 60 seconds, (Figure 2). The opposite effect of sol-gel surface modification related to wetting compared with plasma modification alone is caused by the presence of non-polar polymer SiO_2 sol-gel on the polymer surface and therefore a significant hydrophobisation of the textile. The effect of irradiation by a laser low capacity resource for 10 minutes in the PET textile sample, which was previously modified by plasma and sol-gel layer before fixation. This, in turn, resulted in an increase in the kinetics of the wettability above the level of the original unmodified PET textile.

We used chemically different pigments for the surface modification of the PET fibres. The kinetics of the wetting of the modified surfaces is presented in Figure 3. The dependences are similar in shape, although that for Hombitec S-100 is situated at the highest level and that for Al-powder at the lowest. We can say that Hombitec S-100 with a content of 1% in the pigment paste demonstrated a contact angle of wetting more than 10 $^{\circ}$ to 30 $^{\circ}$ greater in the given time than other pigments evaluated.

The surface modification of textile materials by pigments causes physical – chemical and geometric changes

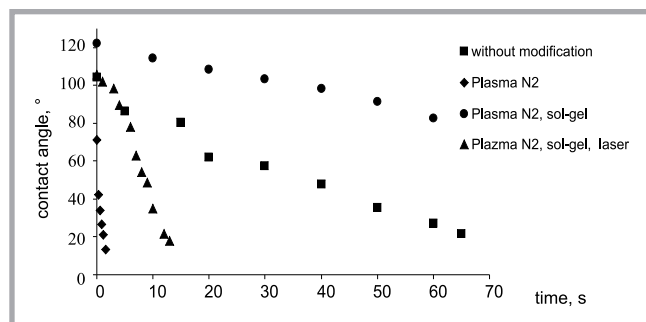


Figure 2. The kinetics of the wetting of the PET textile by water after different surface modification.

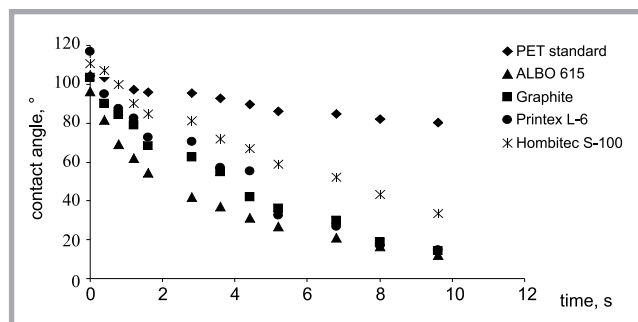


Figure 3. Kinetics of the wetting of the PET textile, modified on its surface by different types of pigments, with a content of 1%.

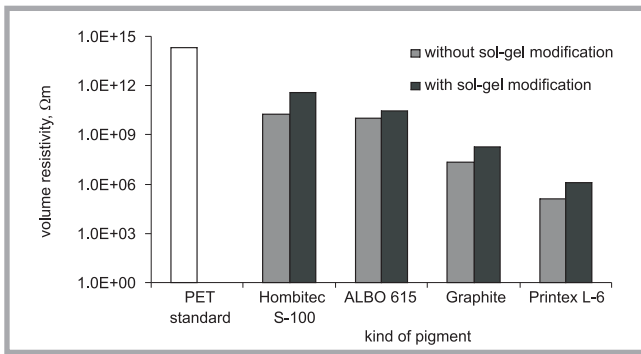


Figure 4. Dependency of volume resistivity of the PET textile on the kind of pigment used with and without sol-gel modification.

