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TG–DSC analysis applied to contemporary oil paints

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Abstract Thermogravimetry coupled with differential scanning calorimetry (TG–DSC) has been commonly used in the field of conservation of Cultural Heritage for the study of art objects, especially for the characterisation of inorganic matrixes. In recent years, thermal analyses have been applied to the study of organic painting materials. The advantages of performing TG–DSC are linked to the fact that it is micro-destructive technique which does not require any treatment prior the analysis and provide useful information in relatively short time. The aim of this study is to describe the application of TG–DSC on the study of oil binders used in contemporary paints. Even if synthetic binders have become increasingly popular in the 20th century, many contemporary artists still prefer the more traditional media: drying oils. Although the wish of recalling traditional methods, much practical knowledge in paint preparation by mixing drying oil and pigments and in the behaviour of the mixture has been lost. This is mainly due to the different composition of contemporary materials in comparison with the traditional ones and may sometimes lead to different drying properties of the oil paint formulations and consequent problems in the art creation and conservation. For answer to this artistic need and in particular to the difficulties outlined by artists themselves in producing and employing oil paints, unpigmented and pigmented oil films were studied after a week, 1 and 2 years of natural drying under laboratory conditions. Thermal analyses were performed in air flow: the focus of this research was, in fact, to study the thermal and oxidative behaviours of young films for better understanding the very first processes leading to the formation of the film.

Keywords TG–DSC · Drying oil · Contemporary oil paints · Linseed oil · Stand oil · Cobalt blue

Introduction

Drying oils are habitually referred as the traditional binding media, known at the Roman times and reintroduced by Van Dijk during the Renaissance [1]. Nevertheless, lipidic binders are quite commonly used in contemporary art, even if since the 1930s many synthetic products (such as acrylic, alkyd, vinyl, etc.) have been introduced and have been rapidly employed by modern and contemporary artists [2–4]. The revival of traditional oil methods is not always associated with a proper knowledge about materials used in oil painting. As a consequence, several contemporary artists have found many difficulties in preparing by themselves oil paints which answer to precise needs: handling properties, quick drying time and stability over time. For a better understanding of the oxidative transformations which lead physical modifications of films, some samples have been prepared ad hoc using manufactured oil media and pigments. Reconstructions were both pigmented and unpigmented oil films, given that the presence of layers containing mainly oil is not so uncommon in contemporary paintings.

Since thermogravimetric and differential scanning calorimetric analyses are valid tools in the study of the thermal and oxidative stability of drying oils [5–11], a TG–DSC method was performed on the reconstructed films to understand the changes occurring in the oil films during the very

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first period after the film laying. The advantage in performing the two analyses simultaneously is associated with the possibility of studying oxidative behaviour and thermal stability both in terms of mass changes and thermal capacity [12]. Other advantages of TG–DSC are linked to the possibility of carrying out micro-destructive analysis (normally the amount of sample ranges between 0.5 and 2 mg); furthermore, the method does not require any pre-treatment and gives useful information in relatively short time [9, 11, 13]. Unlike previous applications of thermal analyses on drying oils [5, 7–9, 11, 14], current samples were not subjected to artificially ageing, generally performed to induce degradation of the films. The purpose of this study was to investigate the thermal and oxidative behaviours of young naturally aged oil paints with particular attention to the drying process and the film formation in the early stages. It is actually well known that the processes occurring during the first stages in the curing of oils are of fundamental importance in relation to the resulting film [6, 15, 16].

The mechanism of drying was studied in different kind of oils, namely, cold-pressed linseed oil, stand oil, poppy seed oil, sunflower oil and castor oil. The first three drying oils have been traditionally used in paints [17]. In particular, CPLO is produced by cold pressing the seeds; the obtained oil is considered the highest quality artist oil [17]. Stand oil is, however, the product of a heating procedure in the absence of oxygen up to 300 °C: the resulting oil, also called pre-polymerised, is a heavy and viscous material [18, 19]. Sunflower oil and castor oil are, however, the typical examples of slow-drying oils widely used in 20th century manufactured artists' oils [17, 18].

Three modern pigments have been chosen for the pigmented films, namely, cobalt blue, chrome green and cadmium yellow. TG–DSC analyses were performed on films after 1 week, 1 and 2 years of natural drying under laboratory conditions.

