Available online at www.sciencedirect.com

International Journal of Thermal Sciences 42 (2003) 963–972

International Journal of Thermal Sciences

www.elsevier.com/locate/ijts

Photopyroelectrical measurement of the thermal properties of knitted textile samples. Influence of composition, structural parameters and water content ☆

Mesures photopyroélectriques des propriétés thermiques d'échantillons textiles. Influence de leur composition, de leur structure et de leur teneur en eau

Angela Limare [a], Thierry Duvaut [b,*], Jean-Marie Bachmann [a]

[a] *Institut français du textile et de l'habillement, 270, rue du Faubourg Croncels, 10042 Troyes cedex, France*
[b] *Laboratoire d'énergétique et d'optique, faculté des sciences, Moulin de la Housse BP 1039, 51687 Reims cedex 2, France*

Received 18 March 2002; accepted 18 January 2003

Abstract

The amplitude and phase of the PPE signal for a strongly scattering sample were calculated using a four-flux model. The sensitivity of both PPE amplitude and phase with respect to the thermal properties and water content of the sample were calculated together with the correlations between the parameters. We show that the water content of a sample can be estimated from the signal amplitude, provided the availability of an *a priori* knowledge of the optical parameters' dependence on the water content. Once the optical characterization is completed, the phase signal can be used for the thermal properties evaluation. The experimental values of the thermal parameters depend on composition, structure and water content. The difference between the results obtained by the photothermal method and those obtained by DSC and Alambeta methods is discussed.

Résumé

L'amplitude et la phase du signal pyroélectrique ont été calculées dans le cas de matériaux diffusants en utilisant un modèle à quatre flux. Les sensibilités de l'amplitude et de la phase par rapport aux paramètres thermiques et hygroscopiques de l'échantillon textile ont aussi été calculées ainsi que les corrélations entre ces paramètres. Nous montrons que la teneur en eau d'un échantillon peut être estimée à partir de l'amplitude du signal, en s'appuyant sur la connaissance a priori de la dépendance des paramètres optiques avec cette teneur en eau. Une fois cette caractérisation optique effectuée, la phase du signal est utilisée pour évaluer les propriétés thermiques de l'échantillon. Les valeurs des paramètres thermiques, issues des mesures expérimentales, montrent une dépendance avec la composition, la structure et la teneur en eau des échantillons textiles. Nous présentons ensuite une discussion critique concernant la comparaison des résultats obtenus avec notre méthode et avec les méthodes Alambeta et calorimétrie différentielle à balayage.

Keywords: Photopyroelectric method; Textile; Thermal properties; Hygroscopic measurements

Mots-clés : Méthode photopyroélectrique ; Textile ; Propriétés thermiques ; Mesures hygroscopiques

---

☆ This work was financially supported by the Region Champagne Ardenne, France.

* Corresponding author.

E-mail addresses: angela.frandas@univ-reims.fr (A. Limare), thierry.duvaut@univ-reims.fr (T. Duvaut), jmbachmann@ifth.org (J.-M. Bachmann).

1290-0729/$ – see front matter © 2003 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.
doi:10.1016/S1290-0729(03)00074-7

Nomenclature

a	phase function parameter	
ASL	absorbed stitch length	
C	volume specific heat	$J \cdot K^{-1} \cdot m^{-3}$
c	specific heat	$J \cdot kg^{-1} \cdot K^{-1}$
c_{dry}	specific heat of the dry sample	$J \cdot kg^{-1} \cdot K^{-1}$
C_{ij}	element of covariance matrix	
d_{air}	air gap thickness	m
e	thermal effusivity	$W \cdot s^{1/2} \cdot K^{-1} \cdot m^{-2}$
e_{dry}	thermal effusivity of the dry sample	$W \cdot s^{1/2} \cdot K^{-1} \cdot m^{-2}$
K_{dry}	absorption coefficient of the dry sample	m^{-1}
K_{H_2O}	absorption coefficient of water at the measuring wavelength	m^{-1}
$l_{1,2}$	estimated sample thickness	m
p_i	parameter i	
P	mass per area	$kg \cdot m^{-2}$
R_{th}	thermal resistance	$m^2 \cdot K \cdot W^{-1}$
$R_{th\ dry}$	thermal resistance of the dry sample	$m^2 \cdot K \cdot W^{-1}$
s_i	root-mean-square of parameter i	
S_λ	water sensitivity factor of the thermal conductivity	
S_c	water sensitivity factor of the specific heat	
T	yarn count	Tex
N_e	yarn number	
X_i	sensitivity coefficient for the parameter p_i	
W	water content	

Greek symbols

λ_{th}	thermal conductivity	$W \cdot m^{-1} \cdot K^{-1}$
ρ	density	$kg \cdot m^{-3}$
ρ_{dry}	density of dry material	$kg \cdot m^{-3}$
ρ_{H_2O}	density of water	$kg \cdot m^{-3}$
ρ_{ij}	correlation coefficient between the parameters p_i and p_j	
σ	scattering coefficient	m^{-1}
σ_{dry}	scattering coefficient of dry material	m^{-1}
χ^2	chi-square	

1. Introduction

The purpose of our study was to provide reliable and meaningful values for thermal parameters of textile samples. To achieve this objective we used the PPE method in the non-contact configuration. Both the model developed for the PPE method, in the case of a strongly scattering sample and the experimental device were validated for thermal characterization of textile samples as described in the joint article [1]. Other photothermal methods have already been used for textile characterization like radiometry [2,3], needing generally higher excitation power. Another method in use is the one called "the skin model" [4] where the thermal resistance is measured by the electrical power needed to keep a fabric at a constant temperature (35 °C).

Photothermal methods depend on both optical and thermal parameters, parameters that can be in principle identified experimentally. In the particular case of textiles, where the interfaces between the layers involved in the experimental cell are not well characterized, some other parameters are added to the already long list of unknown parameters. The number of parameters that can be simultaneously identified is limited by the correlations that may exist between all these parameters. In order to characterize thermally textile samples it is convenient to obtain additional information on the samples optical properties from complementary measurements.

In the particular case where a selective wavelength is used, the optical parameters provide an additional information about the sample. This is the case here since a diode laser emitting at a wavelength corresponding to an absorption band of water was used in our experiment. Therefore, optical properties provide an indirect, but immediate measurement of the water content, which is interesting information while measuring thermal parameters.

