Lidija Černe[1], Barbara Simončič[1], Odon Planinšek[2]
[1] Oddelek za tekstilstvo, Naravoslovnotehniška fakulteta, Univerza v Ljubljani
[2] Fakulteta za farmacijo, Univerza v Ljubljani

Uporaba Zismanovega modela za določitev kritične površinske napetosti apretiranih vodo- in oljeodbojnih tekstilij

Izvirni znanstveni članek

Poslano *april 2008* • Sprejeto *junij 2008*

Izvleček

Namen raziskave je bil preučiti uporabnost Zismanovega modela za določitev kritične površinske napetosti, γ_c, apretiranih vodo- in oljeodbojnih ploskovnih tekstilij. V raziskavo sta bili vključeni dve bombažni tkanini v vezavah keper in platno, ki sta bili apretirani z olje- in vodoodbojnim sredstvom na podlagi fluoroogljikovih polimerov ter kombinacijo olje- in vodoodbojnega ter vrhunskega apreturnega sredstva. Na tkaninah so bili izmerjeni statični in dinamični stični koti različnih n-alkanov, njihove vrednosti pa skupaj uporabljene za grafično določitev γ_c . Po pričakovanju so najnižje vrednosti γ_c pripadale tkaninam apretiranim s fluoroogljikovimi polimeri. Dodatek vrhunskega apreturnega sredstva v apreturi kot tudi povečanje odprte površine tkanine sta povzročila povečanje vrednosti γ_c. Tudi s pranjem apretirane tkanine se je vrednost γ_c povečala, kar pomeni, da se je njena odbojnost zmanjšala. Termična obdelava po pranju, ki je bistveno pripomogla k boljši urejenosti apreturnega filma, je vplivala na ponovno znižanje vrednosti γ_c in s tem na ponovno povečanje odbojnosti tkanine. Smiselnost dobljenih rezultatov je potrdila možnost združitve vrednosti statičnih in dinamičnih stičnih kotov kljub različnim načinom njihove določitve in s tem uporabnost Zismanovega modela za grafično določitev vrednosti γ_c apretirane ploskovne tekstilije.

Ključne besede: ploskovna tekstilija, vodo- in oljeodbojna apretura, kritična površinska napetost, Zismanov model, stični kot, goniometrična metoda, metoda tankoplastnega pronicanja.

The use of Zisman model in determining the critical surface tension of the water and oil repellent finished textiles

Original Scientific Paper

Received *April 2008* • Accepted *June 2008*

Abstract

The object of this research was to investigate the use of Zisman model in determining the critical surface tension, γ_c, of finished water and oil repellent textiles.

The research included two cotton fabrics in plain and twill weave, which were finished with oil and water repellent finish based on fluorocarbon polymers, as well as with a combination of oil and water repellent and easy-care finishes. The static and dynamic contact angles of the n-alkanes were measured on the textiles and combined to graphically determine the value γ_c. As expected, the lowest values of γ_c were obtained for fabrics treated with the fluorocarbon polymers. The addition of the easy-care finish as well as the increase in open surface within the fabric, both increased the value γ_c. The value of γ_c also increased with washing of the chemically finished fabrics, what indicates the lowering of its repellency. Heat treatment after the washing, which dramatically contributed towards better distribution of the finishing network, once again contributed to reduction of the value γ_c. The consistency of the results obtained confirmed the possibility of joining the values of static and dynamic contact angles, despite the differences in their meth-

Vodilni avtor/corresponding author:
dr. Barbara Simončič
tel.: +386 1 200 32 31
e-mail: barbara.simoncic@ntf.uni-lj.si

ods of acquisition, and hence also confirmed the validity of Zisman model to graphically determine the value γ_c of finished flat fabrics.

Key words: flat textile, oil and water repellent finish, critical surface tension, Zisman model, contact angle, goniometry, thin-layer wicking

Introduction

Chemical finishing involves the latest textile valorisation processes. Through these the fibres are coated with a range of different functional finishes, such as easy-care and durable press, softening, antimicrobial, antistatic, flame-retardant, and water and oil repellent and soil-release finishes. With these we can greatly improve the comfort of natural and synthetic fibres and greatly increase the added value of the final products [1–5].

The modification of the fibre surface through chemical finishing causes changes in the physical and chemical fibre properties. The important property is the surface free energy, which quantitatively defines surface characteristics. From this value we can deduct the fibre wetting and wicking properties. To what extent the surface free energy will be affected by the application of finishes depends on the chemical structure of the latter. While nonpolar finishes lower the surface free energy and hence reduce fibre wetting, polar finishes modify this parameter only depending on the presence of functional groups in the agent.

We cannot directly measure the fibre surface free energy, but we can calculate it from the results of the measurements of contact angle, θ, formed by different polar and nonpolar liquids on the textile surface. For this we use Fowkes, Owens-Wendt-Kaelble, Wu, van Oss-Chaudhury-Good, Li-Neumann-Kwok and Zisman model [6]. The surface free energy can also be determined by measuring the rate of thin-layer wicking of liquid into the porous structure of the solid, according to van Oss [7] and Chibowski [8].

A great contribution towards the rational use of contact angle measurements came from Zisman and his co-workers [9]. He investigated the surface wettability of low energy solids. He dis-

1 Uvod

Kemijska apretura vključuje najsodobnejše postopke plemenitenja tekstilij, pri katerih na vlakna nanesemo različna funkcionalna apreturna sredstva, kot so mehčalna, vrhunska, protimikrobna, antistatična, ognjevarna, vodo- in oljeodbojna ter sredstva za lažje odstranjevanje nečistoč. Z njimi lahko v veliki meri izboljšamo uporabne lastnosti naravnih in sintetičnih vlaken ter s tem pomembno vplivamo na povečanje dodane vrednosti končnih izdelkov [1–5].

Modifikacija površine vlaken s kemijskimi apreturnimi sredstvi vpliva na spremembo fizikalnih in kemijskih lastnosti vlaken. Med njimi je pomembna površinska prosta energija, ki kvantitativno opiše površinske lastnosti, iz njene vrednosti pa lahko sklepamo na omočljivost vlaken. V kolikšni meri se bo površinska prosta energija spremenila zaradi nanosa apreturnega sredstva, je odvisno od njegove kemijske strukture. Medtem ko nepolarna apreturna sredstva znižajo površinsko prosto energijo vlaken in s tem zmanjšajo njihovo omočljivost, pa je njena sprememba pri nanosu polarnih apreturnih sredstev odvisna od prisotnih funkcionalnih skupin v sredstvu.

Površinske proste energije vlaken ne moremo neposredno izmeriti, lahko pa jo izračunamo iz rezultatov meritev stičnih kotov, θ, ki jih različne polarne in nepolarne tekočine tvorijo na površini tekstilije. Pri tem lahko uporabimo Fowkes-ov, Owens-Wendt-Kaelblejev, Wu-jev, Van Oss-Chaudhury-Good-ov, Li-Neumann-Kwok-ov ali Zisman-ov model [6]. Površinsko prosto energijo je možno določiti tudi na podlagi meritev hitrosti tankoplastnega pronicanja tekočine v porozno strukturo trdne snovi, ki temelji na modelih van Ossa [7] in Chibowskega [8].

K racionalni uporabi rezultatov meritev stičnih kotov je veliko prispeval Zisman s sodelavci [9]. Preučeval je omočljivost površin trdnih snovi nizkih energij. Ugotovil je, da je cos θ ponavadi premosorazmerno odvisen od površinske napetosti homologne serije čistih tekočin, zato je predlagal naslednjo odvisnost:

$$\cos\theta = a_Z - b_Z\gamma_L = 1 - \beta_Z(\gamma_L - \gamma_c) \qquad (1)$$

V enačbi (1) sta a_Z in b_Z odsek na ordinatni osi in naklon premice, γ_L je površinska napetost tekočine in γ_c kritična površinska napetost.