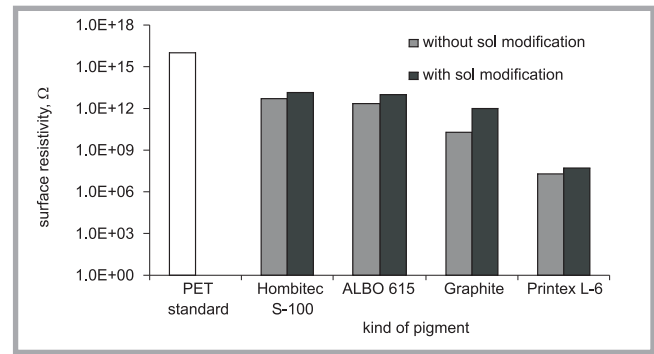


Figure 5. Dependency of surface resistance of the PET textile on the kind of pigment with and without sol-gel modification.

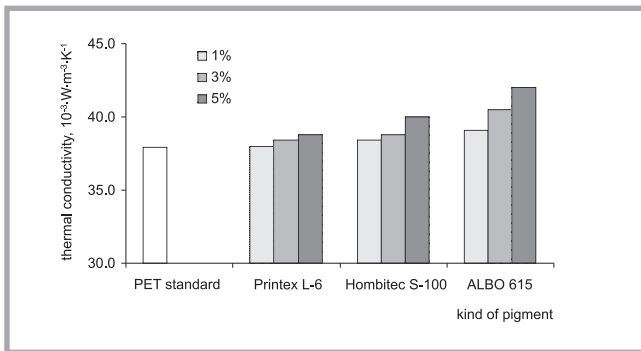


Figure 6. Dependence of the thermal conductivity of the modified PET textiles on the kind and content of pigments.

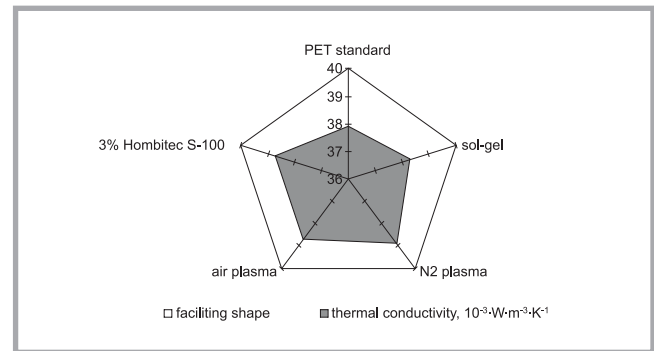


Figure 7. The effects of the kind of surface modification of the PET textiles on their thermal conductivity.

on their surfaces. Consequently, the surface properties change their values. The conditions of managing the surface modification of textile materials affect the qualitative and quantitative character of surface wetting. The surface modification of PET fabrics with pigments makes their surface hydrophilic.

Assessing the volume and surface electrical resistivity

The surfaces of the PET fabrics were pigmented by standard methods used during textile finishing and covered by polymer gel made from $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ using the sol-gel method. The pigments were selected taking into consideration changes in their electrical properties, especially the volume and surface resistance and the surface's electrostatic potential. For operative reasons it was necessary to prevent the accumulation of electrostatic charges on the textile material surfaces, and to allow the electrical resistance to reach an adequate level. The pigments used were electro-conductive, and had micro- and nano-dimensions.

The dependency of electrical volume and surface resistance on the type of pigment used for the PET fabric surface modification was evaluated and is presented in,

Figures 4 and 5. The dependence proves that Printex L-6 is highly efficient and qualitatively changes the material properties in regard to electrical resistivity. The effect of the remaining pigments used – graphite, ALBO 615 and Hombitec S-100 on the change of electrical properties is significantly smaller compared to Printex L-6. However, each pigmentation of the surfaces carried out by us decreased the electrical volume and surface resistance compared to that of the original unmodified PET fabric.

A tendency towards lower values of the volume and surface resistances was expected due to the sol-gel modification of the pigmented PET fabrics. Figures 4 and 5 illustrate the tendency towards a modest increase in these values by about 100 units. Such a modest increase preserves the qualitative character of the PET fabrics when considering their electrical properties. The sol-gel modification of pigmented fabrics should restrain pigment abrasion. This will be the subject of future experiments.