Experimental

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) were performed simultaneously using a Netzsch 409/C apparatus. Data were collected with STA Netzsch software and then elaborated with Origin 8 software.

The temperature program used was set up experimentally from 30 °C, 10 °C/min to 550 °C (560 °C). The instrument was purged with a mixture of air and N_2 at a flow rate of 40 mL/min.

The sample mass ranged between 0.5 and 2 mg; samples were massed in aluminium crucible by the TG internal balance. Alumina was used for the internal calibration.

Three replicates were performed for each sample.

Materials and methods

Drying oils (cold-pressed linseed oil, stand oil, poppy seed oil, walnut oil, castor oil, sunflower oil) and pigments (cobalt blue, $CoAl_2O_4$; cadmium yellow, CdS and chrome green, Cr_2O_3) were purchased from Kremer, Germany. In the case of the pigmented paints, the amount of added oil was varied depending on the pigment characteristics for obtaining a buttery consistency. Once ready, both the unpigmented and pigmented paints were applied on glass slides as a thin layer (approximately 30-μm thick). The slides were kept in laboratory conditions and subjected to natural drying for 2 years. The list of the analysed samples is provided in Table 1.

Results and discussion

TG–DSC curves were evaluated considering both the mass loss expressed as percentage and the heat flow of samples as a function of temperature.

The TG–DSC curves for fresh unpigmented CPLO and stand oil layers are displayed in Figs. 1 and 2. Their thermal and oxidative behaviours are comparable. The thermal results, however, are similar to those observed by Chiantore and Lazzari [9] for drying and oxidative degradation of linseed oil. The TG curves of the fresh oils show in both cases a first strong mass loss between 250 and 400 °C, followed by a second loss above 400 °C. These mass variations are related to two oxidative decompositions, the latter leading to combustion and complete volatilisation of the organic fraction [9, 10]. At the same time, the DSC curves present two exothermic peaks at approximately 380 and 430 °C, related to the oxidative decompositions [10, 11, 20].

For the 1-year-old CPLO and stand oil layers (Figs. 3 and 4), mass losses recorded by the thermogravimetric curve occur between 250 and 400 °C and above 400 °C, raising the same considerations for fresh oil. A slight mass variation is, however, visible between 100 and 200 °C: this

Table 1 Laboratory—prepared oil paint films

Abbreviation	Description
CPLO	Cold-pressed linseed oil
SToil	Stand oil
POP	Poppy seed oil
SUN	Sunflower oil
CAS	Castor Oil
CGoil	Linseed oil + chrome green
CBoil	Linseed oil + Cobalt blue
CYoil	Linseed oil + cadmium yellow

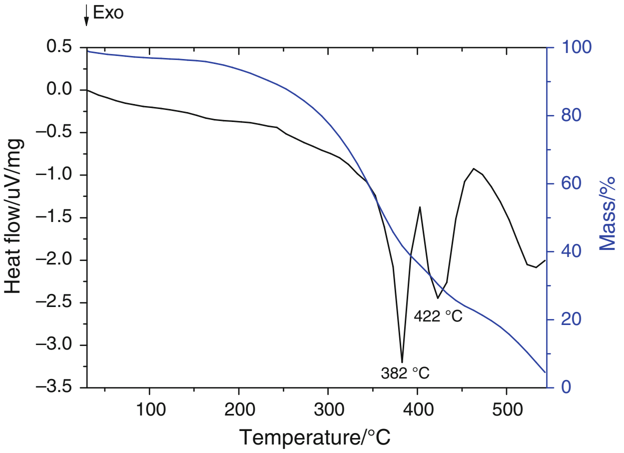

Fig. 1 TG–DSC curves of fresh cold-pressed linseed oil. TG–DSC curves of the analysed samples

