Journal of Thermal Analysis and Calorimetry, Vol. 66 (2001) 315–327

DSC APPLICATION IN THE CONSERVATION FIELD

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Abstract

Differential scanning calorimetry (DSC) has been scarcely used in conservation field and in particular, in the study of painting layers. However DSC is a micro-destructive technique (sample from .05 to 1 mg can be analysed) because no pre-treatment of the sample is required and so it can give rapid and useful information. The aim of the present work is, in fact, to describe useful applications of DSC on the study of materials used in art. The analyses have been conducted under oxygen flow in order to register the thermo-oxidative reactions of the organic binder or protective. In the first part of the paper, materials of different chemical composition have been analysed to build up a data base of DSC profiles. Standard painting layers artificially degraded by treatment with ultraviolet light (365 nm) for 21 days and with NO_x (5 ppm) have been analysed. Comparing the behaviour of the treated to the reference sample, it is useful to study what kind of changes the treatments have produced on the sample. Another possible application of DSC is the study of the formation of the film; analysing the raw, liquid binders and the different naturally aged films an evolution of the chemical structure can be registered.

As a conclusion, DSC analyses on standard used in artistic field allow to investigate their thermal behaviour and to understand the effect of natural and artificial ageing.

Keywords: artificial degradation, DSC, painting binders

Introduction

The first attempt to find out if it is possible to identify materials used in art objects and to study the ageing characteristics of these materials by means of thermal analysis occurred in 1979 [1, 2]; the sample is heated under oxygen to register the thermal behaviour. Interesting works have been undertaken successively [3–7] which plainly demonstrated that differential scanning calorimetry (DSC) is a valid technique for studying oxidative degradation of organic matters (mediums, adhesives, and films substances) in paintings. DSC analyses are affected by many factors such as the nature of the inorganic pigment, the presence of mixture of binders and protective, the degradation story of the sample. These aspects limit its application in the diagnostic for Cultural Heritage and, in fact, in literature it is sometimes used to study the chemi-

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1418–2874/2001/ $ 5.00
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cal–physical properties of materials used as consolidating or protective in conservation and restoration field [8].

The aim of the work is to evaluate DSC potentialities for the analyses of such materials. To this extent different classes of materials have been analysed. Materials belonging to the same class show similar patternship and this allows to associate DSC profiles to the chemical composition of the binder-protective. Moreover this evidence allows to compare painting layers subjected to artificial degradation treatment in order to simulate effective environmental actions which can produce variations visible through DSC and to understand how the stability of the materials is changed. DSC analyses of painting layers from the starting liquid materials to the naturally completely polymerised matrix allow to understand the chemical changes during the formation of the film.

DSC is a micro-destructive technique as it needs very limited amount of the sample (0.5 mg), it does not require any pre-treatment of the sample and it gives – for that reason – very rapid responses.

Experimental

In the present work, DSC 7 (Perkin Elmer) based on the power compensation principle and TGA7 (Perkin Elmer) have been used to study the oxidative degradation of materials used in artistic field.

Analyses have been conducted from 50 to 600°C with a heating rate of 10°C min^{-1} in oxygen flow (40 mL min^{-1}).

0.1–1 mg of sample were weighed directly in an open aluminium pan and an empty similar pan was used as reference. Indium was used to calibrate the oven. At least two replicates have been effectuated for every typology of sample.

Materials and methods

Chinese standards (tung oil, Chinese lacquer, deer and donkey glue, peach gum and beeswax) are from The Center for the Conversation and the Restoration of Cultural Properrty of Xia'n (China).

Samples of standard painting layers made of linseed and walnut oils, egg, fish glue, dammar, mastic, sandarac were prepared by the Opificio delle Pietre Dure (Florence, Italy). The samples have been prepared by spreading a thin and homogeneous film of pure standard onto glass slides; the films were dried naturally in the laboratory and then underwent to artificial degradation by treatment with ultraviolet light (365 nm) for 21 days and with NO_x (5 ppm) for 15 days at 30°C.

Results and discussion

DSC profiles have been evaluated considering the following parameter:

- T_{peak} is the temperature at the minimum of the peak

• T_{onset} gives an idea about the temperature in which degradation starts. Where there is an overlay of more than one peak, the software gives T_{onset} of the principal peak characterised by the minimum T_{peak}.