When defining the series of sample to investigate, only one parameter characterizing composition, structure or water content was changed. In this way we attempted to understand and to quantify the influence of each parameter on the optical and thermal properties of the textile sample.

The purpose of our work was not only to collect experimental data but also to develop an expert system capable of predicting properties from the structural data.

We can define a multitude of thermal parameters for a given sample. These parameters are related one to another. We have studied the behaviour of all these parameters on the structural data and water content, trying to obtain simple relations that can be used for prediction. Depending on the aspect that we want to characterize we choose the most adapted parameters. For example, the thermal effusivity and resistance were chosen when samples are compared because they are not depending on the thickness, and specific heat and thermal conductivity were chosen when the water influence was study because they depend linearly on water content.

The results obtained by using the PPE method were compared to those obtained by Alambeta [5] and differential scanning calorimetry DSC, and the differences discussed.

2. Theoretical background

2.1. Direct model

In the model developed previously we describe the textile material as an equivalent, homogeneous sample, having from macroscopic point of view the same radiative properties [1]. The radiative transfer equation for such an equivalent homogeneous material is solved in a 1D geometry using the four-flux approach. The basic idea behind this methodology is to divide the radiances within the material into four components: two directional components obtained from the incident flux upon reflections and transmissions on the two interfaces of the sample and two isotropic components on each half-space [6,7]. The optical fluxes were calculated at each point of the sample by using the appropriate boundary conditions [8].

Once the optical behaviour of textile samples was mastered, we proceeded by modelling the thermal response of the pyroelectric sensor placed in the vicinity of the sample illuminated by a collimated beam. The heat source generated by the absorption of the incident radiation in the sample can be calculated at each point from the divergence of the optical flux at that point. Then the temperature field in each layer was calculated, and the PPE signal related to the optical, thermal and geometrical properties of the sample.

2.2. Inverse problem

The best fits between experimental and theoretical curves were determined according to the maximum likelihood estimation technique [9]. The fitting was conducted according to a Levenberg–Marquardt algorithm [10,11]. Noise variance at each experimental point was used as weighting factor when calculating the χ^2 factor. The stop criterion of the fitting procedure was the χ^2 factor smaller than one.

Direct modelling of the experiment leads to a minimum number of significant parameters. Parameter fitting may yield meaningless results if some amount of compensation between the various parameters occurs. A theoretical technique of estimation is employed and a reference covariance matrix (C_{ij}) is calculated using the starting parameters. Then the sensitivity coefficients X_i for the parameter p_i were calculated [12] from:

$$X_i = p_i \cdot \frac{\partial S(p_1, \ldots, p_i, \ldots, p_j, \ldots)}{\partial p_i} \tag{1}$$

where $S(p_1, \ldots, p_i, \ldots, p_j, \ldots)$ is the amplitude or phase of the signal.

Even when the contribution of the unknown parameters to the signal is considerable, the parameters may be difficult to identify due to the fact that they are too correlated. The accuracy of the estimated parameters p_i (estimated error standard deviation s_i) and the correlation coefficients between the different parameters ρ_{ij} are calculated from the elements of the covariance matrix (C_{ij}):

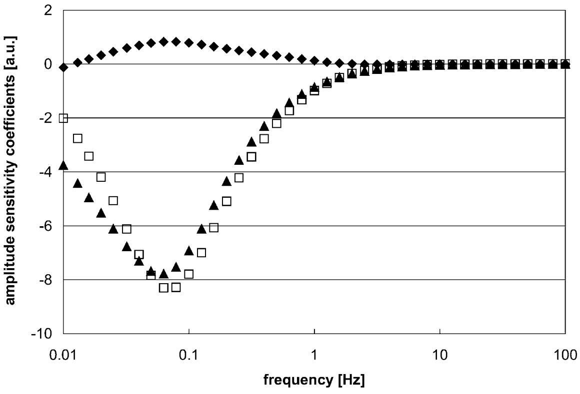
$$s_i = \sqrt{C_{ii}} \quad \text{and} \quad \rho_{ij} = \frac{C_{ij}}{\sqrt{C_{ii}C_{jj}}} \tag{2}$$

It is possible to identify the parameters if all the estimated error standard deviation s are smaller than 100% of the initial parameter value and if the correlation coefficients are not all of them larger than 0.9 [9–12].

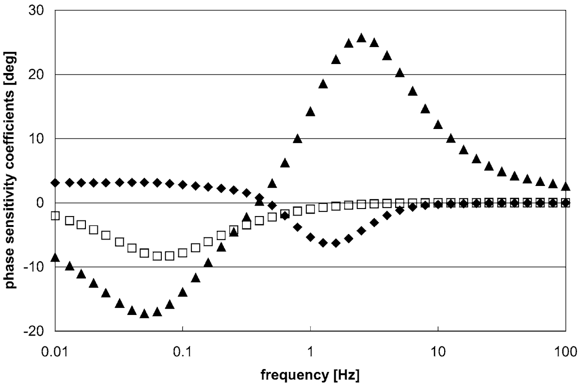
2.3. Sensitivity coefficients of the amplitude and phase for the unknown parameters

Correlation analysis applied to the PPE signal has shown that in the particular case of highly scattering and very low conductive samples such as textiles materials, it is impossible to identify all the sample's related parameters. The thermal characterization of a sample is possible only if the optical parameters of the samples are known *a priori* to the photothermal measurement.

Fig. 1(a), (b) displays the sensitivity coefficients of the amplitude and phase for the unknown parameters (thermal conductivity, specific heat and air gap thickness), calculated from the theoretical model [1] and using Eq. (1). The thermal parameters of the sensor were: thermal conductivity 1.2 W·m^{-1}·K^{-1}, volume specific heat 3.28 × 10^6 J·K^{-1}·m^{-3} and thickness 0.2 mm, corresponding to the values of the PZT ceramic used in the PPE experiment. The other input parameters were: $\lambda_{\text{th}} = 0.2$ W·m^{-1}·K^{-1}, volume specific heat $C = 2 \times 10^5$ J·K^{-1}·m^{-3}, optical absorption coefficient $K = 210$ m^{-1}, the scattering coefficient $\sigma = 3640$ m^{-1}, geometrical factor $a = 0.77$, sample thickness $l = 1$ mm, air gap thickness $d_{\text{air}} = 0.5$ mm. The lateral heat loss in the sensor/sample assembly was included in the value of



(a)



(b)

Fig. 1. Sensitivity coefficients of amplitude (a) and phase (b) for the unknown parameters: thickness of the air gap d_{air} (triangles), thermal conductivity λ_1 (diamonds) and volume specific heat C_1 (empty squares).