Kritična površinska napetost, γ_c, je definirana kot najvišja površinska napetost, ki jo lahko ima tekočina, da še popolnoma omoči trdno snov ($\theta = 0°$) [6, 9]. Ta površinska napetost tekočine je enaka γ_c in je merilo površinske proste energije trdne snovi. Tekočine z $\gamma_L < \gamma_c$ se po površini trdne snovi popolnoma razširijo in tvorijo $\theta = 0°$, tekočine z $\gamma_L > \gamma_c$ pa na površini neporozne trdne snovi oblikujejo kapljo s končnim stičnim kotom večjim od 0°. Ker je pri cos $\theta = 1$ vrednost $\gamma_L = \gamma_c$, lahko enačbo (1) zapišemo kot:

$$\gamma_c = \frac{a_Z - 1}{b_Z} \qquad (2)$$

covered that the cosine of θ is normally directly proportional to the surface tension of the homologous series of liquids and hence suggested the the following relationship (Equation 1).

In Equation 1, a_z and b_z are the intersection on ordinate axis and the slope of the line, γ_L is the liquid surface tension and γ_c the critical surface tension.

The critical surface tension, γ_c, is defined as the maximum surface tension of liquid still allowing it to completely wet the solid (θ = 0°) [6, 9]. This surface tension is equal to γ_c and is a measurement of the solid surface free energy. Liquids with $\gamma_L < \gamma_c$ spread completely over the solid surface and generate θ = 0°; liquids with $\gamma_L > \gamma_c$ form a droplet with end contact angle greater than 0° on the surface of non-porous solid. Since $\gamma_L = \gamma_c$ for cos θ = 1, Equation (1) could be written as (Equation 2).

According to Equations (1) and (2), we can determine γ_c graphically by measuring the contact angles formed between the solid and various hydrocarbons with increasing surface tension, γ_L. For this reason, in the plot of cos θ versus γ_L, we draw a straight line through the experimental points, determine its slope and intersection on ordinate axis and calculate γ_c with the use of Equation (2). Zisman model is practically useful towards the determination of γ_c for nonpolar solids when using nonpolar liquids, such as n-alkanes. It is less appropriate for the determination of γ_c of polar solids with polar liquids.

From the literature [6, 10–14] it is apparent that Zisman model has already been applied to the determination of γ_c of perfluorated and silanized solids when combined with homogenous series of liquids, such as alkanes, alkylbenzenes and siloxanes, whose surface tensions are below 35 mN/m. Because of the simplicity of the model, its application towards determining the absorptive characteristics of finished water and oil repellent fabrics is of great technological relevance. It involves quick and simple graphical determination of fabric surface free energy and factors affecting its change without the use of complicated models for surface free energy components calculation. However, a limitation thereof arises due to the porous structure of textiles. On porous surfaces

V skladu z enačbama (1) in (2) lahko γ_c določimo grafično na podlagi meritev stičnih kotov, ki jih na površini trdne snovi tvorijo različni ogljikovodiki z naraščajočo površinsko napetostjo, γ_L. V ta namen v grafu odvisnosti cos θ od γ_L skozi eksperimentalne točke narišemo premico, ji določimo naklon in odsek na ordinatni osi ter s pomočjo enačbe (2) izračunamo γ_c. Zismanov model ima praktično uporabnost pri določitvi γ_c nepolarnih trdnih snovi z uporabo nepolarnih tekočin, na primer n-alkanov, veliko manj pa je uporaben za določitev γ_c polarnih trdnih snovi s polarnimi tekočinami.

Iz literaturnih virov [6, 10–14] je razvidno, da se je Zismanov model že uveljavil za določitev γ_c perfluoriranih in silaniziranih trdnih neporoznih snovi z uporabo homogenih serij tekočin, in sicer alkanov, alkilbenzov in siloksanov, katerih površinske napetosti so nižje od 35 mN/m. Zaradi preprostosti modela ima njegova vpeljava za določitev omočljivosti apretiranih vodo- in oljeodbojnih tekstilij velik tehnološki pomen. Z njim lahko namreč brez uporabe zapletenih modelov za določitev komponent površinske proste energije trdne snovi hitro in preprosto grafično določimo površinsko energijo tkanine ter dejavnike, ki vplivajo na njeno spremembo. Vendar pa pri tem obstaja omejitev povezana s porozno strukturo tekstilij. Na porozni površini namreč tekočina oblikuje kapljo stalne oblike s statičnim stičnim kotom le v primeru, če je prisotna kapilarna depresija, ki prepreči, da bi tekočina pronicala v pore. Pogoj za to je stični kot tekočine večji od 90°. V primeru stičnega kota manjšega od 90°, poteče kapilarni dvig, zaradi katerega tekočina pronica v pore trdne snovi z določenim dinamičnim stičnim kotom, ki je v območju od 0 do 90°. Če za določitev γ_c uporabimo homogeno serijo nepolarnih tekočin z naraščajočimi površinskimi napetostmi, kot to priporoča Zismanov model, bodo tekočine z nižjimi površinskimi napetostmi pronicale v tekstilijo, tiste z višjimi površinskimi napetostmi pa na njeni površini oblikovale kapljo. Če za grafično predstavitev uporabimo le vrednosti statičnih oziroma dinamičnih stičnih kotov tekočin, je število eksperimentalnih točk premajhno, kar vzbuja dvom o pravilnosti lege premice skozi te točke.

V literaturnih virih še nismo zasledili hkratne uporabe statičnih in dinamičnih kotov, saj se eksperimentalni metodi za njihovo določitev med seboj bistveno razlikujeta. Zato je bil namen raziskave preučiti možnost združitve vrednosti statičnih in dinamičnih stičnih kotov za grafično določitev vrednosti γ_c apretirane ploskovne tekstilije ter s tem potrditi ali ovreči uporabnost Zismanovega modela pri plemenitenju tekstilij.

2 Eksperimentalni del

2.1 Tkanine

Pri eksperimentalnem delu smo uporabili dve 100 % bombažni tkanini, in sicer eno v vezavi keper (tkanina A) in drugo v veza-

the liquid forms a droplet of stable shape with a static contact angle only in case of capillary depression, as this prevents the liquid from wicking into the pores. The necessary condition for this to happen is a liquid contact angle greater than 90°. In the event of contact angles smaller than 90°, capillary action takes place, due to which the liquid penetrates into the pores of the solid at a given dynamic contact angle between 0 and 90°. If for the determination of γ_c we use a homogenous series of nonpolar liquids with increasing surface tensions, as suggested by Zisman model, the liquids with lower surface tension will penetrate into the textile, while those with higher surface tension will form a droplet on the fabric surface. If we only use the static or dynamic contact angles for the graphical presentations, the number of experimental points is too small and generates uncertainty about the relevancy of the line drown through these points.

In the literature we still have not found evidence that static angles could be used in conjunction with dynamic angles, as the experimental methods for their determination are very different. Because of this, the object of this research was to investigate the possibility of joining the values of static and dynamic contact angles for the graphical determination of the value γ_c of finished fabrics and hence to confirm or deny the applicability of Zisman model in the finishing of textiles.

2 Experimental

2.1 Fabrics

In the experimental work we used two 100 % cotton fabrics, one woven in twill weave (fabric A) and one in plain weave (fabric B). The construction parameters of the fabrics are given in Table 1. The fabrics were first bleached, mercerized and neutralized, and so prepared for finishing.

2.2 Finishing

*The fabrics were finished with a water and oil repellent finish (finish 1) and with a multifunctional finish which consisted of water and oil repellent and easy-care finishes (finish 2). As a water and oil repellent finish we used fluorovi platno (tkanina B). Konstrukcijski parametri tkanin so podani v preglednici 1. Tkanini sta bili predhodno beljeni, merceizirani in nevtralizirani ter tako pripravljeni za apretiranje.

Table 1: Structural properties of fabrics.