• A, area of the peak

• H, height of the peak

• Peak ratio is the ratio between the height of the two principal peaks

• W, width of the peak

• W/H is the ratio between the width and the height to describe the shape of the peaks

DSC analyses of standard films

Figures 1–4 report the DSC profiles of a large number of characteristic materials used in the artistic field. The curves are able to give evident discrepancies between different families of binders. It can be noticed that substances of similar structure produce very similar curves.

Siccative oils

Siccative oils demonstrate the same patternship composed of two large peaks. They are mixtures of tryglicerides with lateral chains containing 16 or 18 carbon atoms with different degrees of unsaturation as reported in Table 1 [9].

Table 1 Triglicerides composition of lipidic binders

Binders	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Eleostearic
N° Carbon	16	18	18	18	18	18
Unsaturation number	0	0	1	2	3	3
Unsaturation position	–	–	9	9, 12	9, 12, 15	9, 11, 13
Walnut	3–7	0.5–3	9–30	57–76	2–16	–
Linseed	6–7	3–6	14–24	14–19	48–60	–
Tung	3	2	11	15	3	59
Egg	27	9	44	13.5	0.5	–

The two unsaturated bonds within the linoleic acid and the three unsaturated sites in linolenic acid are the principally factors of the drying properties. The drying mechanism involves the loss of one hydrogen atom from the methylene carbon between the two double bonds and the reaction with oxygen leading to the final formation of ether or carbon–carbon bonds between the different chains [9].

Comparing linseed and walnut oils behaviour, the former has the higher degradation temperature in the high molecular mass region. In previous works [3–5] the two thermal peaks have been explained associating the first peak to the combustion of materials rich in oxygen, as, for instance, the dicarboxylic acids which are formed during the natural ageing of the film, and the second peak related to the high temperature combustion of the reticulated structures. Consequently, the second peak temper-

ature has been considered to be related to the siccative capacity of the film and, from a chemical point of view, to the content of linolenic and linoleic acids present in the lateral chains of the triglycerides structure. Another factor which is worthwhile to be considered is the peak ratio (Table 2) between the height of the last and the first peak, the trend of which is to increase from walnut to linseed oil, increasing respectively the level of polymerisation.

Table 2 Peak ratio of linseed, walnut and tung oil standard samples

	Peak ratio	St. dev.
Linseed	1.70	0.50
Walnut	0.79	0.08
Tung oil	0.44	0.01

Tung oil is equally unsaturated as linseed oil but it has more tendency to form heterogeneous phases when drying [10]. Experimentally it dries in a very short time probably due to the high content of conjugated double bonds, but this rapid rate of drying in moist air seems not due to the classical oxidation and polymerisation, but rather to the formation of a colloidal state in which moisture acts as a coagulant. In

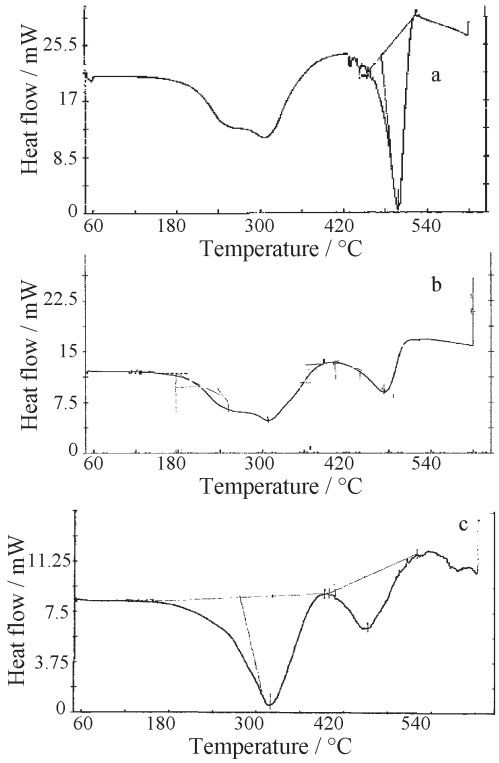

Fig. 1 DSC curves of standard binders' films: a – linseed oil; b – walnut oil; c – tung oil

fact, considering the DSC profiles of tung oil it seems that there is a formation of a lower MW film with a larger distribution with respect to those obtained from the other two types of oils (Fig. 1).