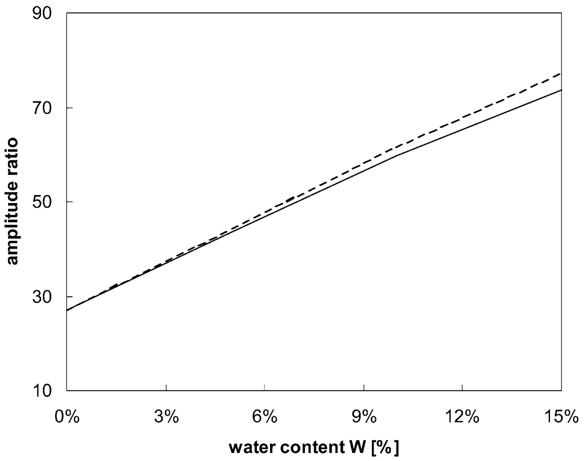


Fig. 2. Numerical simulation of the amplitude ratio versus water content: assuming that the thermal parameters are varying with the water content (solid line) and for constant thermal parameters (dashed line).

the heat exchange coefficient ($h = 18$ W·m^{-1}·K^{-1}), allowing the use of a one-dimensional model.

We observe that the parameters are strongly correlated in the signal amplitude. Considering typical values of optical and thermal parameters for cotton we obtain for the amplitude the following absolute values of correlation coefficients: $\rho(d_{\text{air}}, \lambda_1) = 0.9$, $\rho(d_{\text{air}}, C_1) = 0.98$ and $\rho(\lambda_1, C_1) = 0.96$. These parameters are less correlated in the signal phase and the correlation coefficients are also depending on the input parameters. For the phase signal we obtain $\rho(d_{\text{air}}, \lambda_1) = 0.3$, $\rho(d_{\text{air}}, C_1) = 0.7$ and $\rho(\lambda_1, C_1) = 0.5$ for dry material and 0.5, 0.9 and 0.8 respectively for cotton with a water content of $W = 15\%$ ($\lambda_{\text{th}} = 0.6$ W·m^{-1}·K^{-1}, $C = 3 \times 10^5$ J·K^{-1}·m^{-3}, $K = 552$ m^{-1}, $\sigma = 3370$ m^{-1}). In conclusion, only the phase was used to evaluate the thermal parameters and the air gap thickness.

2.4. Estimation of the water content from the PPE amplitude

For a given type of sample, only the equations that govern the dependence of the optical parameters on the water content are really necessary, not the absolute values. In other words, the way in which optical parameters influence the signal amplitude and the fact that the absorption and the scattering coefficients are correlated through their dependence on the water content, offer us the possibility of estimating optical parameters from the PPE amplitude. The PPE amplitude provides an indirect, but immediate measurement of the water content, which is an interesting information when measuring thermal parameters in non stationary conditions.

The optical and scattering thickness (the products between the respective optical coefficients and the thickness) are dimensionless parameters. At a particular wavelength corresponding to a water absorption band, these parameters are very sensitive to the water content. If we suppose a simple, linear dependence on the water content:

$$K \cdot l = P_{\text{dry}}[A + B \cdot W], \qquad \sigma \cdot l = P_{\text{dry}}[C + D \cdot W] \quad (3)$$

the parameters involved have the following meaning: A is related to the optical absorption coefficient of the dry material (K_{dry}) and its density ρ_{dry} and characterizes the substance, B depends on the optical absorption coefficient of water $K_{\text{H}_2\text{O}}$ at the measuring wavelength (in our case $\lambda = 1.94$ µm) divided to its density $\rho_{\text{H}_2\text{O}}$, C characterizes the dry material and its scattering coefficient and D describes the reduction of the scattering surface due to the fibres that stick together due to water adsorption (experimental values for D are negative). P_{dry} is the mass per area of the dry material. While the linear dependence of absorption thickness function of water content is evident at a wavelength characterizing water absorption, the linear dependence of the scattering coefficient is justified only by the experimental data and is probably valid only in a restricted range of water content.

In the joint article [1] we observed that the signal amplitude has constant sensitivities to optical absorption and scattering coefficients at high and low frequencies, but these sensitivities have different signs.

If we know the dependence of the optical parameters on water content from complementary measurements it is possible to determine the water content W from the ratio of the maximal amplitude (at low frequencies) and the "plateau" amplitude obtained at high frequencies.

Fig. 1 represents the theoretical variation of the amplitude ratio obtained from the one-dimensional theoretical model described in [1]. The numerical simulation was calculated as a function of water content considering $Kl = 0.21 + 2.28^{*}W$ and $\sigma l = 3.64–1.8^{*}W$ (typical values for one of the cotton samples). The parameter describing the phase function of the scattering was considered to be independent of water content: $a = 0.77$. The other input parameters were: $\lambda_{\text{th}} = 0.2–0.6$ W·m^{-1}·K^{-1}, volume specific heat $C = 2 \times 10^5–3 \times 10^5$ J·K^{-1}·m^{-3}; sample thickness $l = 1$ mm, air gap thickness $d_{\text{air}} = 0.5$ mm. The solid line represents the theoretical results obtained considering that the thermal parameters are changing function of water content, and the dashed line was obtained considering the thermal parameters constant. We observe only a small difference between the curves, consistent with the fact that the amplitude ratio is not very sensitive to the variation of thermal parameters with the water content. This is due to the fact that the induced variations on the amplitude are almost compensating one another due to the anti-correlation of these parameters as we can see in Fig. 1(a). If we consider also a lack of precision on the thickness of the air gap d_{air}, the dashed curve is translated above and bellow the solid line due to the correlation with volume specific heat C. This correlation will determine an imprecision on the water content W estimated this way.