Fabric	T_t (*tex*)		Density[a)] (n/cm)		Weave	Mass per unit area (g/m^2)
	warp	weft	warp	weft		
A	28	28	46	23	twill	216
B	28	28	28	23	plain	165

[a)] *Density is expressed as a number of threads on cm.*

2.2 Apretiranje

Na tkanine smo nanesli olje- in vodoodbojno apreturo (apretura 1) ter večnamensko olje- in vodoodbojno ter vrhunsko apreturo (apretura 2). Kot olje- in vodoodbojno sredstvo smo uporabili fluorogljikove polimere (FCP), kot vrhunsko apreturno sredstvo brezformaldehidni derivat imidazolidinona (BDI) in kot aditiv modificirani aminofunkcionalni polisiloksan (APS). Za povečanje pralne obstojnosti FCP polimernega filma na blagu smo dodali poliizocianatno reaktivno zamreževalo (RZ). Kot katalizator (K) pri suhem zamreženju BDI smo uporabili magnezijev klorid ($MgCl_2 \times 6\ H_2O$). Apreturna sredstva in dodatki so bili dobavljeni pri proizvajalcu CHT (Nemčija). Vrednost pH impregnirnih kopeli od 5 do 6 smo uravnali z ocetno kislino (CH_3COOH).

Pri apretiranju smo uporabili impregnirni postopek, ki smo ga izvedli s polnim omakanjem na dvovaljčnem fularju pri sobni temperaturi, sledilo je ožemanje med valji fularja z 82 ± 2 % ožemalnim učinkom, nato sušenje pri temperaturi do 110 °C in kondenziranje 1,5 minute pri temperaturi 150 °C v sušilno-kondenzacijskem stroju. Kombinacije in koncentracije apreturnih sredstev v impregnirni kopeli so prikazane v preglednici 2. Na tkanino A smo nanesli apreturi 1 in 2 (vzorca sta označena z A-1 in A-2), na tkanino B pa le apreturo 1 (vzorec je označen z B-1).

Table 2: Concentration, c, of finishing agents.

Finish	*c* (g/l)				
	FCP	RZ	BDI	K	APS
1	40	2.5	0	0	0
2	40	2.5	80	15	10

2.3 Nega apretiranih tkanin

Pranje apretirane tkanine smo izvedli v gospodinjskem pralnem stroju pri 60 °C z 18 g/l pralnega praška Persil® color power 1,5 ure. Pranje smo ponovili desetkrat. Vzorce smo po končanem

carbon polymers (FCP), while as an easy-care finish we used formaldehyde-free derivates of imidazolidine (BDI) and, as an additive, modified amino functional polysiloxane (APS). To increase the wash resistance of the FCP on the fabric, we added polyisocyanate reactive crosslinking agent (RZ). As a catalyst (K) of the crosslinking of the BDI in pad-dry-cure method, we used magnesium chloride ($MgCl_2 \times 6 H_2O$). The finishing media and additives were purchased from the supplier CHT (Germany). The pH values of the impregnation baths, ranging from 5 to 6, were balanced with acetic acid (CH_3COOH).

For the finishing we used an impregnation process, which was carried out by fabric padded at 82 ± 2% wet pickup with the finishing agents at room temperature, followed by drying at temperatures up to 110 °C and finally condensation for 1.5 minutes at a temperature of 150 °C in a dryer. The composition and concentration of the finishes in the impregnation bath is shown in Table 2. Fabric A was treated with finishes 1 and 2 (the samples are labelled as A-1 and A-2), while fabric B only with finish 1 (sample B-1).

2.3 Care of the finished fabric

Washing of the finished fabrics was carried out for 1.5 hours in a domestic washing machine at 60 °C with 18 g/l of the washing powder Persil® color power. The washing was repeated 10 times. The samples were afterwards rinsed out with cold water 6 times and then followed water pump out, a short squeezing and air drying. The washed samples were then heat treated in a dryer at 100 °C for 3 minutes.

programu še 6-krat spirali s hladno vodo. Sledilo je črpanje vode in kratko ožemanje ter nato sušenje na zraku. Oprane vzorce smo nato toplotno obdelovali v sušilno-kondenzacijskem stroju pri 100 °C 3 minute.

2.4 Meritve stičnih kotov tekočin

Statični stični koti

Stične kote sedeče kaplje tekočine na površini tkanine (slika 1) smo določili goniometrično z aparatom FIBRO DAT 500/1100 (slika 2). Med tekočinami smo izbrali n-alkane z naraščajočo površinsko napetostjo, in sicer od n-pentana (C5) do n-heksadekana (C16), mešanico n-heksadekana in parafinskega olja v razmerju 35 : 65 (C16/PO) ter parafinsko olje (PO). Tekočine smo kupili pri proizvajalcu Aldrich Co. Lastnosti tekočin so zbrane v preglednici 3.

Meritve smo opravili tako, da smo na površino tkanine z mikropipeto avtomatsko nanašali kaplje tekočine dovolj majhnega volumna (do 8 µl), da smo se tako izognili deformaciji oblike kaplje zaradi gravitacije. S pomočjo slikovne analize smo časovno spre-

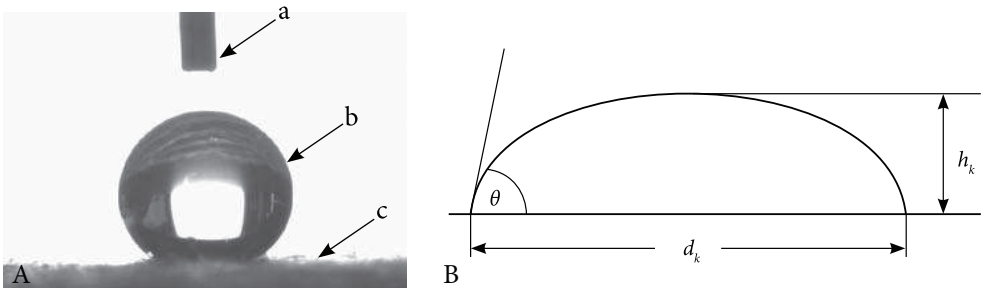

Figure 1: Snap-shot of liquid drop deposited on textile surface (A) and scheme of sessile drop dimensions (B). a – needle, b – sessile drop, c – textile surface.

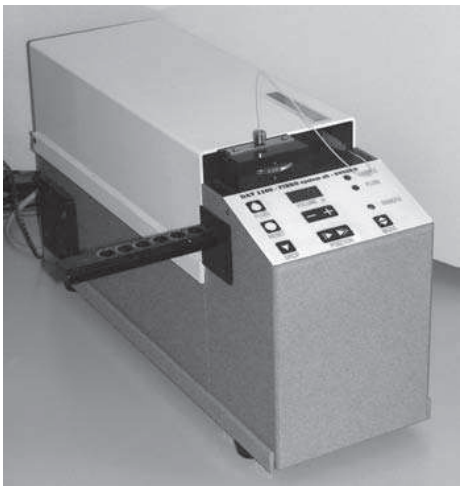

Figure 2: Contact angle apparatus FIBRO DAT 500/1100 (Fibro, Sweden).

Table 3: Surface tension, γ_L, viscosity, η, and density, ρ, of liquids at 20 °C [7, 15].

Liquid	Abbrev.	γ_L (mN/m)	η (mPa s)	ρ (g/cm³)
n-pentane	C5	16.0	0.234	0.626
n-hexane	C6	18.4	0.317	0.661
n-heptane	C7	20.1	0.410	0.684
n-octane	C8	21.6	0.541	0.699
n-nonane	C9	22.9	0.713	0.717
n-decane	C10	23.8	0.907	0.730
n-dodecane	C12	25.4	1.493	0.749
n-tetradecane	C14	26.6	2.322	0.763
n-hexadecane	C16	27.5	3.451	0.773
n-hexadecane/paraffin oil mix (35 : 65)	C16/ PO	28.7	– [a)]	– [a)]
Paraffin oil	PO	31.2	110–230	0.838

[a)] *No reference data.*

2.4 Measurement of liquid contact angles

Static contact angles

The static contact angles of liquid droplets on the fabric surface (Figure 1) were determined goniometrically with the apparatus FIBRO DAT 500/1100 (Figure 2). For the liquids we picked n-alkanes with increasing surface tension, from n-pentane (C5) to n-hexadecane (C16), a mixture of n-hexadecane and paraffin oil in a ratio of 35 : 65 (C16/PO) and paraffin oil (PO). The liquids were purchased from the supplier Aldrich Co. The liquid properties are collected in Table 3.