Tung oil presents a minor peak ratio than the other two oils and this seems to indicate a major effect of the natural degradation with respect to the other oils.

Glue

Fish glue, deer glue and donkey glue belong to the same family. Glue is produced by heating skins, bones and muscle tissues at about 80–90°C; in that way the collagen which is the main component is partially degraded and acquired adhesive properties [10]. Collagen is a fibrous protein in which the linear polypeptide chains are more or less parallel with each other including very strict structure formed by frequently repeated glycine-proline-hydroxyproline sequences. Collagen consists of three protein strands held together through strong hydrogen bonding. Glue is formed by the breaking down of the inter chain hydrogen bonds due to the water action. Glues can be obtained both from animal and from fish with the difference that fish glue seems to have lower structural stability than the animal glue. This can be related to the lower proportion of hydroxyproline and proline residues. Comparing the DSC profiles of the three glue (Fig. 2) it can be noticed that deer and donkey glues show one large peak

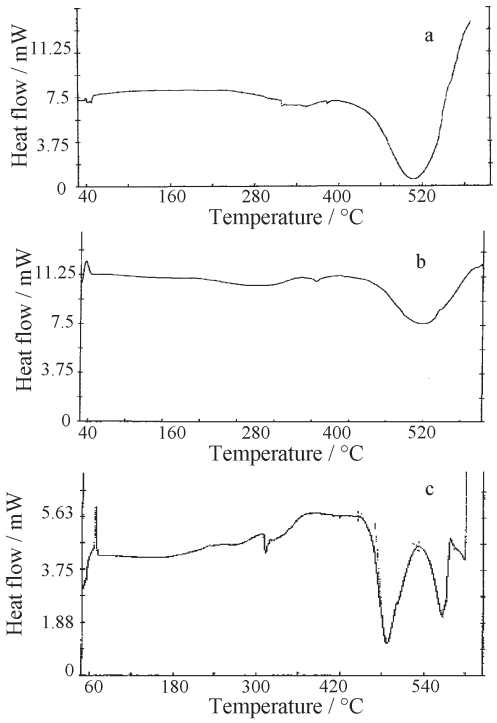

Fig. 2 DSC curves of standard binders' films: a – deer glue; b – donkey glue; c – fish glue

while fish glue presents two more sharp peaks in the high molecular mass region. It seems as in the two animal glues there is a large distribution of high molecular masses, while in fish glue appears a mixture of separated narrow distribution of molecular mass compounds.

Resins

Dammar, mastic and sandarac are three natural resins used as protective in the conservation fields. They are of terpenic nature, in particular, sandarac is a diterpenic resin while dammar and mastic are triterpenic one. Sandarac is a cupressaceae resin and is formed of 70% by polymerised communic acid (a diterpenic compound with two double bonds conjugated responsible of the polymerisation) and the remaining percentage by different kinds of diterpenoid. The nature of triterpenoid found in resins is 'non-polymerisable' but 'oxidizable' [9]. Dammar is composed of a large proportion of triterpenoid compounds and a proportion of polymeric hydrocarbon, mastic has some compounds in common with dammar with a more varied composition. The three profiles (Fig. 3) have a large band at the beginning, a more or less irregular zone and the high molecular mass degradation peak. Dammar and mastic are very

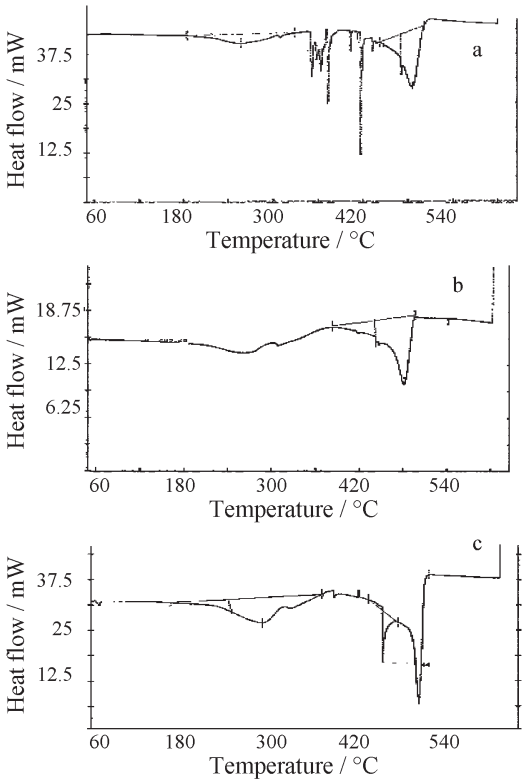

Fig. 3 DSC curves of standard protectives' films: a – sandarac; b – mastic; c – dammar

similar chemically and this chemical similarity is clear even from the DSC curves. Comparing the other two binders, the sandarac curve presents sharp peaks that seem to show the presence of well-defined structured compounds.