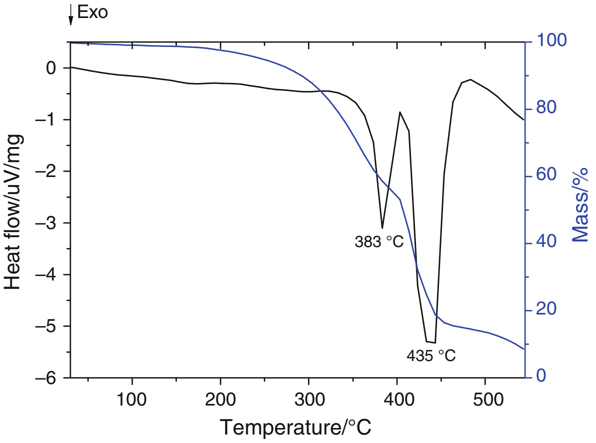

Fig. 2 TG–DSC curves of fresh stand oil. TG–DSC curves of the analysed samples

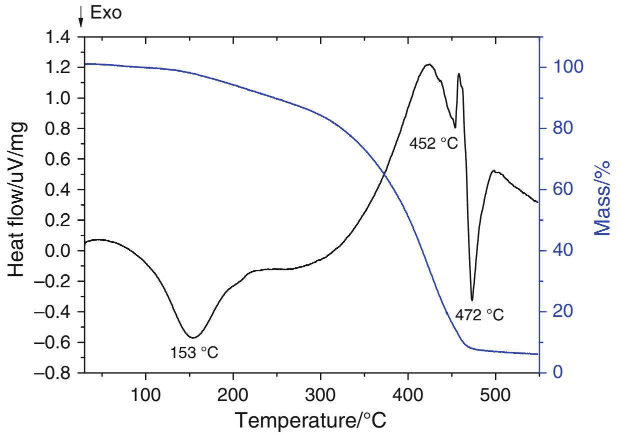

Fig. 3 TG–DSC curves of 1-year cold-pressed linseed oil layer. TG–DSC curves of the analysed samples

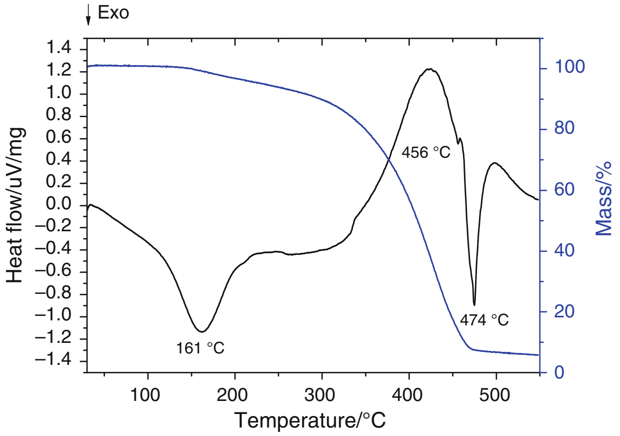

Fig. 4 TG–DSC curves of 1-year stand oil layer. TG–DSC curves of the analysed samples

is possibly related to the decomposition of hydroperoxide groups with formation of radicals, whose reactions with double bonds C=C lead to an exothermic process of cross linking [9, 21]. This event occurs approximately at 160 °C. The slightly evident mass loss associated to this exothermic peak is less than 8%, but was not observed in fresh oil. This is explainable considering that the unsaturated C=C bonds from oleic, linoleic and linolenic acids [19] were not exposed to oxygen atmosphere before the analysis (fresh oil was taken directly from the container). During the drying process, a first compulsory stage called induction period is present and it involves the absorption of oxygen. This period is attributed to the presence of natural antioxidants in the drying oils and only after the oxygen absorption the formation of peroxides and hydroperoxides is possible [16, 19].

Another important consideration comes from the comparison between TG–DSC curves of the 1-year-old CPLO and the one of the stand oil layer. Both the samples are obtained from linseed oil but whilst the first is the result of a cold preparation, stand oil is the result of a heating procedure in anaerobic condition. The mass loss curves are extremely similar and show three main ranges of mass variations as described before. DSC curves exhibit the exothermic peak related to peroxides decomposition at 153 °C for CPLO and 161 °C for the pre-polymerised oil. Both oils undergo a double oxidative decomposition: these exothermic events occur at approximately 450 and 470 °C. The last variation occurs in both cases at 420 °C and it is a melting step. This similarity in the TG–DSC curves could be an indication that the global process of oxidation leads to the formation of the same products, even in layers resulting from drying oils subjected to different preparation treatments. The same behaviour was observed also for poppy seed oil (Fig. 5), sunflower oil (Fig. 6) and castor oil layers after 1 year of natural drying.