For the measurements to take place, we used a micrometric syringe to position drops of liquid of relatively small volume (up to 8 µl), in order to avoid deformations due to gravity, on the fabric surface. With the help of photographic analysis we followed the changes in height, diameter, surface area and volume of the droplets. The contact angle, θ , was determined with the height-width method [16, 17] according to the[6], (Equation 3), where h_k is the height of the droplet and d_k its width.

Static contact angles were determined for the liquids that did not spread over the fabric surface and that rather formed stable droplets. On the basis of the contact angle measurements of these liquids in the period of time between 0 mljali spreminjanje višine, premera, ploščine in volumna kaplje. Stični kot, θ, smo določili z metodo višina-širina [16, 17] po naslednji enačbi [6]:

$$\tan\frac{\theta}{2} = \frac{2h_k}{d_k} \qquad (3)$$

kjer je h_k višina kaplje in d_k širina kaplje.

Statične stične kote smo določili za tekočine, ki se po površini tkanine niso razširjale, temveč so oblikovale kaplje stalne oblike. Na podlagi meritev stičnih kotov teh tekočin v časovnem območju od 0 do 60 sekund, smo njihove ravnotežne stične kote določili kot povprečne vrednosti kotov, dobljenih v časovnem območju od 30 do 60 sekund. Če se ravnotežje po 30 sekundah meritev ni popolnoma vzpostavilo, smo vrednosti stičnih kotov podali kot približne. Zaradi eksperimentalnih napak, ki bi lahko bile posledica hrapavosti in heterogenosti površine uporabljenih tkanin, smo za vsako tekočino opravili najmanj deset meritev stičnih kotov, pri čemer smo tekočino nanašali na različna mesta tkanine, kot rezultat pa smo podali srednjo vrednost stičnega kota z natančnostjo ±3°. Meritve smo opravili pri temperaturi 20 °C.

Metoda tankoplastnega pronicanja

Metoda tankoplastnega pronicanja (TLW), ki jo je razvil van Oss s sodelavci [7], pozneje pa sta jo preoblikovala Chibowski in Holysz [8, 18], temelji na fenomenu pronicanja tekočine v porozno strukturo trdne snovi, adherirane na steklen nosilec. Z njo lahko na podlagi meritev hitrosti tankoplastnega pronicanja tekočine določimo parametre poroznosti ploskovne tekstilije [19, 20] kot tudi

and 60 seconds, we obtained the average values of their balanced contact angles in the period between 30 and 60 seconds. If the equilibrium did not fully balance out after 30 seconds, we indicated the results as approximate. Because of experimental errors, which could arise due to the surface roughness and heterogeneity of the fabrics used, we carried out at least 10 measurements for each liquid, whereby the liquid was placed on different spots on the fabric. The quoted result is then the mean value with an accuracy of ± 3°. The measurements were carried out at a temperature of 20 °C.

Thin-layer wicking method

The thin-layer wicking method (TLW), developed by van Oss et al [7] and further elaborated by Chibowski and Holysz [8, 18], is based on the phenomenon of liquid wicking into the porous structure of a solid deposited on a glass plate. This way, by measuring the thin-layer wicking rate, we can determine the porosity parameters of the fabric, as well as the contact angle, θ, at which the liquid penetrates into the pores of the fabric [19, 20]. θ is the dynamic contact angle, which can be taken under given conditions as being equal to Young contact angle. This allows us, through correct application of the thin-layer wicking method, to use the value θ to calculate the surface free energy of the solid.

The TLW measurements were carried out with the use of a tensiometer K12 (Krüss, Germany) and software Krüss 121 (Figure 3). Just like for the static contact angle measurements, we used n-alkanes with increasing surface tension (Table 3). Based on the measurements of the liquid mass, m, rising into the pores of the vertically placed fabric sample, versus time, t, we determined the rate of capillary action, as defined by Washbourn equation [21], (Equation 4).

In Equation 4, m^2/t is the rate of capillary rise, ρ is the liquid density, θ the contact angle between the liquid and the pore walls, and C the constant depending on the porous structure of the fabric.

In Equation 4 there are two unknowns, C and θ. We solved the difficulties presented by the existence of two unknowns, C and θ, according to van Oss, whereby we determined C by assum-

Figure 3: Tensiometer K12 (Krüss, Germany).

stični kot, θ, s katerim tekočina pronica v pore ploskovne tekstilije. θ je dinamični stični kot, ki ga lahko pri določenih pogojih enačimo z ravnotežnim Young-ovim stičnim kotom. To daje možnost, da ob pravilni izvedbi metode tankoplastnega pronicanja vrednosti θ uporabimo za izračun površinske proste energije trdne snovi.

Meritve TLW smo izvedli s pomočjo procesnega tenziometra K12 (Krüss, Nemčija) in programske opreme Krüss 121 (slika 3). Tako kot pri meritvah statičnih stičnih kotov smo za merjenje uporabili n-alkane z naraščajočo površinsko napetostjo (preglednica 3). Na podlagi meritev naraščanja mase tekočine, m, ki se dviga v pore vertikalno postavljenega vzorca tkanine, v odvisnosti od časa, t, smo določili hitrost kapilarnega dviga, ki jo opiše modificirana Washburnova enačba [21]:

$$m^2 = \frac{C\rho^2\gamma_L \cos\theta}{\eta}\, t \qquad (4)$$

V enačbi (4) je m^2/t hitrost kapilarnega dviga, ρ je gostota tekočine, θ stični kot, ki ga oblikuje tekočina na stenah por, in C konstanta trdne snovi, v našem primeru tkanine, ki je odvisna od njene porozne strukture.

V enačbi (4) sta dve neznanki, prva je C in druga θ. Enačbo smo v skladu s priporočili van Ossa rešili na tak način, da smo pri določitvi konstante C uporabili tekočino, v našem primeru n-pentan, za katero smo predpostavili, da se spontano razširja po površini trdne snovi in je zato $\cos\theta = 1$. Vrednost C, ki se na ta način izračuna iz enačbe (4), smo uporabili za izračun $\cos\theta$ tekočin, v našem primeru višjih n-alkanov, ki se po površini iste trdne snovi niso razširjali spontano in so zato oblikovali $\cos\theta < 1$.

Tenziometrične meritve smo izvedli tako, da smo krajši rob vzorca vpeli v nosilec tako, da je bila njegova lega vzporedna površini tekočine (slika 4). Po vzpostavitvi stika vzorca s tekočino smo pri

ing that n-pentane spontaneously spreads on the surface of the solid and therefore forms a cos θ = 1. The value of C, which is then calculated from Equation 4, is subsequently used to calculate cos θ for the higher n-alkanes, which do not spontaneously spread on the fabric surface and which hence possess a cos θ < 1.

To carry out the tensiometric measurements, we gripped the short side of the sample in the holder so that it was positioned perpendicular to the liquid surface (Figure 4). After the contact between the sample and the liquid, we measured the mass of absorbed liquid at time intervals until the sample was saturated with the liquid. For each fabric sample we carried out at least 10 measurements at 20 °C for each individual liquid, from which we gave the results as the average value measured.