Once the optical parameters are known, either from a direct measurement with a spectrophotometer or via assessment from the ratio of the maximal and the plateau

Table 1
The characteristics of jersey knitted samples measured at 20 °C and 65% RH. Parameters l_1 and l_2 are the sample thickness obtained when applying a pressure of 1 g·cm^{-2} and 10 g·cm^{-2}, respectively

Sample reference	Yarn count T (tex)	Diameter ϕ [mm]	Absorbed stitch length ASL [cm]	Mass per aria [g·m^{-2}]	l_1 (1 g·cm^{-2}) [mm]	l_2 (10 g·cm^{-2}) [mm]	CM_1 (1 g·cm^{-2})	CM_2 (10 g·cm^{-2})	l_{eq} [mm]
C21	71.4	0.42	54	364	1.66	1.39	0.42	0.50	0.69
C22	71.4	0.42	60	332	1.79	1.50	0.35	0.42	0.63
C23	71.4	0.42	66	297	1.87	1.58	0.30	0.36	0.56
C41	25	0.28	29.7	200	1.13	0.80	0.44	0.62	0.49
C42	25	0.28	33	176	1.13	0.82	0.38	0.53	0.43
C43	25	0.28	36.3	162	1.10	0.82	0.36	0.49	0.40
C51	20	0.22	26.1	182	0.98	0.73	0.35	0.47	0.34
C52	20	0.22	29	171	1.07	0.80	0.30	0.40	0.32
C53	20	0.22	31.9	157	1.07	0.81	0.28	0.36	0.30
M1	20	0.21	27	167	0.74	0.58	0.37	0.47	0.28
M2	20	0.21	30	137	0.77	0.57	0.29	0.40	0.23
M3	20	0.21	33	125	0.75	0.56	0.27	0.37	0.21
PA1	15.6	0.2	31.5	167	0.81	0.7	0.41	0.48	0.34
PA2	15.6	0.2	35	158	0.86	0.74	0.37	0.43	0.32
PA3	15.6	0.2	38.5	146	0.89	0.8	0.33	0.37	0.29
P1	16.7	0.15	25.2	141	0.52	0.32	0.29	0.47	0.15
P2	16.7	0.15	28	121	0.45	0.33	0.28	0.39	0.13
P3	16.7	0.15	30.8	109	0.41	0.32	0.28	0.36	0.12
L1	71.4	0.65	54	264	1.85	1.21	0.66	1.02	1.23
L2	71.4	0.65	60	227	1.79	1.21	0.59	0.87	1.06
L3	71.4	0.65	66	208	1.79	1.21	0.54	0.80	0.97

amplitudes, we can proceed with the thermal parameters evaluation from the signal phase.

3. Experimental results

We defined and prepared a series of samples as various as possible and which could allow the study of the influence of only one parameter. The results presented here concern jersey knitted sample of cotton (C), modal (M), polyamide (*PA*), polyester (*PES*) and wool (L). There were three values of absorbed stitch length (*ASL*)[1], for each type of yarn count (T)[2] a typical one and the two others characterized by ±10% spread of the typical value (see Table 1). Modal is a regenerated cellulose with the yarn made of fibres. Polyester samples have a yarn composed of 36 filaments and polyamide samples have a yarn composed of two yarns, each of 38 filaments. Samples C2 have 2 yarns per stitch, each of them having a yarn number (N_e)[3] of 28. In wool samples two yarns are twisted together, leading to a yarn of an yarn number of 28. The rest of the samples have 1 yarn per stitch. The thickness for each knitted sample was measured at two pressures (1 g·cm^{-2} and 10 g·cm^{-2}) according to the International Standard [13].

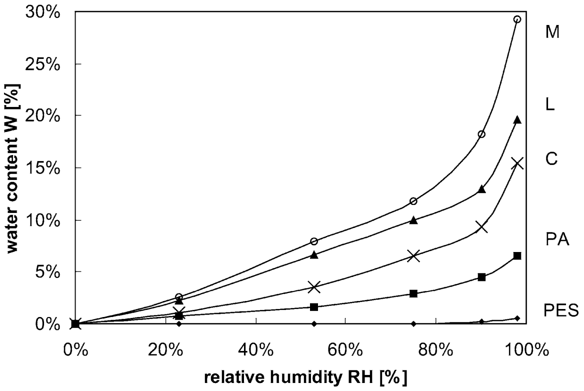


Fig. 3. Sorption isotherms for each type of textile composition.

Five replicates of each type of sample were conditioned under different relative humidities imposed by salt solutions: 23%, 53%, 75%, 90% and 98% RH. The samples were previously dried in an oven at 80 °C for at least 4 days. Then the water content of each sample was obtained by weighting. The results for each type of material are shown in Fig. 3. The samples can be classified according to their capacity to retain water as follows: modal, wool, cotton, polyamide, polyester (from the most hydrophilic to the less one).

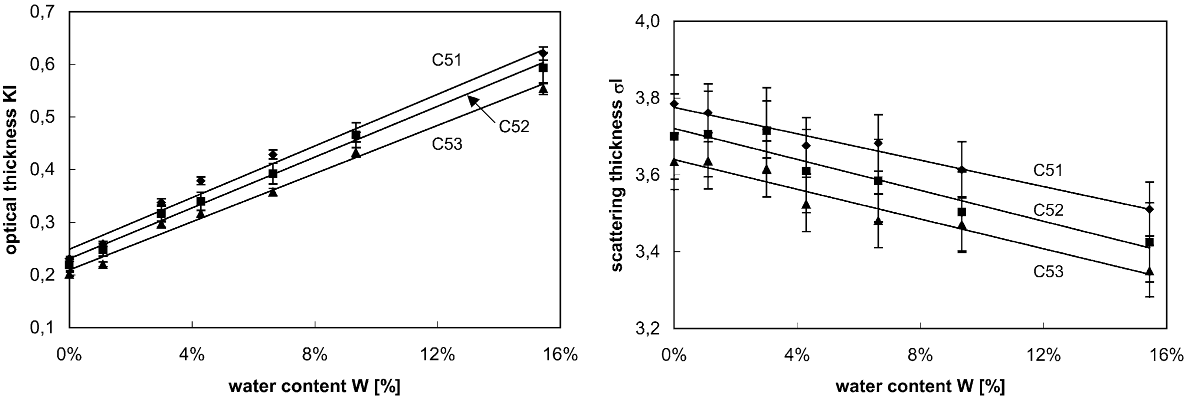
The directional–hemispherical radiative parameters were measured using a two-beam spectrophotometer (Lambda 9 Perkin–Elmer) equipped with integrating sphere. Three macroscopic values are accessible experimentally: τ', $\tau'^{\cap}$ and $\rho'^{\cap}$. The optical absorption and the scattering coefficients were identified using a least-square minimization program based on a Levenberg–Marquart algorithm [10,11]. Using an isotropic function for scattering, the numerical fit

---

[1] Absorbed Stitch Length = the length in cm of 100 stitches. The smaller this value the tighter the fabric.