Table 2 contains the results of TG and DSC performed on several unpigmented and pigmented oil layers. Except

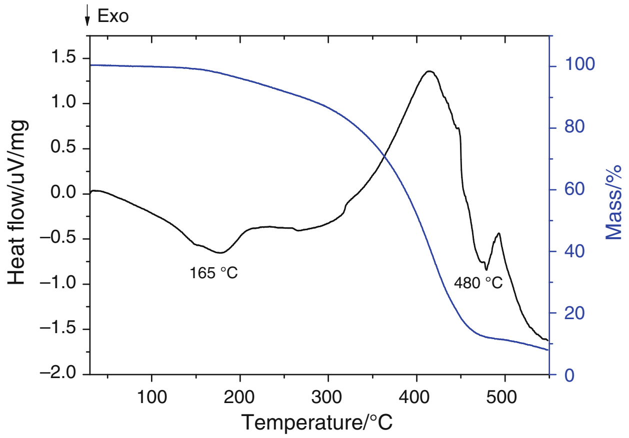

Fig. 5 TG–DSC curves of 1-year poppy seed oil layer. TG–DSC curves of the analysed samples

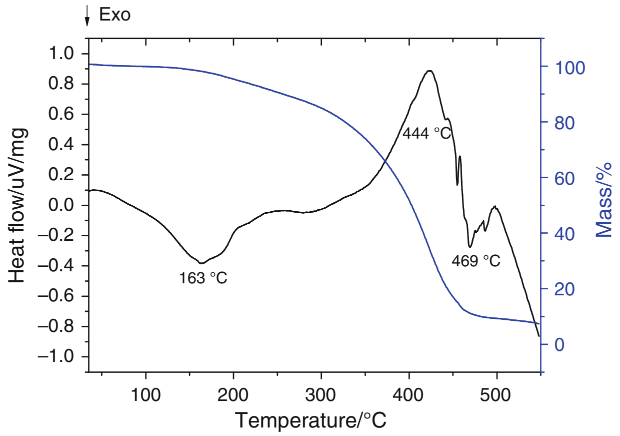

Fig. 6 TG–DSC curves of 1-year sunflower oil layer. TG–DSC curves of the analysed samples

for fresh oils, the recorded TG curves showed a slight mass loss in the range between 100 and 200 °C, appearing in correspondence to the exothermic DSC peak at around 150–160 °C: as seen before, this change is related to the decomposition of hydroperoxide groups and the auto-oxidation process of unsaturated fatty acids present in the oil composition [19, 22]. Between 250 and 400 °C and between 400 and 550 °C, two more evident mass losses occur, which are linked to the oxidative decomposition with final combustion. After TG analyses, the percent mass loss was calculated. Depending on the age of the films and the presence of pigments, the variations in the mass loss values are rather different. In general, the percentage of mass lost after performing TG analyses decreases over time. Measurements were performed at several ranges of curing conditions (fresh, 1 week, 1 and 2 years). This trend was observed in all oil samples. For example, the layer made of cadmium yellow in linseed oil presents values decreasing over time: 84.5% after 1 week, 84.1 and 82.8% after 1 and 2 years, respectively. A possible explanation for the different thermal behaviour of older films is due to the chemical transformations occurring in the film layers during drying processes. As autoxidation and polymerisation occur throughout the film, cross-linking reactions give rise to the formation of polymer matrix and then to new volatile molecules, which are subjected to fragmentation and elimination with ageing [22]. For unpigmented oil films, the total percent mass variation was higher than 90%, whilst for pigmented layers, values vary from approximately 80% for cobalt blue and cadmium yellow films to 40% of chrome green film. These differences are likely due to the differences in composition of the painted layers, in particular, to the varied amount of oil and pigments in the formulations.