3 Results and discussion

In Table 4 and in Figure 5 we show the results of the contact angle measurements of the n-alkanes on the surface of samples A-1, A-2 and B-1. From the results it is evident that finishing process, textile care and fabric construction parameters [22] all influence the absorption rate. While on the surface of the A-1 sample all n-al-

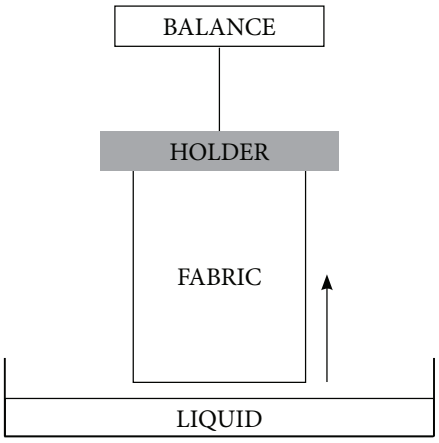

Figure 4: Schematic description of thin layer wicking into the vertical set sample. ↑ represents the direction of liquid penetration.

različnih časih merili maso navzete tekočine toliko časa, dokler se vzorec ni nasitil s tekočino. Za vsak vzorec tkanine smo s posamezno tekočino opravili najmanj 10 meritev pri temperaturi 20 °C ter kot rezultat podali povprečno vrednost meritev.

3 Rezultati in razprava

V preglednici 4 in na sliki 5 so predstavljeni rezultati meritev stičnih kotov n-alkanov na površini vzorcev A-1, A-2 in B-1. Iz rezultatov je razvidno, da tako apretura, način nege kot tudi konstrukcij-

Table 4: Static contact angles, θ, of n-alcanes obtained with FIBRODAT on the finished fabrics A and B.

Liquid	θ [a] (°)						
	A-1 [b]					A-2 [c]	B-1 [d]
	0P [e]	1P	1P+T [f]	10P	10P+T		
C10	98.2	/ [g]	≈ 97.7	/	/	/	/
C12	106.7	/	105.2	/	≈ 86.2	/	/
C14	107.6	/	105.0	/	102.1	/	≈ 96.0
C16	108.8	/	106.3	/	105.5	≈ 82.3	≈ 108.7
C16 / PO	116.0	110.9	112.6	≈ 94.7	109.4	111.7	112.0
PO	124.3	120.3	118.1	113.4	115.2	118.1	119.4

[a] *Average values of 10 measurements between 30 and 60 s.*

[b] *A-1 – fabric in twill weave, finished with FCP,*

[c] *A-2 – fabric in twill weave, finished with multifunctional finish,*

[d] *B-1 – fabric in plain weave, finished with FCP.*

[e] *P – number of washing cycles.*

[f] *T – heat treatment after washing.*

[g] *Capillary sorption.*

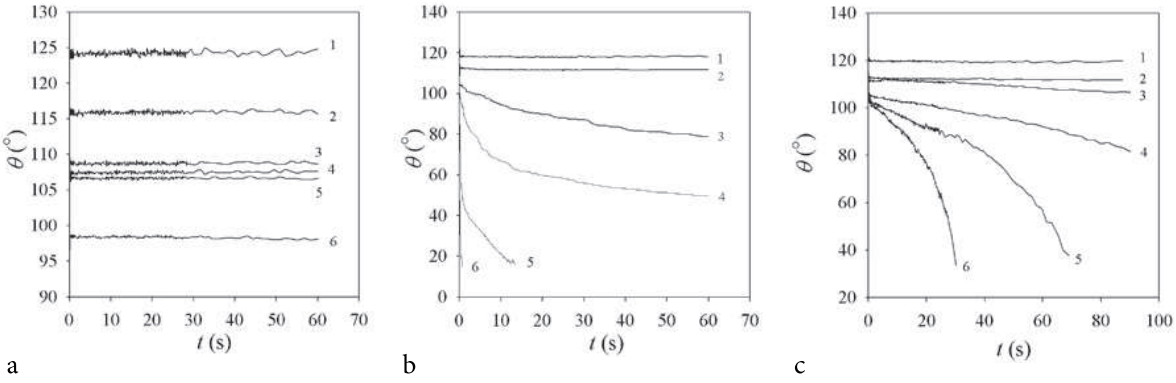

Figure 5: Time dependence of contact angles, , of some n-alcanes on samples A-1 (a), A-2 (b) and B-1 (c). 1 – PO, 2 – C16/PO, 3 – C16, 4 – C14, 5 – C12, 6 – C10.

kanes higher than C9 (Figure 5a) formed stable contact angles, on samples A-2 and B-1 only C16/PO and PO did so (Figures 5b and 5c). For boundary cases, such as C16 on sample A-2, and C14 and C16 on sample B-1, we found that eventually the contact angles as well as the droplet volume decreased over time, while the drop surface remained unchanged. This indicates that the liquid partially penetrated into the fabric pores, though it did not spread over its surface. For these liquids we indicated the measured contact angles as approximate (Table 4).

In Figure 6 we show the measurements of the rate of thin-layer wicking of the n-alkanes into the samples A-1, A-2 and B-1. From the values of m^2/t of n-pentane for each sample we obtained the constant, C, through Equation 3 and from m^2/t of higher n-alkanes we obtained the dynamic contact angles. The results are collected in Tables 5 and 6. From the comparison between the contact angles in Tables 4 and 6, we can in this case discredit the rule that a n-alkane which does not rise into the vertically placed sample due to capillary depression forms a static contact angle on the fabric surface. C9, C10 and C12 did not, for instance, rise into sample B-1 when applying the TLW method, while their pendant droplets in the goniometric measurements did penetrate into the sample porous structure. Based on these results, we decided to include also those static contact angle values which were indicated as approximate in Table 4 into all further consideration.

For the determination of γ_c for each sample according to Zisman model, we graphically pre-

Table 5: Constants, C, of A-1, A-2 and B-1 samples, calculated from Eq. (4) from capillary sorption velocities of n-pentane into the vertical positioned samples.

Sample [a]	Treatment	C ×10^7 (cm^5)
A-1	0P [b]	1.397
	1P	2.704
	1P+T [c]	1.826
	10P	3.256
	10P+T	2.448
A-2	0P	1.777
B-1	0P	0.445

[a] A-1 – fabric in twill weave, finished with FCP, A-2 – fabric in twill weave, finished with multifunctional finish, B-1 – fabric in plain weave, finished with FCP.

[b] P – number of washing cycles,

[c] T – heat treatment,

ski parametri tkanine vplivajo na omočljivost vzorcev in to potrjuje rezultate naše predhodne raziskave [22]. Medtem ko so na površini vzorca A-1 statične stične kote oblikovali vsi n-alkani višji od C9 (slika 5a), pa na vzorcih A-2 in B-1 le C16/PO in PO (sliki 5b in 5c). Za mejne primere, to je C16 na vzorcu A-2 ter C14 in C16 na vzorcu B-1, smo ugotovili, da sta se stični kot in volumen kaplje s časom sicer počasi zmanjševala, površina kaplje pa je ostala nespremenjena. To je bil pokazatelj, da je tekočina sicer delno pronicala v pore tkanine, ni pa se razširila po njeni površini. Za te tekočine smo izmerjene stične kote obravnavali kot približne (preglednica 4).

Na sliki 6 so prikazani rezultati meritev hitrosti tankoplastnega pronicanja n-alkanov v vzorce A-1, A-2 in B-1. Iz vrednosti m^2/t za n-pentan smo iz enačbe (4) izračunali vrednosti konstant, *C*, za posamezni vzorec, iz vrednosti m^2/t za višje n-alkane pa dinamične stične kote. Rezultate smo zbrali v preglednicah 5 in 6. Iz pri-

