Thermal characterization of nonhomogeneous materials

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In this paper we want to discuss some applications of the photothermal techniques to the inhomogeneous materials. We provide some examples of nondestructive characterization of materials at different scale of inhomogeneity: the paper and the steel samples.

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Introduction

Photothermal techniques have been widely used for the nondestructive evaluation of the thermophysical properties of nonhomogeneous materials. In this paper we want to discuss some examples of photothermal characterization of materials at different “scale” of inhomogeneity.

Paper samples

Paper samples have been only recently investigated by photothermal techniques [1]. One important problem in paper making technology is that paper undergoes thermal and photochemical reactions, which drastically shortens its useful life. These reactions are responsible for the breaking of chemical bonds in the cellulose fibers, thus damaging the texture structure, and for the changes in chromophore content. The chromophores are chemical groups responsible for absorbing light in the ultraviolet (UV)-visible (VIS) part of the spectrum, thus contributing to the yellowing of the paper. These reasons motivated the use of photothermal techniques to characterize the optical and the thermal properties of aged paper samples, so to find a correlation between these properties and the aging state of the paper.

Table I. Best fit parameters: $D_s$ is the thermal diffusivity, $\beta_a$ and $\beta_s$ are the absorption and the scattering coefficients

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$D_s$ [cm$^2$/sec]</th>
<th>$\beta_a$ [cm$^{-1}$]</th>
<th>$\beta_s$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBA 00</td>
<td>6.9 $10^{-4}$</td>
<td>31</td>
<td>710</td>
</tr>
<tr>
<td>KBA 10</td>
<td>7.7 $10^{-4}$</td>
<td>36</td>
<td>430</td>
</tr>
<tr>
<td>KBA 20</td>
<td>1.1 $10^{-3}$</td>
<td>39</td>
<td>360</td>
</tr>
<tr>
<td>KBA 32</td>
<td>9.0 $10^{-4}$</td>
<td>55</td>
<td>400</td>
</tr>
<tr>
<td>KBA 42</td>
<td>9.3 $10^{-4}$</td>
<td>59</td>
<td>350</td>
</tr>
<tr>
<td>LA 00</td>
<td>6.5 $10^{-4}$</td>
<td>14</td>
<td>1100</td>
</tr>
<tr>
<td>LA 10</td>
<td>9.5 $10^{-4}$</td>
<td>18</td>
<td>720</td>
</tr>
<tr>
<td>LA 20</td>
<td>8.5 $10^{-4}$</td>
<td>22</td>
<td>780</td>
</tr>
<tr>
<td>LA 32</td>
<td>7 $10^{-4}$</td>
<td>30</td>
<td>730</td>
</tr>
<tr>
<td>LA 42</td>
<td>1.1 $10^{-3}$</td>
<td>34</td>
<td>450</td>
</tr>
</tbody>
</table>

Table I. Best fit parameters: $D_s$ is the thermal diffusivity, $\beta_a$ and $\beta_s$ are the absorption and the scattering coefficients.

The photothermal deflection technique has been applied to two different sets of samples: the “LA” samples made of pure cellulose and the “KBA” samples made of a high content of lignin. These samples have been artificially aged by using a special treatment; they have been kept in a oven at 90°C for long time (0, 10, 20, 32 and 42 days), in a high humidity atmosphere ($\approx 60\%$). The experimental results have been explained by considering the scattering phenomenon that reduces the light penetration inside the sample and shifts the photon distribution towards the surface. The analysis of the obtained results shows a clear correlation between aging and thermophysical properties of the paper (see tab.I).

As a result the absorption coefficient value tends to increase with aging due to the production of chromophores absorbing the UV-VIS portion of the light spectra. Moreover the KBA samples reveal a higher absorption coefficient with respect to the LA ones, due to the higher content of lignin which strongly absorbs the radiation around 400 nm. On the contrary, the scattering coefficient reveals the opposite tendency showing lower values with the aging level. In fact, due to the breaking of the paper fibers, the structure becomes more homogeneous as revealed by the loss of scattering power and by the enhancement of the heat transport efficiency that means a higher thermal diffusivity.