[2] Yarn Count = the mass in grams of 1000 meters of yarn, actually linear mass.

[3] Yarn Number = the length in km of 1 kg of yarn. The larger this value, the finer the yarn.



(a) (b)

Fig. 4. Optical (a) and scattering (b) thickness of cotton samples $C5$ as a function of water content W.

Table 2
Optical absorption and scattering related parameters at $\lambda = 1.94$ µm characterizing the effect of water in the sample

Sample reference	A [$\text{m}^2\cdot\text{kg}^{-1}$]	B [$\text{m}^2\cdot\text{kg}^{-1}$]	C [$\text{m}^2\cdot\text{kg}^{-1}$]	D [$\text{m}^2\cdot\text{kg}^{-1}$]	a
C21	0.99	15.2	17.5	−10.0	0.37
C22	1.05	14.6	18.8	−11.1	0.56
C23	1.15	14.9	19.9	−10.4	0.71
C41	1.34	15.6	21.0	−10.9	0.62
C42	1.42	14.4	23.1	−11.3	0.73
C43	1.32	15.0	24.6	−11.1	0.81
C51	1.35	14.3	21.7	−10.4	0.56
C52	1.36	15.0	23.0	−12.4	0.70
C53	1.37	15.4	24.8	−11.8	0.77
M1	1.47	14.9	18.9	−2.5	0.77
M2	1.63	16.0	21.6	−3.5	0.82
M3	1.64	15.2	23.3	−9.0	0.90
PA1	0.95	16.6	23.2	−1.2	0.34
PA2	0.95	16.4	24.8	−1.9	0.38
PA3	0.95	17.2	26.5	−3.9	0.43
PES1	0.27	–	10.9	–	0.86
PES2	0.32	–	11.3	–	0.76
PES3	0.36	–	11.4	–	0.76
L1	1.53	14.3	12.4	−12.9	0.95
L2	1.57	13.2	13.4	−12.3	1.04
L3	1.74	15.1	14.1	−14.1	1.15

did not converge, while with the Henyey–Greenstein function we encountered numerical problems related to its integration. The best results were obtained with a linearly anisotropic phase function. When calculating the macroscopic radiative parameters, the relevant parameters from global optical point of view are the dimensionless products: optical thickness (*Kl*) and scattering thickness (σl). Therefore the identified values obtained from the least-squared minimization program were *Kl*, σl and a (the phase function parameter). The corresponding optical absorption and scattering coefficients can be then calculated for any value of the sample thickness.

An example of how the optical and scattering thickness depend on water content is given in Fig. 4(a), (b) for cotton C5. We observe a linear dependence of these parameters on the water content. From these types of curves it is possible to determine the coefficients defined in Eq. (3). The results for all the samples are given in Table 2, together with those for the phase function parameter a which is independent of water content.

We observe that depending on composition, the samples have different dry absorption coefficients. Within a group of samples having the same yarn count we observe similar values for A and C. The influence of the absorbed stitch length (*ASL*) is contained in the factor P (mass per area) which multiplies the coefficients A and C and for obtaining the absorption thickness and scattering thickness of the dry material. For samples having the same composition like, for instance, cotton (groups $C2$, $C4$, $C5$), the A and C coefficients depend on the yarn type. There is a significant difference between the group $C2$ (two yarns per stitch) and the groups $C4$ and $C5$ (one yarn per stitch).

Coefficient B should be the same for all the samples since it depends only on the properties of water. The optical absorption coefficient for water at $\lambda = 1.94$ μm is about 15000 m^{-1}, which divided by the density of water gives a value of 15 $\text{m}^2{\cdot}\text{kg}^{-1}$ for B. Polyester absorbs a small quantity of water which means that the linear fitting should be done in a very small range of W (0–0.5%). This is the reason why we do not have any value of B and D parameters for this material, the optical coefficients (absorption and scattering) being considered as constant. Coefficient D characterizes the reduction of the scattering surface due to water presence. Its value is more important for materials based on natural fibres (cotton and wool), than the artificial (modal) and synthetic (polyamide) ones. For modal the small D coefficient can be due to its important swelling, the samples volume is increasing by a factor of 1.5 at 30% water content.

The geometrical parameter is increasing showing a more pronounced forward tendency the looser the fabric (larger *ASL*) and the finer the yarn.

Five samples from each specimen were equilibrated at each relative humidity (0%, 23%, 53%, 75%, 90%, 98%), than measured using the PPE experimental set-up [14]. A 200 μm thick and 20 mm diameter PZT ceramic provided with high reflectance gold electrodes, was used as a pyroelectric sensor. The textile sample is a disk clamped between two PVC rings. The PPE signal data were measured by a Stanford Research SR850 lock-in amplifier. The diode laser (Applied Optronics Corp., maximum power 1 W at 1.8–2.2 μm) was electronically modulated by the internal generator of the lock-in. The experiment was computer controlled via a RS 232 interface and a LabView 6.01 program. The experimental data were processed and inversed by a Mathematica 3.0 program based on a Levenberg–Marquart algorithm.

The optical parameters measured previously were introduced into the one-dimensional PPE model. The thermal parameters were identified from the PPE phase in the frequency range 0.01–100 Hz with 10 points per decade. The parameters characterizing the sensor were the same as those considered in Section 2.3. The parameters identified from the phase were validated only if the amplitude also satisfied the condition of χ^2 less then one.

From the PPE phase three parameters are accessible: the air gap thickness and two thermal parameters, in our case the thermal conductivity and the volume specific heat. Other thermal parameters can be calculated from the previous two such as: the thermal resistance, the thermal effusivity, the thermal diffusivity and the mass specific heat. The thermal parameters identified from the phase signal were retained only if the amplitude also satisfied the χ^2 criterion.