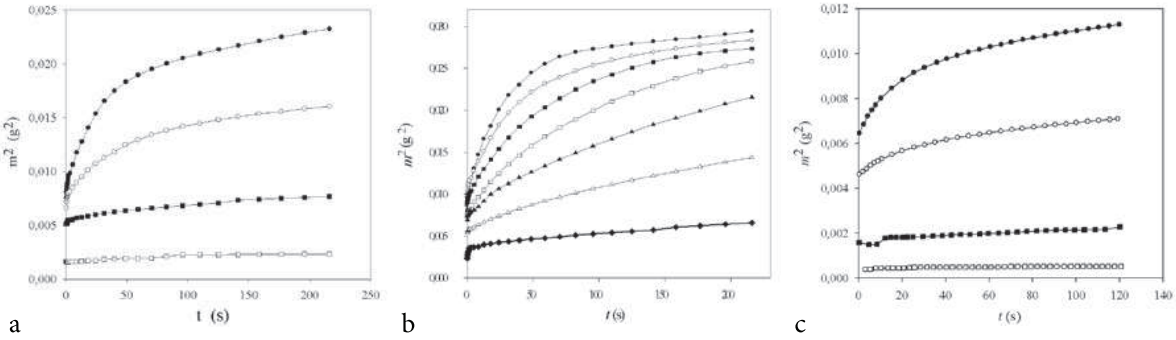

Figure 6: Plots of mass increase, m^2, versus time, t, in thin-layer wicking of n-alcanes into the vertical set samples A-1 (a), A-2 (b) and B-1 (c). • C5, ○ C6, ▪ C7, ▫ C8, ▲ C9, △ C10, ◆ C12.

sented the plots of the liquid contact angle versus its surface tension in Figures 7 and 8. To this end we plotted both static and dynamic contact angles in the same plot and investigated the possibility to treat them together, despite the differences between the experimental methods used to measure them. The criterion for this was the reasonability of the γ_c values obtained with both methods, as well as the correlation coefficient, r^2, of the line drawn through the experimental points.

merjave stičnih kotov v preglednicah 4 in 6 je razvidno, da pri tem ne velja pravilo, da n-alkan, ki zaradi kapilarne depresije ne pronica v vertikalno postavljen vzorec, oblikuje statični stični kot na površini tega vzorca. Tako na primer C9, C10 in C12 v vzorec B-1 niso pronicali pri uporabi TLW metode, delno pa je pronicala sedeča kaplja teh tekočin pri goniometričnih meritvah. Na podlagi teh rezultatov smo se tudi odločili, da približno določene vrednosti statičnih stičnih kotov v preglednici 4 prav tako vključimo v nadaljnjo obravnavo.

Za določitev γ_c posameznega vzorca smo v skladu z Zismanovim modelom na slikah 7 in 8 grafično predstavili odvisnosti stičnih

Table 6: Contact angles, θ, of n-alcanes, obtained by TLW-V method on A-1, A-2 and B-1 fabric samples.

Liquid	θ (°)						
	A-1 [a]					A-2 [b]	B-1 [c]
	0P [d]	1P	1P+T [e]	10P	10P+T		
C6	65.4	37.7	61.0	33.2	51.1	42.5	63.9
C7	85.0	45.4	77.9	41.7	73.2	48.9	67.0
C8	88.7	57.7	85.2	49.3	81.1	55.2	87.1
C9	/ [f]	70.4	86.6	68.9	85.4	62.7	/
C10	/	76.6	/	76.9	88.6	72.3	/
C12	/	85.6	/	77.4	/	82.7	/
C14	/	88.2	/	86.9	/	/ [g]	/
C16	/	89.7	/	88.9	/	/	/

[a] *A-1 – fabric in twill weave, finished with FCP,*

[b] *A-2 – fabric in twill weave, finished with multifunctional finish,*

[c] *B-1 – fabric in plain weave, finished with FCP.*

[d] *P – number of washing cycles.*

[e] *T – heat treatment after washing.*

[f] *Capillary depression,*

[g] *The values were not determined.*

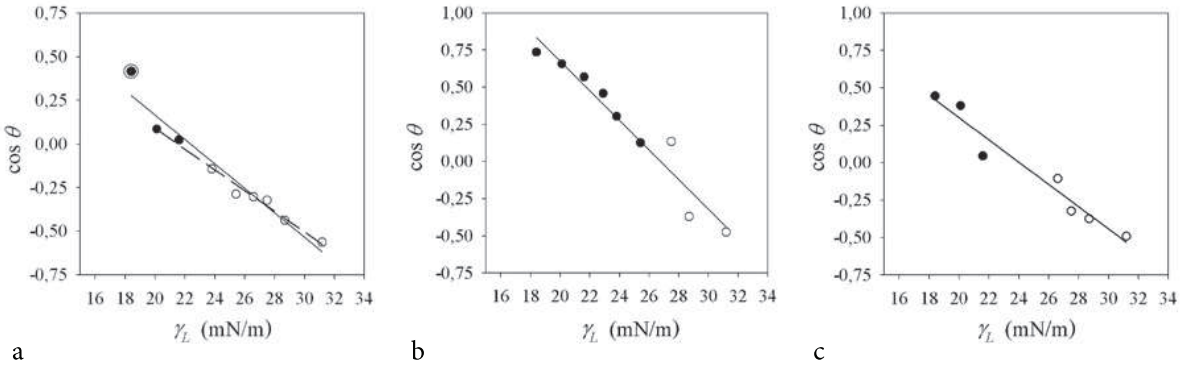

Figure 7: Plots of cos of contact angle, θ, versus liquid surface tension, γ_L, for fabric samples A-1(a), A-2 (b) and B-1 (c).
○: contact angles obtained by goniometric method, •: contact angles obtained by TLW method. ———: all scatters included, – – – –: the encircled scatter was not considered.

From Table 7 we see that all values of γ_c lie between 4.72 and 16.99 mN/m, which is consistent with the literature [11], where for low energy surfaces with end –CF_3 groups, the determined values for γ_c lie between 6 and 20 mN/m. We obtained the lowest values for γ_c (respectively 4.72 and 8.09 mN/m) for the unwashed sample A-1. This is also understandable, as this is the sample on which the n-alkanes display the largest contact angles, and at

kotov tekočin od njihove površinske napetosti. Pri tem smo na isti graf narisali tako statične kot dinamične stične kote in preučili možnost, da jih obravnavamo skupaj kljub različnim eksperimentalnim metodam za njihovo določitev. Merilo za to je predstavljala smiselnost vrednosti γ_c pri njihovi medsebojni primerjavi, pa tudi korelacijski koeficienti, r^2, premic, ki smo jih narisali skozi eksperimentalne točke.
Iz preglednice 7 je razvidno, da so vse vrednosti γ_c preučevanih vzorcev v območju 4,72–16,99 mN/m, kar je v skladu z literaturnimi podatki [11], v katerih so bile za površine nizkih energij s

Table 7: The critical surface tension, γ_c, of A-1, A-2 and B-1 fabric samples, determined graphically by Zisman model from static contact angle measurements obtained by goniometric method (Table 4) as well as dynamic contact angles obtained by TLW method (Table 6).

Sample [a]	Treatment	a_z [d]	b_z [e]	γ_c (mN/m)	r^2
A-1	0P [b]	1.566 (1.281) [f]	0.070 (0.060) [f]	8.09 (4.68) [f]	0.974 (0.992) [f]
	1P	2.757	0.105	16.73	0.988
	1P+T [c]	1.675	0.072	9.38	0.967
	10P	2.641	0.097	16.92	0.987
	10P+T	1.895	0.077	11.62	0.965
A-2	0P	2.668	0.100	16.68	0.968
B-1	0P	1.797	0.075	10.63	0.975

[a] *A-1 – fabric in twill weave, finished with FCP, A-2 – fabric in twill weave, finished with multifunctional finish, B-1 – fabric in plain weave, finished with FCP.*
[b] *P – number of washing cycles,*
[c] *T – heat treatment,*
[d] *a_Z – intersection on ordinate axis (Eq 2),*
[e] *b_Z – slope of the line (Eq 2),*
[f] *The value of γ_c when the encircled scatter in Figure 7a was not considered.*