DSC analyses of degraded film

To evaluate the effects produced by degradation, standard of pure binders (linseed oil, walnut oil, egg, fish glue) and protectives (dammar, mastic and sandarac) have been analysed.

Siccative oils

Concerning oils it can be observed that UV treatment does not produce significant variation. Probably the UV treatment adopted in this work is not sufficient to degrade oils film. NO_x treatment affects T_{onset} of the first peak (Table 3) and it produces, especially in walnut, a change in the shape of the curve. In fact, the first peak is the sum of two degradation transitions and after NO_x treatment, the shape of the second transitions becomes narrow.

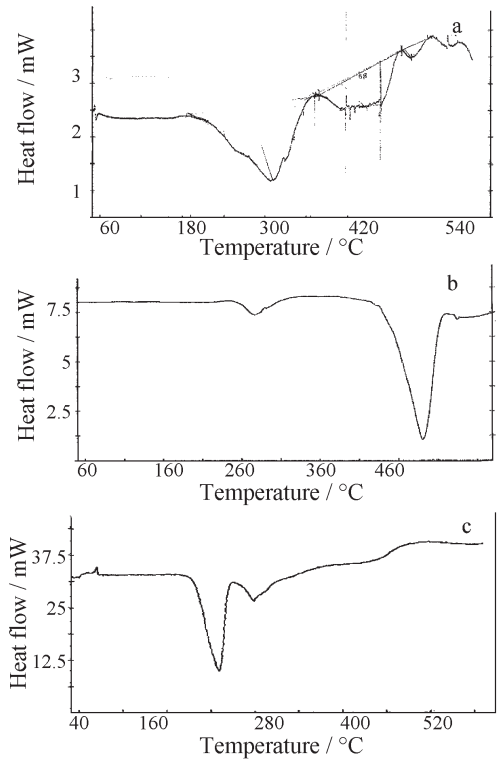

Fig. 4 DSC curves of standard binders' film: a – egg; b – peach gum; c – beeswax

Table 3 DSC parameters of linseed and walnut oils

	Treatment	$T_{1\,(onset)}$	$T_{1\,(peak)}$	$T_{2\,(onset)}$	$T_{2\,(peak)}$
Linseed oil	T=0	209	305	473	496
	St. dev.	9	1	4	2
	NO_x	272	309	483	498
	St. dev.	14	10	1	4
Walnut oil	T=0	198	306	438	475.1
	St. dev.	1	4	4	0.1
	NO_x	256	317	434.91	478.3
	St. dev.	5	4	0.06	0.7

Fish glue

Concerning fish glue samples, UV treatment changes the shape of the first peak which becomes wider (Fig. 5).

NO_x treatment does not reveal any effects.

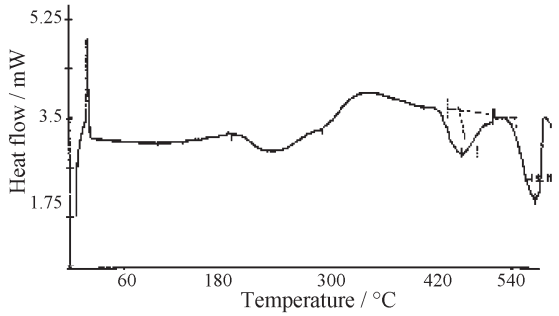

Fig. 5 DSC curves of UV treated fish glue

Egg

In egg samples UV and NO_x exposure seems to increase the last peak area (Fig. 6) with respect to the others two. Moreover the complexity of the central region increases with appearance of many sharp peaks.

Resins

Concerning resins degraded samples have a DSC profile very different with respect to the natural film.