Unfortunately, especially when a large surface area must be analyzed, one needs quick techniques, which can give information about the local aging level of a paper foil.

Fig. 1 Photoluminescence spectra obtained for: (1) LA 00; (2) LA 20; (3) LA 42. The exciting wavelength was 360 nm.

In this case we may use the photoluminescence technique:
the UV light is used to excite electronic states of the paper.

These states decay through radiative emission whose spectra allows to identify the active chromophores taking part to the luminescence process. In Fig.1 the luminescence spectra is shown for three different LA samples.

As one can see, the aging treatment causes both an intensity decrease and a broadening of the spectra that reveal a change in the chromophore type responsible for the emission. The same measurement has been repeated on a paper sheet coming from a book, more than 200 years old, as shown in Fig. 2. In this case the aging effect is responsible also for the appearance of a second peak in the emission spectra at $\lambda=550$ nm, in addition to that located at around $\lambda=440$ nm.

![Fig. 2 Photoluminescence spectra obtained on (1) a paper sheet more than 200 years old and, for comparison, on (2) the LA 00 sample.](image)

The emission intensity peaks obtained by scanning the exciting beam from the external to the internal border are shown in fig.3.

![Fig. 3 Photoluminescence intensity peak as a function of the exciting beam position on the 200 years old paper: (1) $\lambda=440$ nm; (2) $\lambda=550$ nm. The negative values of the distance refer to points close to the external edge, while those positive are relative to those close to the internal part.](image)

The data reveal lower intensity peak values for the measurements obtained on the external part of the paper. In our opinion, this is an effect related to the humidity penetration, which is responsible for a more relevant degradation in the external border than in the remaining part of the foil. Of course the intensity peak values do not follow a monotonic behavior but exhibit a certain degree of scattering, due to local inhomogeneities of the paper. We want now to show the use of the photothermal signal autocorrelation for the evaluation of the homogeneity level of a paper sample. The signal is in this case obtained by using photothermal radiometry. The pump beam and the infrared detector are fixed, while the paper sample is moved along one direction, so to be heated from the border to the center. A 10 cm scan has been performed and the data were collected with a step of 10 $\mu$m. In Figs.4 and 5 are shown two particular scans obtained respectively close to the external edge and inside the paper. The signal taken close to the edge reveal a decrease of the phase which is due to presence of a homogeneous and compact strip, probably produced by the humidity, which vanishes in the center of the foil.

![Fig. 4 Photothermal phase signal as a function of the pump beam position.](image)

On the contrary the data reported in Fig. 5 reveal a quite constant value of the phase apart from a certain degree of scattering due to the local structural inhomogeneities of the paper.

![Fig. 5 Photothermal phase signal as a function of the pump beam position](image)

The measured scan has been divided into 1.5 cm slots and then the autocorrelation has been calculated for each slot. In Fig 6 the autocorrelation curves are plotted vs the autocorrelation distance. Two distinct analyses can be done: one for short distance (micron scale), and one for long distance (millimetric range). At short distance, all curves drastically decrease from 1 to 0.5, in similar way, within a distance of 30–40 $\mu$m (half-width correlation length). This means that the paper may be considered homogeneous in the scale of 30–40 $\mu$m, which probably corresponds to the average size of the cellulose fibers. This analysis has been more accurately repeated by dividing the scan in slots 1.5 mm long and by calculating their relative autocorrelation. The half width length of their autocorrelation is reported in Fig. 7 as a function of the position. As one can see, the data show a large dispersion around a mean value that is however almost the same everywhere showing that in a range given by the correlation length, the paper structure can be...
considered approximately homogenous.