The results for the thermal resistance per unit area (expressed as the ratio of the sample thickness and the thermal conductivity) for dry samples are presented in Fig. 5. The values were calculated using two values of the sample thickness, those obtained experimentally (l_1 and l_2). The values of thermal resistance are the same within the experimental errors, meaning that the thermal insulation of a sample is constant regardless the arbitrary value of the considered thickness. We observe that for a given type of sample, the thermal resistance is increasing with the *ASL* since it the sample is containing more air. The samples of the series cotton $C2$ and wool have the same *ASL* values and comparable sample thickness, but in terms of thermal insulation wool samples are better than cotton ones.

The results for the thermal effusivity for the dry samples are presented in Fig. 6. The thermal effusivity is another parameter independent of the samples thickness. Intuitively, the thermal effusivity, which is a parameter characterizing the interface, should not depend on the thickness of the layer beyond that interface. This observation is important in the handle evaluation of a tissue, where the thermal effusivity is related with the warm–cool feeling [15]. We observe that samples made of synthetic materials like polyamide and polyester have larger values of thermal effusivity, therefore a "cooler" contact. The cellulose based samples (made

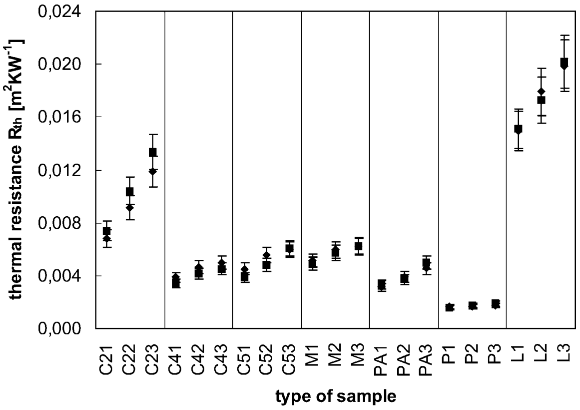


Fig. 5. Thermal resistance of dry samples identified from the PPE phase and for two values of sample thickness: l_1 (diamonds) and l_2 (squares).

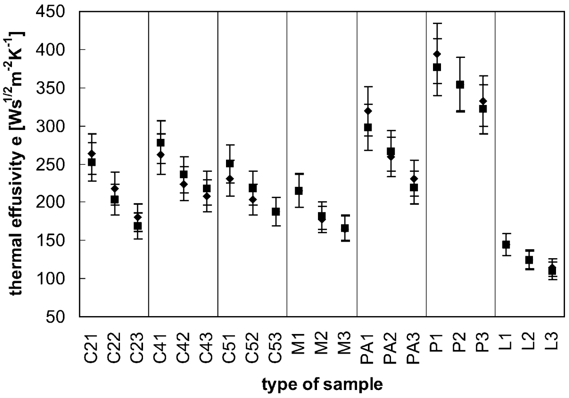


Fig. 6. Idem as Fig. 5 but for the thermal effusivity.

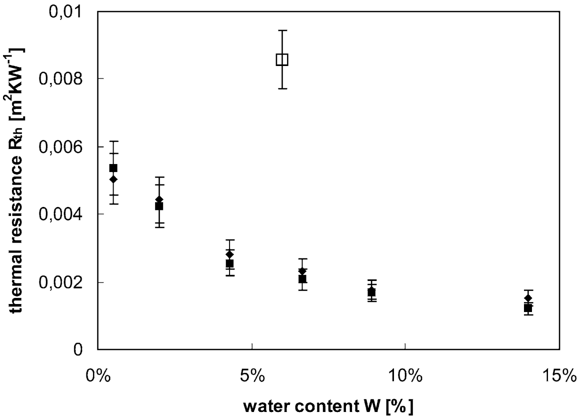


Fig. 7. Thermal resistance of cotton samples $C53$ as a function of water content W. The values are calculated from the PPE phase using the two estimated values of sample thickness: l_1 (diamonds) l_2 (squares). The empty square represents the value obtained with Alambeta at ambient humidity (65% RH).

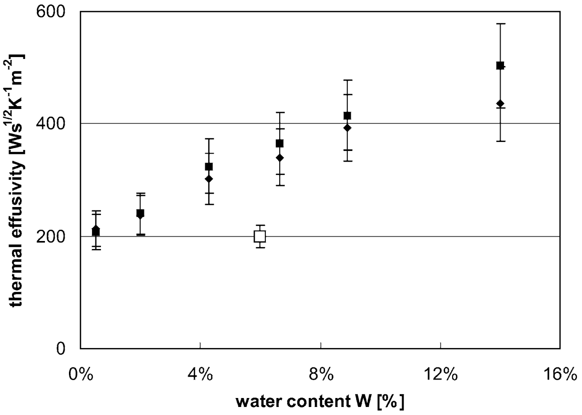


Fig. 8. Idem as Fig. 7 for the thermal effusivity.

of cotton and modal) have intermediate values of thermal effusivity being between the “cool” touch of synthetic samples and the “warm” touch of wool samples. For the same type of sample, the thermal effusivity is decreasing when the samples become less compact (larger *ASL*).

Alambeta measurements were performed for samples equilibrated at ambient humidity (laboratory conditioned at 65% ± 5% RH, 20 °C) by using a Zweigle T675 instrument. In the Alambeta measurement, the sample is placed between two metal plates and submitted to a constant pressure. DSC measurements were performed on two replicates preconditioned at 0%, 75% and 98% using a TA Instruments Modulated DSC.

Figs. 7, 8, 9 show the water dependence of several thermal parameters for one of the cotton samples ($C53$) from PPE, Alambeta and DSC measurements. We knew that the DSC method is not adapted for fibrous materials, but we nevertheless wanted to have an idea about the order of magnitude obtained for such samples.

In Figs. 7 and 8 we observe that when taking up water the thermal resistance of the sample is decreasing and the thermal effusivity is increasing. From the point of view of the comfort the textile becomes less thermally insulating and it has a cooler touch when its water content increases. The Alambeta measurement yields a larger value for the thermal resistance and a lower value for the thermal effusivity than the values obtained from the PPE method. This result suggests that there could be a contact resistance at the metal plate/textile interfaces which is not taken into account into the model of the Alambeta signal. Due to the fact that the thermal resistance is over evaluated, the other calculated thermal parameters are incorrect as, for example, the specific heat (Fig. 9). The values of the specific heat from the PPE experiment, calculated using the two values of the thickness are essentially the same. The values obtained for dry samples are close to those given in literature: 1230–1340 J·kg^{-1}·K^{-1} [16]. The values obtained from the DSC experiment are different from those acquired in the PPE measurements. DSC gives better results for samples containing water due to a better thermal contact between the sample and the Al pan. The same remark applies to all the other samples. The results confirm the fact that although DSC method is extremely accurate for compact materials, it is not well adapted for fibrous materials.