The most affected element is the shape of the peaks which can be described by comparing their height and width. It can be noticed that in mastic and sandarac UV treated samples the first shoulder, present in undegraded samples (Fig. 3) disappears while in dammar its W/H ratio increases (Table 4). Both in sandarac and in mastic the W/H value related to peak 3 decreases. Comparing the curves, in fact, from a wide

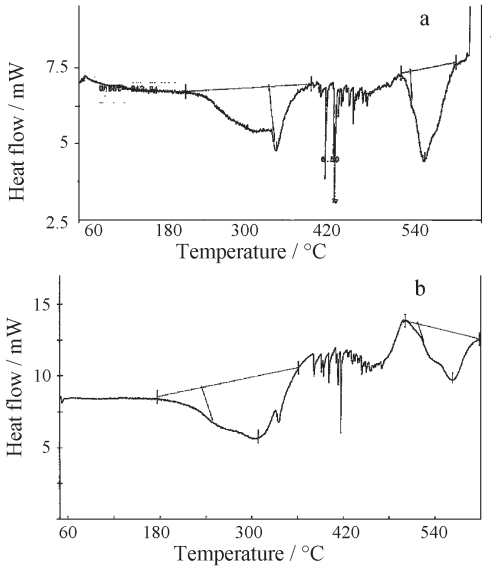

Fig. 6 DSC curves of treated egg: a – UV treated sample; b – NO_x treated sample

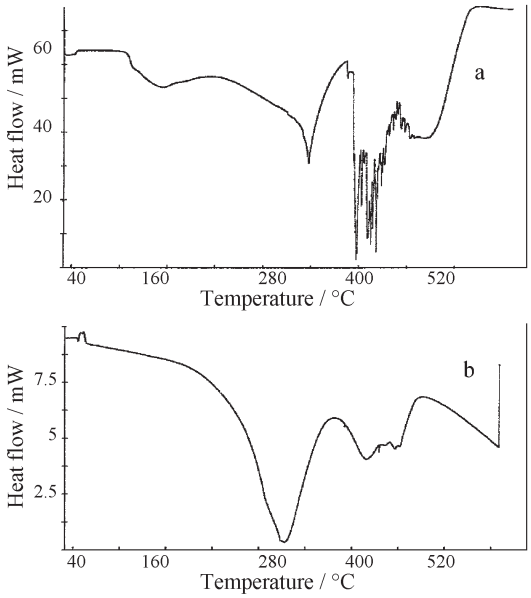

Fig. 7 DSC curves of tung oil: a – sticky material; b – one-month aged film

profile, a sharp peak appears suggesting that a homogenisation of the composition could have happened. In dammar, almost the same results are obtained with the sharp peak slightly shifted toward lower temperatures.

In dammar and mastic, NO_x exposure does not produce any effect unless in the central zone where medium sharp peaks appear from the wide signals. In sandarac the effects are more evident in the central zone as well with an increasing complexity of peaks.

DSC studies of film formation

DSC and TG profiles are useful to understand the dynamics of formation of painting film. For that reason layers at different natural ages have been analysed. Besides thermal parameters obtained by DSC analyses, simultaneous losses of mass have been registered by TG.

Comparing tung oil films, at different ageing time, there is a clear evolution from the fresh liquid tung oil to the one-month and the two-year naturally aged films. In the fresh tung oil, the profile is irregular with many sharp peaks indicating the presence of pure compounds, while in the one-month film two different large peaks are distinguished (Fig. 7), and in the two-year aged tung oil the peaks are more defined (Fig. 1c).

Chinese lacquer is a liquid water in oil emulsion produced by trees belonging to the *Anarcadiaceae* family [9]. Lacquer has siccative capacity due to the presence of substituted phenol with saturated or unsaturated C15 or C16 lateral chains.

In Chinese lacquer the DSC profile presents an intense signal between 400–500°C; the peak is very large in the sticky material (Fig. 8), while it becomes