Compared to the TG curves, the DSC curves are more varied both in the endothermic and exothermic peaks as reported in Table 2. The exothermic peak at around 150 °C, not present in fresh oils, is visible in all the cured samples: this peak is an index of a fundamental importance for studying the rate of cross linking in the film. The exothermic process of cross linking happened after the decomposition of hydroperoxides groups and the further formation of radicals reacting with the double bonds C=C [9, 21]. With curing, it is possible to notice that the hydroperoxide peak changes in size, becoming broader. Whilst 1-year-old CPLO and stand oil films showed a well resolved peak at 153 and 161 °C, respectively (Figs. 3 and 4), the trend of the curve changed and broadened for pigmented and cured oil films, as reported for cobalt blue in linseed oil in Fig. 9. This provides an interesting indication on the rate of cross linking. The concentration of hydroperoxides, which initially increased whilst\ the autoxidation took place, decreased with age (to almost disappear) from the occurrence of the formation of new bonds and the cure of the formed film. Figure 7 depicts the comparison of hydroperoxide peak for fresh oil (not present), 1-year-old CPLO film (153 °C) and 1-year-old film composed of cobalt blue in CPLO (broad peak at 159 °C). The process of cross-linking and film formation probably occurs within the first 2 years since the paint laying, as suggested by the broadening of the hydroperoxide peak.

The influence of the chemical composition of the pigments in the autoxidation processes was clearly observed in the DSC curves. In fact, the melting transition and oxidative decomposition peaks are shifting and changing in shape according to the mixing pigments. (see Figs. 8 and 9). Cobalt blue in particular is considered as a catalyst in the film formation: in fact, it can affect the drying process thanks to reduction–oxidation (redox) mechanism which is able to promote polymerisation [23–26].

Table 2 TG–DSC results for analysed unpigmented and pigmented oil samples

Samples	Age of the film	TG results		DSC results	
		Weight loss regions	Total weight losses/%	Exothermic peaks	Endothermic peaks
CPLO	Fresh	/1/250–400 °C;/2/>400 °C	95.6	382 °C; 422 °C	400 °C; 475 °C
	1 week	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	95.4	151 °C; 450 °C; 470 °C	418 °C; 451 °C; 493 °C
	1 year	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	93.8	153 °C; 452 °C; 472 °C	422 °C; 457 °C; 497 °C
	2 years	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	92.1	154 °C; 453 °C; 472 °C	423 °C; 455 °C; 498 °C
SToil	Fresh	/1/250–400 °C;/2/>400 °C	94.9	383 °C; 444 °C	403 °C; 475 °C
	1 week	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	94.8	158 °C; 451 °C	413 °C; 482 °C
	1 year	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	93.7	161 °C; 456 °C; 474 °C	422 °C; 496 °C
	2 years	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	92.3	160 °C; 457 °C; 477 °C	424 °C; 497 °C
POP	1 week	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	94.2	151 °C; 438 °C; 471 °C	411 °C; 486 °C
	1 year	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	92.1	152 °C; 178 °C; 445 °C; 475 °C	414 °C; 492 °C
	2 years	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	91.7	154 °C; 451 °C; 476 °C	417 °C; 498 °C
SUN	1 week	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	94.6	148 °C; 478 °C	404 °C; 474 °C
	1 year	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	93.8	155 °C; 453 °C; 488 °C	414 °C; 485 °C
	2 years	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	92.3	156 °C; 459°; 489 °C	419 °C; 489 °C
CAS	1 week	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	94.1	159 °C; 458 °C; 469 °C	406 °C; 478 °C
	1 year	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	93.6	153 °C; 464 °C; 478 °C	425 °C; 502 °C
	2 years	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	93.5	156 °C; 465 °C; 480 °C	415 °C; 499 °C
CBoil	1 week	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	83.4	153 °C; 37 °C; 455 °C	434 °C; 451 °C; 478 °C
	1 year	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	80.8	155 °C; 421 °C; 443 °C; 458 °C	436 °C; 450 °C; 479 °C
	2 years	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	78.3	158 °C; 422 °C; 448 °C; 461 °C	435 °C; 453 °C; 484 °C
CYoil	1 week	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	84.5	151 °C; 390 °C; 405 °C; 456 °C	302 °C; 437 °C; 482 °C
	1 year	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	84.1	156 °C; 391 °C; 408 °C; 455 °C	303 °C; 438 °C; 487 °C
	2 years	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	80.2	158 °C; 401 °C; 409 °C; 459 °C	303 °C; 441 °C; 486 °C
CGoil	1 week	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	47.3	153 °C; 392 °C; 499 °C	387 °C; 439 °C
	1 year	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	43.5	151 °C; 397 °C; 501 °C	391 °C; 449 °C
	2 years	/1/100–250 °C;/2/250–400 °C;/3/>400 °C	40.1	151 °C; 409 °C; 508 °C	395 °C; 450 °C