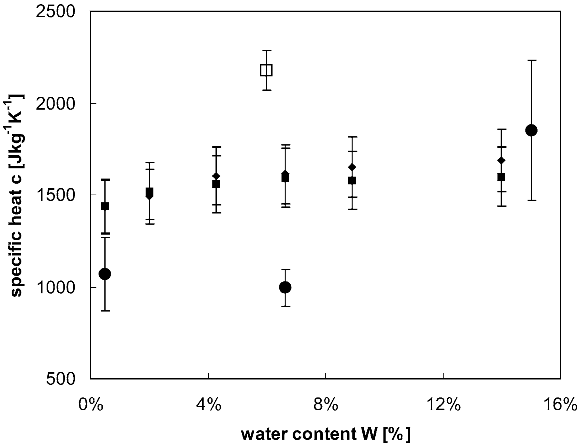


Fig. 9. Idem as Fig. 7 for the specific heat. Circles represent values obtained by DSC.

By representing all thermal parameters versus water content we observed that two of them are well represented by linear functions: the thermal conductivity and the specific heat. This behaviour of the thermal conductivity implies a parallel model of the heat flow in the wet fabric, while the behaviour of mass specific heat is normal for a mixture of two components. The density dependence on water content is $\rho = \rho_{\text{dry}}(1 + W)/f(W)$, where ρ_{dry} is the density of the dry sample and $f(W)$ is the relative variation of the volume, a factor depending on the water content.

Figs. 10 and 11 illustrate how the thermal conductivity and the specific heat depend on the water content. Data concerning only the typical samples (having the central value of the *ASL*) are shown.

Based on the observation that the experimental values for thermal resistance, thermal effusivity and specific heat are the same regardless the considered thickness we are

Table 3
Parameters related to the effect the water content on the thermal properties

Sample reference	ρ_{dry} [kg·m^{-3}]	λ_{dry} [W·m^{-1}·K^{-1}]	S_λ	c_{dry} [J·kg^{-1}·K^{-1}]	S_c
C21	497	0.111	10.3	1439	0.95
C22	497	0.069	18.0	1398	0.91
C23	497	0.045	29.6	1358	0.85
C41	344	0.153	11.8	1427	0.81
C42	344	0.100	17.6	1408	0.94
C43	344	0.076	26.0	1414	0.91
C51	500	0.082	11.5	1424	0.83
C52	500	0.056	18.4	1430	0.90
C53	500	0.046	26.0	1443	0.98
M1	546	0.061	10.4	1565	1.05
M2	546	0.045	14.0	1564	1.05
M3	546	0.040	16.0	1540	1.07
PA1	487	0.105	2.99	1693	0.86
PA2	487	0.093	1.13	1637	1.94
PA3	487	0.086	3.95	1633	2.31
P1	945	0.093	–	1752	–
P2	945	0.074	–	1763	–
P3	945	0.061	–	1795	–
L1	193	0.080	8.1	1330	1.27
L2	193	0.064	10.9	1312	1.30
L3	193	0.050	12.6	1215	1.48

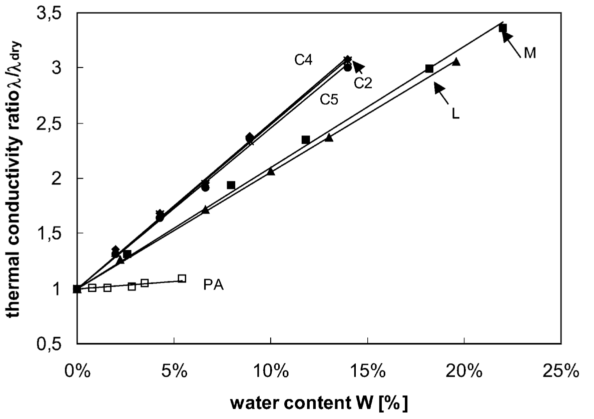


Fig. 10. Thermal conductivity ratio of textile samples versus the water content. Only data for samples having the central value of the *ASL* are shown.

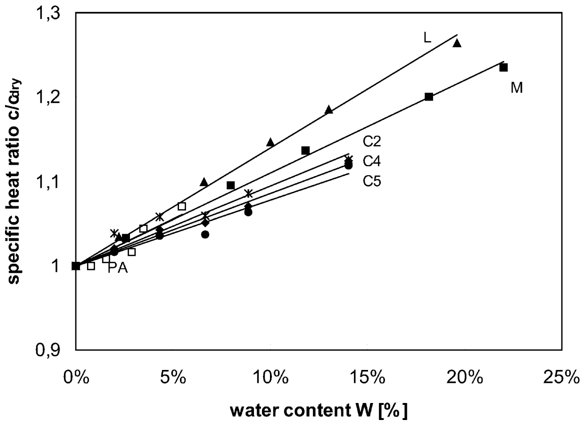


Fig. 11. Specific heat ratio of textile samples versus the water content.

going to show only these parameters dependence on the water content. The thermal resistance at any water content is obtained from its dry value and the thermal conductivity slope versus water content S_λ: $1/R_{\text{th}} = 1/R_{\text{th dry}}(1 + S_\lambda W)$. The thermal effusivity depends on both water sensitivities S_λ and S_c: $e^2 = e^2_{\text{dry}}(1 + S_\lambda W)(1 + S_c W)(1 + W)/f(W)$.

The values of the thermal resistance, thermal effusivity and specific heat for all dry samples are listed in Table 3, together with the values of the slopes giving the sensitivities of the thermal conductivity and specific heat with respect to the water content. We observe that for dry samples thermal resistance increases and thermal effusivity decreases with the *ASL* (as already discussed when presenting Figs. 5 and 6), which is normal since the sample is less compact, including steadily more air. The sensitivity factor for the thermal conductivity S_λ increases with the *ASL*, the influence of water being more pronounced in a less conducting sample. The specific heat behaviour is not depending on the structure, c_{dry} and S_c being constant with *ASL* and yarn count, depending only on the composition.