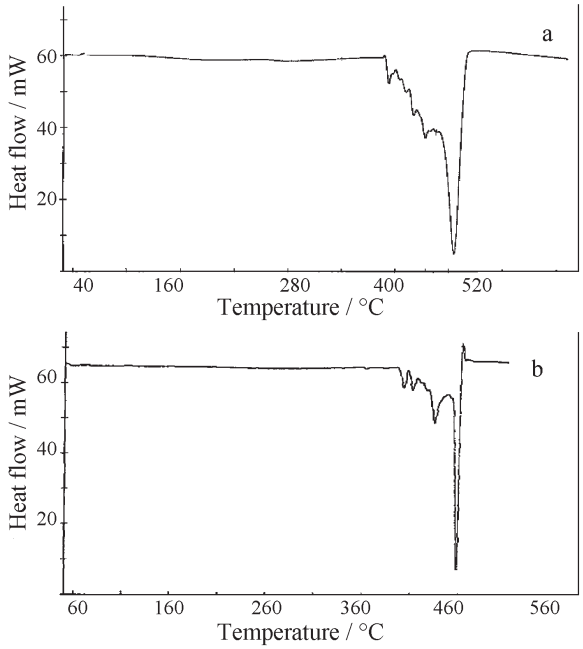

Fig. 8 DSC curves of Chinese lacquer: a – sticky material; b – one-year aged film

Table 4 DSC parameters of resins samples[a]

Sample	Treatment	$T_{1\ (onset)}$	$T_{1\ (peak)}$	W_1/H_1	$T_{2\ (onset)}$	$T_{2\ (peak)}$	W_2/H_2	$T_{3\ (onset)}$	$T_{3\ (peak)}$	W_3/H_3
Sandarac	T=0	271.2	257.6	8.13	416.19	416.90	0.42	470.02	486.2	0.70
	UV	–	–	–	381.28	382.24	1.33	484.37	485.8	0.18
Mastic	T=0	230.3	263.7	6.25	–	–	–	438.62	480.0	0.90
	UV	–	–	–	358.89	359.74	2.00	479.88	481.4	0.16
Dammar	T=0	232.9	280.5	3.95	441.28	442.29	0.96	481.00	491.1	0.43
	UV	230.5	275.8	6.29	416.18	416.89	0.26	479.46	492.4	0.60

[a]for this series of samples, only one DSC measurement has been effectuated

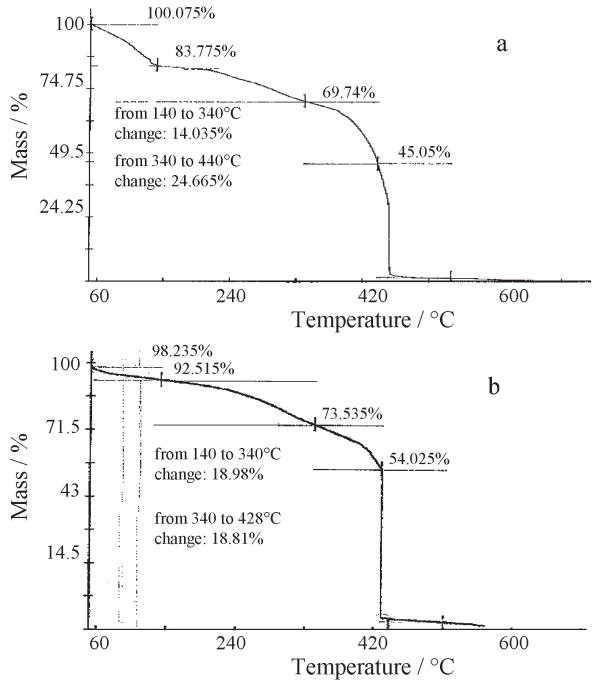

Fig. 9 TG profiles of Chinese lacquer: a – sticky material; b – one-year aged film

sharper in the one-year naturally aged film. This is evident when comparing the TG profiles (Fig. 9): in the liquid lacquer there is a high mass loss (20%) between 60 and 150°C, and one defined loss between 440 and 500 °C, while in the aged sample there is a minor loss (6%) in the beginning region and a complete decomposition of the material near 430°C.

Conclusions

A large data base of DSC curves has been created.

DSC profiles of compounds belonging to the same class are similar and this allows to relate the chemical properties of the sample to the curve and to use DSC profiles in order to obtain information on the stability of the material towards oxidative degradation.

As the curves are function of the degradation parameter of the sample, DSC analyses are very useful to verify the state of the material and to optimise the artificial degradation processes.

DSC can also be used to study the natural polymerisation and the degradation state of the materials, together with other analytical techniques (FTIR, Raman, …)

This research was supported by CNR (Italian Council of Research) – Progetto Finalizzato Beni Culturali (1996–1999). The authors wish to thank Dr. Fan Juan for carrying out part of DSC analyses.

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