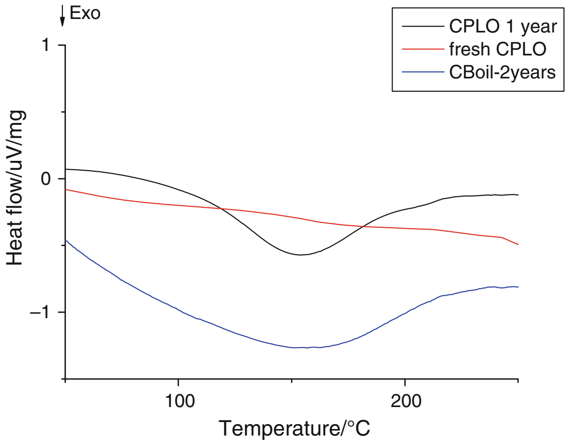

Fig. 7 Comparison of the DSC exothermic peak at 150 °C between fresh CPLO, 1-year CPLO and 2-year CBoil. TG–DSC curves of the analysed samples

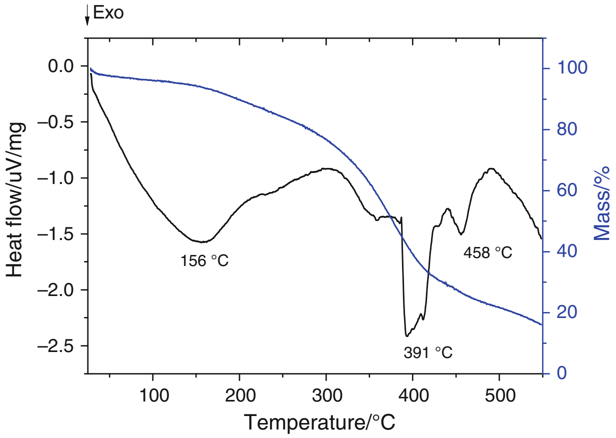

Fig. 8 TG–DSC curves of 1-year cadmium yellow linseed oil layer. TG–DSC curves of the analysed samples

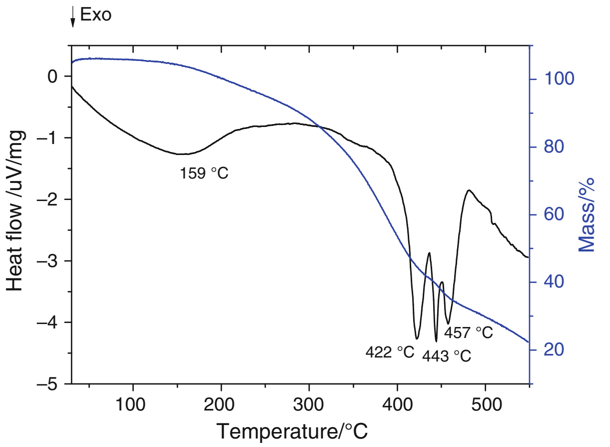

Fig. 9 TG–DSC curves of 1-year cobalt blue linseed oil layer. TG–DSC curves of the analysed samples

Concluding remarks

TG–DSC analyses carried out on unpigmented and pigmented young films successfully allowed for the understanding of the thermal behaviour and oxidative stability within 2 years since the film laying. In particular, this study shows that following the formation and the transformation of the hydroperoxide groups useful information is provided:

- within a week from the paint preparation, autoxidation of the unsaturated fatty acids present in drying oils takes place;
- the formation of the film starts after a week from the paint laying and likely in 2 year of curing the film appears to be thermally stable;
- both the previous processes are speeded up if catalyst-containing pigments (such as cobalt blue) are present in the paint layer.

In particular, DSC analysis can be suitable for the prediction of oxidative stability and for the evaluation of the film formation considering the very first stages since oil layers have been painted out.