The thermal conductivity for any considered thickness can be calculated by multiplying the value of thickness by the inverse of the thermal resistance. The volume specific heat is the product of the specific heat and the density obtained from the mass per area divided by the thickness. Then, the thermal diffusivity which is the ratio λ/C can be calculated for any water content and any thickness. An important parameter when calculating the density is the geometrical one, i.e., $f(W)$. A significant variation of the volume with the water content was observed only for modal: 1.5 at 98% RH and $W = 30\%$. For all the other samples it was constant and equal to unity.

4. Conclusion

The PPE method has proven again its potential in the optical and thermal characterization of materials. By using as excitation source a diode laser centred on an absorption band of water, the method provides an indirect measurement for water content provided the variation of the optical parameters is known. Then, the complete characterization of the sample could be done in two steps, firstly, the optical parameters and the water content are estimated from the amplitude, then the thermal parameters are identified from the phase. Therefore, the PPE method is applicable for dynamic measurements such as monitoring the water uptake or the drying out of a sample and assessing their influence on the thermal parameters. We emphasize again the fact that the method provides information about all the thermal parameters of the sample.

Due to the capability of the pyroelectric sensors to respond to very small temperature variations, low levels of excitation radiation can be used. This prevents unwanted phenomena like desorption of water during the measurement.

Despite these advantages the use of the PPE method will mostly be restricted to laboratory since it is time consuming and sensitive to vibrations (pyroelectric materials are also piezoelectric). Moreover, the method is not a true non-contact one, the distance between sensor and sample has to be controlled in the sub-millimetre range.

A series of test samples were produced specially with the major objective to investigate the effect of each structural parameter. The results obtained for different materials and for different yarn count and absorbed stitch length are consistent. The hydrophilic and hydrophobic character of the textiles is noticeable as a variation of the optical parameters in particular that of the absorption coefficient.

The yarn count affects the optical parameters: a larger yarn count corresponds to higher optical absorption and scattering coefficients. The absorbed stitch length determines a decrease of the optical absorption and scattering coefficients and an increase of the geometrical parameter of the phase function.

The identified thermal conductivity, the thermal diffusivity and the volume specific heat depend on the value assumed for the sample thickness while others such as: thermal resistance, thermal effusivity and mass specific heat do not. The last ones are useful when classifying textiles on the base of only comfort related factors such as the thermal insulation properties or the “warm-cool” feeling given by the thermal resistance and effusivity respectively.

The other parameters require that a particular value is chosen for the sample thickness. The thermal conductivity is obtained from the inverse of thermal resistance multiplied by the thickness, and the volume specific heat from the mass specific heat, mass per area, thickness and the volume variation factor function of water content. The thermal diffusivity, which is the ratio of the thermal conductivity and the volume specific heat is less sensitive to the water content and the structural parameters.

The PPE results were compared to those obtained by Alambeta method. The later has the advantage of being extremely easy to use and almost instantaneous, but samples can only be measured at ambient humidity. If only a classification of the insulation properties is needed, Alambeta method can be used, but the quantitative results are affected by an insufficient consideration of heat transfer at interfaces. For instance, the calculated values for the specific heat are over estimated relative to those in literature which on their turn are close to the values obtained by PPE method.

The method can be easily extended to other semi-transparent, scattering, fibrous samples such as nonwoven textile and paper.

References

[1] A. Limare, T. Duvaut, J.-F. Henry, C. Bissieux, Non-contact photopyroelectric method applied to thermal and optical characterization of textiles. Four-flux modelling of a scattering sample, Internat. J. Thermal Sci., submitted together with this article.

[2] R. Hüttner, T. Bahners, E. Schollmeyer, A. Weber, W. Backer, B. Bein, J. Pelzl, Detection of thermal waves by infrared radiometry as a tool for on-line characterization of thermal process in polymeric coatings and textiles, High Temp. High Press. 29 (1997) 379–384.

[3] R. Hüttner, T. Bahners, E. Schollmeyer, A. Weber, W. Backer, B. Bein, J. Pelzl, Modulated photothermal infrared radiometry as a tool for on-line characterization of polymeric coatings in textile processes, Progr. Natural Sci. Suppl. 6 (1996) S735–S738.

[4] M.J. Pac, Les surfaces textiles aux échelles micro, méso et macroscopiques : Propriétés thermiques et tribologiques, Ph.D. Thesis, University of “Haute Alsace”, Mulhouse, Fr., 2001.

[5] I. Hess, J. Dolezal, New method and equipment for measuring thermal properties of textiles, Text. Mach. Soc. Japan 42 (1989) 71–75.

[6] R. Siegel, J.R. Howell, Thermal Heat Transfer, Hemisphere/McGraw-Hill, New York, 1992.

[7] M.N. Ozisik, Radiative Transfer and Interaction with Conduction and Convection, Wiley, New York, 1973.

[8] C. Bissieux, J.-F. Henry, P. Egée, Caractérisation radiative de matériaux semi-transparents diffusants à l’aide d’un modèle à quatre flux, Rev. Gen. Therm. 392 (1994) 470–478.

[9] J.V. Beck, K.J. Arnold, Parameter Estimation in Engineering and Science, Wiley–Interscience, New York, 1977.

[10] K. Levenberg, A method for the solution of certain problems in least-squares, Q. Appl. Math. 2 (1944) 164–168.

[11] D.W. Marquardt, An algorithm for least squares estimation of non-linear parameters, J. Soc. Indust. Appl. Math. 2 (1963) 431–441.

[12] P.R. Bevington, Data Reduction and Analysis for the Physical Sciences, McGraw-Hill, New York, 1969.

[13] International Standard: ISO 9863-2 (1996).

[14] T. Duvaut, A. Limare, J.-M. Bachmann, Photothermal device for water dynamics measurement and thermophysical characterization. Application on textile samples, Rev. Sci. Instrum. 73 (2002) 1299–1303.

[15] S. Kawabata, Textile Machinery Society of Japan, Osaka, Japan, 1980.

[16] J. Brandrup, E.H. Immergut (Eds.), Handbook of Polymers, Wiley–Interscience, New York, 1989.