Assessing the thermal conductivity

The effect of the surface modification of the PET fabric by pigmentation was also evaluated considering the change of the

thermal-conductive properties. The thermal conductivity λ was assessed with dependence on the kind of pigment and pigment content in the pigmenting paste, (Figure 6). We indicated that the thermal conductivity of PET fabric with its surface modified by Printex L-6 and Hombitec S-100 pigments is at the level of the thermal conductivity of PET fabric without surface modification. A more important change in thermal conductivity occurred in PET fabric modified on its surface by ALBO 615 pigment, tending to higher values in comparison with PET fabric without surface modification. A higher content of ALBO 615 pigment caused an increase in thermal conductivity.

As can be seen, surface changes influence thermal conductivity. Plasma and pigment increase the thermal conductivity of PET standard, (Figure 7). It should be emphasised here that, as mentioned previously, due to the working mode of the Alambeta device, the results obtained are valid under the given circumstances of these experiments.

Conclusions

Deliberate surface modifications of PET fibre materials causes structural change

in the surface layers, and a corresponding change in the surface's functional properties. Our experiments proved the following:

1. Plasma modification is the most effective method for the hydrofilisation of the surface of PET fibre materials.
2. The laser effect on the surface of PET textile causes higher wetting ability compared to that of the original unmodified PET textile, probably due to the violating relief created on the material's surface.
3. Sol-gel surface modification of PET textile has a significant hydrophobic effect.
4. The pigmentation of the PET fibre surface material by nano-pigments qualitatively changed their electro-conductive character, even at a low pigment content.
5. The formation of sol-gel nano-film on the surfaces of the pigmented materials tested made the electro-conductive surface hydrofobic
6. The effect of sol-gel modification of PET fabrics, aiming to change the electrical properties of PET fabrics, is very modest, which corresponds with the decrease in hydrophilicity.
7. Hombitec S-100 - nano-pigment increases the thermal conductivity of PET fabrics with surface modification, when compared to unmodified PET fabrics. The environmental at conditions for heat transfer has changed by pigmentation.



Acknowledgments

This research was performed thanks to the Grant Agency of Slovakia VEGA (No.1/2451/05) and the Grant Agency APVV (No. 20-011404).

References

1. Amberg-Schwab S. Hoffmann M., Bader H.: *Kunststoffe*, 1996, 86, pp.600-664.
2. Textor T., Bahners T., Schollmeyer E.: *Technische Textilien* Vol. 45(2002) pp.169-172.
3. Textor T., Bahners T., Schollmeyer E.: *Technische Textilien* Vol. 44(2001) pp.304-306.
4. Kričevskij G.E.: *Chimičeskaja tehnologija tekstilnych materialov*, Moskva 2001, Tom 3.
5. Siegel J., Kotal V., Slepíčka P., Švorčík V.: *Chemické listy* Vol. 100(2006) p.642.
6. Seeram R. et al: *Electrospinning and Nanofibres*. National university of Singapore, Singapore, 2005, Hong Kong.

Received 15.11.2007 Reviewed 15.01.2008

Next XIPS

The 7th in series meeting

on the

X - Ray Investigation of Polymer Structure XIPS' 2007

is scheduled for the the second half of 2007

For further information please contact:

Prof. Andrzej Włochowicz Ph. D., D. Sc.

UNIVERSITY OF BIELSKO-BIAŁA
Faculty of Textile Engineering
and Environmental Protection
Institute of Textile Engineering and Polymer Materials
ul. Willowa 2, 43-309 Bielsko-Biała
tel. +48 33 8279 114, fax. +48 33 8279 100
e-mail: awlochowicz@ath.bielsko.pl

or

Prof. Janicki Jarosław Ph. D., D. Sc.

UNIVERSITY OF BIELSKO-BIAŁA
Faculty of Textile Engineering
and Environmental Protection
Institute of Textile Engineering and Polymer Materials
ul. Willowa 2, 43-309 Bielsko-Biała
tel. +48 33 8279 114, fax. +48 33 8279 100
e-mail: jjanicki@ath.bielsko.pl