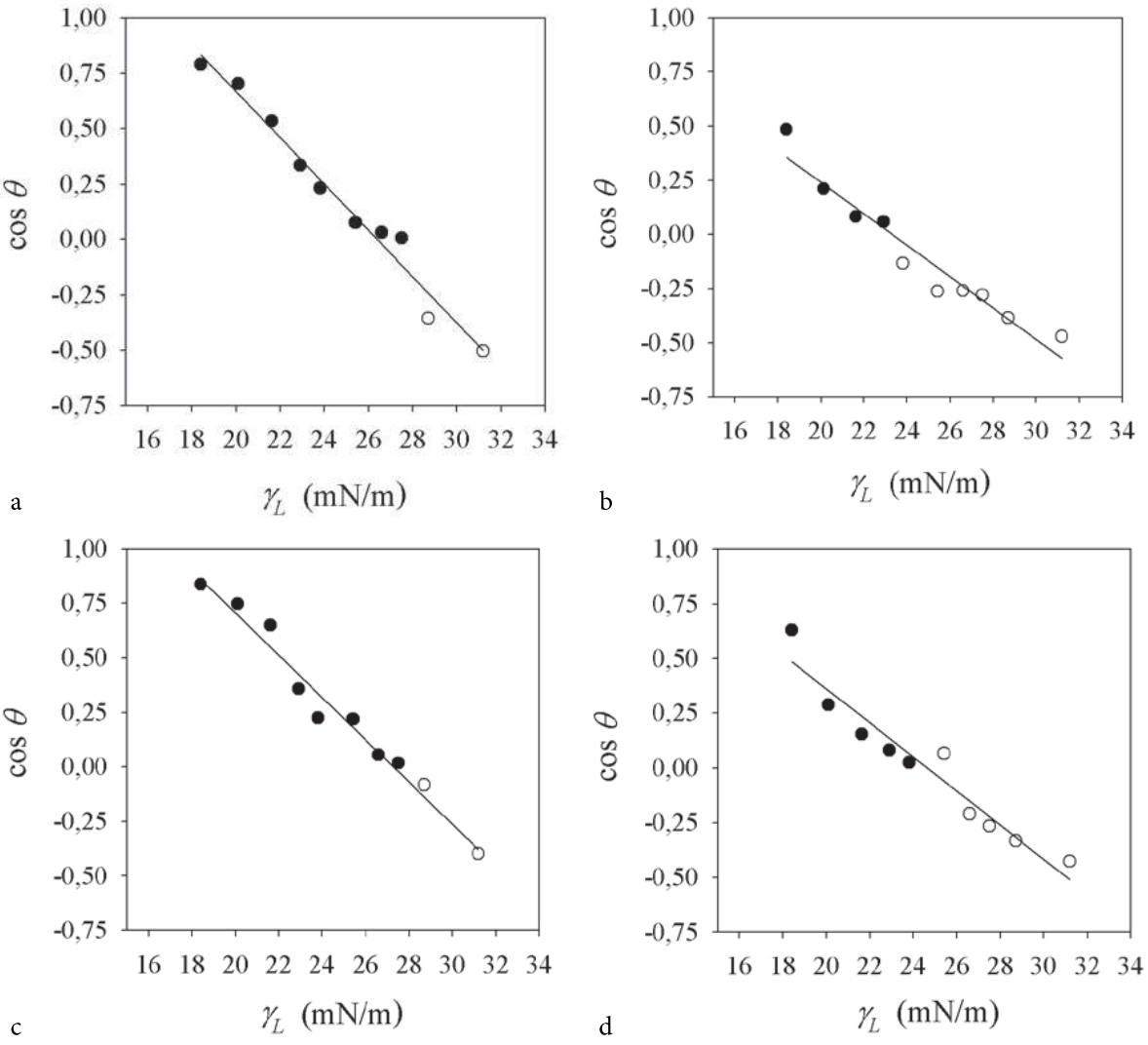

Figure 8: Plots of cos of contact angle, θ, versus liquid surface tension, γ_L, for fabric samples A-1 after washing and heat treatment. a) 1P, b) 1P+T, c) 10P, d) 10P+T. ○: contact angles obtained by goniometric method, •: contact angles obtained by TLW method.

the same time the fewest n-alkanes wick into it. The results are consistent with the properties of the applied finish 1, as well as with the fabric construction parameters. Finish 1, which contains only FCP with very low surface tension, affects the greatly reduced surface free energy of the finished fabric, and the twill weave itself affects the closing of its surface structure. We obtained a somehow higher value for γ_c (10.68 mN/m) in the case of sample B-1. It is in the contrary to sample A-1 in plain weave, for which surface open area is grater and also has a lower mass per unit area. This is also the reason for the higher γ_c, while the FCP in fin-

končnimi $-CF_3$ skupinami določene γ_c od 6 do 20 mN/m. Najnižje vrednosti (4,72 oziroma 8,09 mN/m) smo dobili pri nepranem vzorcu A-1. To je tudi razumljivo, saj je to vzorec, na katerem tvorijo n-alkani najvišje stične kote, hkrati s tem pa vanj pronica najmanj n-alkanov. Rezultati so v skladu z lastnostmi nanesene apreture 1 kot tudi s konstrukcijskimi parametri tkanine. Apretura 1, ki vključuje le FCP z izredno nizko površinsko napetostjo, vpliva na močno znižanje površinske proste energije apretirane tkanine, vezava keper pa povzroča zaprtost njene površine. Nekoliko višjo vrednost γ_c (10,68 mN/m) smo dobili v primeru vzorca B-1. Le-ta se od vzorca A-1 razlikuje po tem, da je to tkanina v vezavi platno, za katero je značilna večja odprta površina, ima pa tudi manjšo ploščinsko maso. To je tudi vzrok za zvišanje γ_c, ob tem pa FCP v apreturi 1 tudi temu vzorcu zagotavlja-

ish 1 grants good water and oil repellent characteristics also to this sample. In the case of sample A-2, the addition of an easy-care finish in finish 2 affects the increased γ_c (16,75 mN/m), which preserves the oil repellency of the sample. These results are also in accordance with the oil repellency test (AATCC 118-1966), which showed that n-tetradecane with γ_L = 26,6 mN/m is the last liquid not wetting the surface in 30 s [23], while n-hexadecane gave us static contact angles yet after 60 s (Table 4). The results confirmed our previous conclusions – finishing has a greater effect on γ_c than the fabric construction parameters [22]. The values of γ_c also change logically depending on the number of washing cycles and heat treatment of sample A-1. Repeated washing increases γ_c. Heat treatment after the sample washing contributed to the re-arrangement of the finished film what reflected in reducing of the γ_c value once again. These results are consistent with the ones obtained through the use of other theoretical models for calculating the surface free energy of solid [22]. From Table 7 it is also noticeable that the values of the correlation coefficient, r^2, are satisfactory and hence confirm the reliability of the results obtained through the combined use of static and dynamic contact angles.

4 Conclusion

In this research we investigated the use of Zisman model for determining the critical surface tension of fabric treated with water and oil repellent finish, as well as with multifunctional finish. From the results we can conclude that Zisman model is useful for determination of surface properties of finished water and oil repellent fabrics, and that for the same series of liquids we can easily combine static and dynamic contact angles, as the values of r^2 suffice for this purpose. We obtained the lowest values of γ_c for unwashed fabric samples treated with FCP (A-1, A-2 and B-1). With washing, the value of γ_c increases, but even after 10 cycles it does not exceed 17 mN/m. Heat treatment greatly improved the orientation of the finishing network, which in turn reduced γ_c. The results show that multifunctional finish (A-2) re-

jo visoko vodo- in oljeodbojnost. V primeru vzorca A-2 dodatek vrhunskega apreturnega sredstva v apreturi 2 vpliva na zvišanje γ_c, ki doseže vrednost 16,75 mN/m, tkanina pa kljub temu ohrani oljeodbojnost. Ti rezultati so v skladu s testom oljeodbojnosti (AATCC 118-1966), ki je pokazal, da je n-tetradekan s γ_L= 26,6 mN/m zadnja tekočina, ki v 30 s ni popolnoma omočila tkanine [23], z n-heksadekanom pa smo že po 60 s dobili statični stični kot (preglednica 4). Rezultati so potrdili tudi naše dosedanje ugotovitve, da je vpliv apreture na vrednosti γ_c večji od vpliva konstrukcijskih parametrov tkanine [22]. Vrednosti γ_c se tudi smiselno spreminjajo v odvisnosti od števila pranj in termične obdelave vzorcev A-1. Pranje vzorca vpliva na zvišanje vrednosti γ_c, ki se z večkratnim pranjem še zviša. Termična obdelava po pranju bistveno pripomore k boljši urejenosti apreturnega filma, kar se kaže v znižanju γ_c. Ti rezultati so v skladu s tistimi, ki smo jih dobili pri uporabi drugih teoretičnih modelov za izračun površinske proste energije trdne snovi [22]. Iz preglednice 7 je tudi razvidno, da so vrednosti korelacijskega koeficienta, r^2, relativno visoke, kar dodatno potrjuje relevantnost rezultatov, dobljenih s kombinacijo statičnih in dinamičnih stičnih kotov ter s tem uporabnost Zismanovega modela.