![Autocorrelation trace calculated on the slots obtained at a distance from the external border given by: ( ) 0 cm; (◊) 1.5 cm; (Δ) da 3.5 cm.](image1)

**Fig. 6** Autocorrelation trace calculated on the slots obtained at a distance from the external border given by: ( ) 0 cm; (◊) 1.5 cm; (Δ) da 3.5 cm.

![Autocorrelation half-width as a function of the pump beam position.](image2)

**Fig 7** Autocorrelation half-width as a function of the pump beam position.

Coming back to fig.6, if one looks at the curves corresponding to higher values of the distance, it is possible to find some fluctuations, which reproduce themselves in a quite periodical way with a characteristic distance of the order of 1mm. These fluctuations indicate the presence of some “large size” inhomogeneity whose size may be evaluated studying the autocorrelation function. On the contrary the autocorrelation of the data measured at the edge (□) does not exhibit any significant fluctuation in the millimeter range; in fact the presence of the strip makes the paper more homogeneous.

**Steel samples**

Other kind of nonhomogeneous materials investigated by photothermal techniques are those subjected to thermal (such as hardening), mechanical (such as grinding) or chemical treatments of the surface, so to induce useful microstructural modifications in near-surface layers, as for example the steel samples. These samples are often subjected to a hardening process in order to increase the surface hardness. We are now interested to point out the correlation between between the grade of hardness and the thermal properties. In a hardened piece a lot of structural changes had place. First of all macroscopically there is a region with a different structure from the bulk. The structure of the martensite introduce distortions into the lattice. The grain size of this new phase is smaller than in the phase at the equilibrium and the number of grain-boundaries is higher in the hardened surface than in the bulk of the piece. This is because during the fast cooling there’s no time for the grain to grow but the nucleation of new grains is favorite. This represents another obstacle for the heat conduction. Moreover if the steel was chemical treated, then the concentration is changed from the starting 0.2% to around 1.1% of carbon that work like a fine dispersion of inclusions. If the steel was also alloyed there is the presence of carbides with a smaller conductivity than the steel, which are also obstacles for the heat conduction. Generally we may say that what works very well to increase the hardness of a piece, on the other hand makes difficult the heat conduction; this is the aim of the anti-correlation between hardness and thermal diffusivity [2].

We have applied photothermal techniques in several configurations to measure the thermal diffusivity of five 20MnCr5 steel samples, so to find the anti-correlation. These samples have the same hardening depth of 0.8mm, but a different surface hardness ranging from 450 HV to 880 HV. The effective thermal diffusivity for these samples is measured by using a standard photothermal deflection. In fig.8 the phase of the lateral deflection signal is plotted as a function of the lateral offset for different working frequencies, for the 20MnCr5 sample n°2. All curves show an asymptotically linear slope as expected [3]. The initial distortion from linearity is due to the probe beam height with respect to the surface (100µm) and the pump beam size (typically tens of micron). By using the least square method on the asymptotic linear piece, it is possible to work out the thermal diffusivity. The experimental results on the average thermal diffusivity are plotted versus the expected hardness in Fig.9 where the expected anti-correlation between thermal diffusivity and hardness is proven [3].

![Phase of the lateral photothermal deflection signal vs the lateral offset for the hardened steel sample n°2.](image3)

**Fig.8** Phase of the lateral photothermal deflection signal vs the lateral offset for the hardened steel sample n°2. The different curves refer to different modulation frequencies.

![Thermal diffusivity – Hardness diagram for 20MnCr5 hardened steels: the hardening depth is 0.8mm. Other nondestructive tests by using photothermal radiometry allow measuring the diffusivity depth profiles.](image4)

**Fig.9**: Thermal diffusivity – Hardness diagram for 20MnCr5 hardened steels: the hardening depth is 0.8mm. Other nondestructive tests by using photothermal radiometry allow measuring the diffusivity depth profiles. The results has
been widely discussed in ref.[4] and [5], and, in this book, in the paper “Photothermal depth profiling by Thermal Wave Backscattering Theory.”

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References