References

1. Vasari G. Le vite de più eccellenti architetti, pittori et scultori italiani. Torino: Einaudi; 1986.
2. Learner TJS. Analysis of modern paints. Los Angeles: Getty Publications; 2004.
3. Pugliese M. I materiali sintetici nell'arte contemporanea. Kermes. 1997;30:21–30.
4. Jones FN, Mao W, Ziemer PD, Xiao F, Hayes J, Golden M. Artist paints—an overview and preliminary studies durability. Prog Org Coat. 2005;52:9–20.
5. Pires J, Cruz AJ. Thecniques of thermal analysis applied to the study of cultural heritage. J Therm Anal Calorim. 2007;87:411–5.
6. Erhardt D, Tumosa CS, Mecklenburg MF. Long-term chemical and physical processes in oil paint films. Stud Conserv. 2005;50:143–50.
7. Odlyha M. Investigation of the binding media of paintings by thermoanalytical and spectroscopic techniques. Thermochim Acta. 1995;269–270:705–27.
8. Burmester A. Investigation of paint media by differential scanning calorimetry (DSC). Stud Conserv. 1992;37:73–81.
9. Lazzari M, Chiantore O. Drying and oxidative degradation of linseed oil. Polym Degrad Stab. 1999;65:303–13.
10. Rudnik E, Szczucinska A, Gwardiak H, Szulc A, Winiarska A. Comparative studies of oxidative stability of linseed oil. Thermochim Acta. 2001;370:135–40.
11. Prati S, Chiavari G, Cam D. DSC application in the conservation field. J Therm Anal Calorim. 2001;66:315–27.
12. Le Parlouer P. Simultaneous TG-DSG: a new technique for thermal analysis. Thermochim Acta. 1987;121:307–22.
13. Thomas PS, Stuart BH, McGowan N, Guerbois JP, Berkahn M, Daniel V. A study of ochres from an Australian aboriginal bark painting using thermal methods. J Therm Anal Calorim. 2011; 103:1336–9.
14. White RE, Thomas PS, Phillips MR, Wuhrer R. A DSC study of the effect of lead pigments on the drying of cold pressed linseed oil. J Therm Anal Calorim. 2005;80:237–9.
15. Bonaduce I, Carlyle L, Colombini MP, Duce C, Ferrari C, Mazzeo R, Prati S, Ribechini E, Selleri P, Tiné MR, Tombari E, Townsend JH. Study on binding media in oil paintings: characterisation of linseed oil by DEMS, TGA and GC-MS. In: Proceedings of ICOM-CC, Interim meeting Scientific Research Working Group, Pisa, 7–8 October 2010; p. 16.
16. Wexler H. Polymerization of drying oils. Chem Rev. 1964; 64:591–611.
17. Mayer R. The artist's handbook of materials and techniques. 5th ed. New York: Viking Press; 1991.
18. Doerner M. The materials of the artists and their use in painting. London: Harvest Books; 1984.
19. Mills JS, White R. The organic chemistry of museum objects. New York: Butterworth Heinemann; 1987.
20. Serifaki K, Boke H, Yalcin S, Ipekoglu B. Characterization of materials used in execution of historic oil paintings by XRD. SEM-EDS, TGA and LIBS analysis. Mater Charact. 2009;60:303–11.
21. Ploeger R, Scalarone D, Chiantore O. Thermal analytical study of the oxidative stability of artists' alkyd paints. Polym Degrad Stab. 2009;94:2036–41.
22. Van den Berg JDJ, Van den Berg KJ, Boon JJ. ICOM committee for conservation 12th triennial meeting, Lyon, France, 29 August–3 September. London: James & James Ltd; 1999. p. 248–53.
23. Turri B, Vicini S, Margutti S, Pedemonte E. Calorimetric analysis of the polymerization process of linseed oil. J Therm Anal Calorim. 2001;66:343–8.
24. Šimůnková E, Brothánková-Bucifalová J, Zelinger J. The influence of cobalt blue pigments on the drying of linseed oil. Stud Conserv. 1985;30:161–6.
25. Tuman JS, Chamberlain D, Scholsky KM, Soucek MD. Differential scanning calorimetry study of linseed oil cured with metal catalysts. Prog Org Coat. 1996;28:251–8.
26. Mallégol J, Lemaire J, Gardette J. Drier influence on the curing of linseed oil. Prog Org Coat. 2000;39:107–13.