4 Sklepi

V raziskavi smo preučevali uporabnost Zismanovega modela za določitev kritične površinske napetosti tkanin, apretiranih z olje- in vodoodbojno apreturo kot tudi z večnamensko apreturo. Iz rezultatov lahko sklepamo, da je Zismanov model uporaben za določitev površinskih lastnosti apretiranih vodo- in oljeodbojnih tkanin in da lahko za isto serijo tekočin združujemo rezultate tako statičnih stičnih kotov kot tudi dinamičnih stičnih kotov v istem grafu, saj so vrednosti r^2 relativno visoke. Najnižje vrednosti γ_c dobimo pri nepranih vzorcih tkanin, apretiranih s fluorogljikovimi polimeri (A-1, A-2 in B-1). S pranjem se γ_c zvišuje in tudi po desetih pranjih ne preseže 17 mN/m. Termična obdelava vzorcev po pranju povzroči ponovno znižanje vrednosti γ_c. Rezultati so pokazali, da večnamenska apretura (A-2) v primerjavi z olje- in vodoodbojno apreturo (A-1) ostaja oljeodbojna, in to kljub višji vrednosti γ_c.

5 Zahvala

L. Černe in B. Simončič se zahvaljujeta Janiju Vidmarju iz Inštituta za celulozo in papir, Ljubljana, Slovenija, za pomoč pri meritvah stičnih kotov na aparatu FIBRO DAT. Raziskavo sta finančno podprla Javna agencija za raziskovalno dejavnost RS (Program P2-213, CRP M2-0104 in financiranje mlade raziskovalke L. Černe) ter Ministrstvo za obrambo RS (CRP M2-0104).

tains oil repellency in comparison with water and oil repellent finish (A-1), despite the higher value of γ_c.

5 Acknowledgments

L. Černe and B. Simončič thank Jani Vidmar from Pulp and Paper Institute, Ljubljana, Slovenia, for assistance with FIBRO DAT contact angle measurements. This work was supported by the Slovenian Research Agency (Programme P2-0213, Project M2-0104 and Young researcher project L. Černe) and the Slovenian Ministry of Defence (Project M2-0104).

6 Literatura

1. KNITTEL, D. in SCHOLLMEYER, E. Technologies for a new century. Surface modification of fibers. *Journal of the Textile Institute*, 2000, vol. 91 (3), p. 151–165.
2. LUO, S. in VAN OOIJ, W. J. Surface modification of textile fibers for improvement of adhesion to polymeric matrices: a review. *Journal of Adhesion Science and Technology*, 2002, vol. 16 (13), p. 1715–1735.
3. BAJAJ, P. Finishing of textile materials. *Journal of Applied Polymer Science*, 2002, vol. 83, p. 631–659.
4. RHEE, H., YOUNG, R. A. in SARMADI, A. M. The effect of functional finishes and laundering on textile materials. I: Surface characteristics. *Journal of The Textile Institute*, 1993, vol. 84 (3), p. 394–405.
5. *Textile Finishing*. Edited by D. Heywood. Hampshire: Society of Dyers and Colourists, 2003, p. 528.
6. Adamson, A. W. *Physical chemistry of surfaces*. 5th edition. Canada: John Wiley and Sons, 1990, p. 777.
7. VAN OSS, C. J., GIESE, R. F., LI, Z., MURPHY, K., NORRIS, J., CHAUDHURY, M. K. in GOOD, R. J. Determination of contact angles and pore sizes of porous media by column and thin layer wicking. *Journal of Adhesion Science and Technology*, 1992, vol. 6 (4), p. 413–428.
8. CHIBOWSKI, E. in GONZÁLEZ-CABALLERO, F. Theory and practice of thin-layer wicking. *Langmuir*, 1993, vol. 9, p. 330–340.
9. FOX, H. W. in ZISMAN W. A. The spreading of liquids on low-energy surfaces. III Hydrocarbon surfaces. *Journal of Colloid Science*, 1952, vol. 7 (4), p. 428–442.
10. *Modern approaches to wettability: theory and applications*. Edited by M. E. Schrader and G. I. Loeb. New York: Plenum Press, 1992, p 451.
11. KISSA, E. Repellent finishes. V: *Handbook of fiber science and technology: Volume II, Chemical procesing of fibers and fabrics: Functional finishes, Part B*. Edited by M. Lewin in S. B. Sello. Marcel Dekker, New York, 1984, p. 144–204.
12. SEDEV, R., FABRETTO, M. in RALSTON, J. Wettability and surface energetics of rough fluoropolymer surfaces. J*ournal of Adhesion*, 2004, vol. 80, p. 497–520.
13. BACHMANN, J., ARYE, G., DEURER, M., WOCHE, S. K., HORTON, R., HARTIGE, K.-H. in CHEN, Y. Universality of a surface tension – contact-angle relation for hydrophobic soils of different texture. *Journal of Plant Nutrition and Soil Science*, 2006, vol. 169, p. 745–753.
14. McCULLOUGH III, D. H., GRYGORASH, R. and REGEN, S. L. Fluorocarbon crowning: Langmuir–Blodgett deposition versus self-assembly at molecularly rough surfaces. *Langmuir*, 2007, vol. 23, p. 9606–9610.
15. *CRC Handbook of Chemistry and Physics*. Edited by D. R. Lide.

79th edition. Boca Raton, Washington: CRC Press, 1998.
16. *Modern approaches to wettability: theory and applications*. Edited by M. E. Schrader and G. I. Loeb. New York: Plenum Press, 1992, p. 451.
17. ČERNE, L. in SIMONČIČ, B. Vpliv načina določitve stičnega kota na površinsko prosto energijo apretirane tkanine. V 38. simpozij o novostih v tekstilstvo in 3. simpozij o novostih v grafiki : zbornik prispevkov [Elektronski vir]. Uredili Barbara Simončič, Aleš Hladnik in Dejana Đorđević. Ljubljana : Naravoslovnotehniška fakulteta, Oddelek za tekstilstvo, 2007, p. 71–75.
18. CHIBOWSKI, E. in HOŁYSZ, L. Use of the Washburn equation for surface free energy determination. *Langmuir*, 1992, vol. 8, p. 710–716.
19. Simončič, B., Černe, L., Dimitrovski, K. in Planinšek O. Uporaba Washburnove enačbe za določitev poroznosti tkanin. *Tekstilec*, 2003, vol. 46 (11/12), p. 335–341.
20. ČERNE, L., DIMITROVSKI, K., PLANINŠEK, O. in SIMONČIČ B. Primjena metode tankoslojne penetracije za određivanje parametra poroznosti tkanine. *Tekstil*, 2004, vol. 53 (12), p. 613–622.
21. Rulison, C. *Wettability studies for porous solids including powders and fibrous materials*. Technical note 302. KRÜSS: Instruments for surface chemistry, Charlotte, Krüss, 1996.
22. SIMONČIČ, B. in ČERNE, L. Vpliv različnih dejavnikov na površinsko prosto energijo. *Tekstilec*, 2004, vol. 47 (1/2), p. 6–12.
23. SIMONČIČ, B. in ČERNE, L. Uporaba Fluorogljikovih polimerov pri sodobnih olje- in vodoodbojnih apreturah. *Tekstilec*, 2001, vol. 44 (9–10), p. 263–270.