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CALORIMETRIC ANALYSIS OF THE POLYMERISATION PROCESS OF LINSEED OIL

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Abstract

In this paper the polymerisation of linseed oil is studied in order to prove the catalytic action of some inorganic pigments. The results show that the calorimetric technique is able to monitor the polymerisation process in the temperature range between 130 and 220°C; reproducible values for isothermal analysis are obtained between 130 and 150°C; finally the results are quantitative and can be justified by kinetic equations.

Keywords: catalytic action, linseed oil, pigments

Introduction

The painting layer of an art work is a mixture of pigments and ligands [1]. Until the middle of the 15th century, the most common technique was tempera painting and protein ligands such as egg, casein, etc. were employed. Afterwards, under the influence of Flemish painters, the use of siccative oils as binding agents was introduced and rapidly spread.

The main siccative oils used in painting are linseed oil, poppy oil and nut oil. Chemically speaking, they are complex mixtures of triglycerides, i.e. esters formed by the combination of one molecule of glycerine with three of higher fatty acids. The acids are generally different from one another and each oil has a different percentage of unsaturated fatty acids.

The principal fatty acids in siccative oils are: oleic acid $C_{18}H_{34}O_2$, with one carbon–carbon double bond; linoleic acid $C_{18}H_{32}O_2$, with two carbon–carbon double bonds; linolenic acid, $C_{18}H_{30}O_2$ with three carbon–carbon double bonds. The latter is the main component of linseed oil. Furthermore, linseed oil contains over 80% of unsaturated fatty acids and is, therefore, classified as a ‘harden dry’ siccative oil [2].

The percentage of unsaturated fatty acids is the base of the chemistry of these materials because it is directly linked to the tendency of the double bond to polymerise. The polymerisation reaction of siccative oils is a three-step radical chain reaction: induction, propagation and termination [3–5].

The oxygen of the air is the initiating agent in the first step of the desiccation process. This step is often preceded by an induction period that is due to the presence

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of natural anti-oxidising agents (fitosteroids and polyphenols), the percentage of which is quite high in siccative oils of vegetable origin [6].

Since the beginning, it was immediately obvious that desiccation time could represent a problem, especially compared to that of the previously employed tempera binders. In fact, the induction period of pure linseed oil is about two days and nearly a month is required to complete the formation of the film.

In our days, vegetable oils are the main components of paints and protective films; nevertheless they are mixed with siccative agents in order to reduce desiccation time [7].

On the other hand, it is well known that some inorganic pigments used in painting have a catalytic action, i.e. are able to induce a strong acceleration and drastically decrease desiccation time.

The aims of the present work were twofold: primarily, we want to verify whether the calorimetric technique is sufficiently sensitive to monitor the polymerisation of linseed oil [8], secondarily, we sought to investigate the catalytic effect of some of the most common inorganic pigments on the polymerisation process and quantify these results.

Experimental

Materials

Pure linseed oil commercially available was used; it was supplied by: Lefranc and Bourgeois.

Commercially pigments supplied by Windsor and Newton, such as minium (Pb_3O_4), chromium yellow ($PbCrO_4$) lead and tin yellow ($PbSnO_4$) and read earth (based on iron oxides) were employed. Lead and iron are known as catalysts for the oxidative polymerisation reaction of linseed oil.

Technique

The polymerisation reaction of linseed oil was monitored with a 828 Mettler DSC. Isothermal analyses and temperature scans were performed.

The scans were carried out on pure linseed oil by heating the system from 25 to 600°C with a rate of 10°C min^{-1} and the reactions were carried out under air, nitrogen and oxygen atmosphere. The aim of these different measurements is to determine the most convenient conditions for a laboratory study of the polymerisation reaction.

Isothermal analyses were carried out on pure linseed oil and on linseed oil/pigment mixtures. Temperatures were selected between 130 and 150°C and the measurements were performed in air. This enabled us to compare the different kinetics of polymerisation.

In the isothermal analysis the conversion grade x% is estimated through the equation:

$$x = \Delta H_t / \Delta H_{TOT} \cdot 100 \tag{1}$$

where ΔH_t is the heat developed during the reaction at the temperature T and time t and ΔH_{TOT} is the total conversion heat at the same temperature.

Results and discussion

The temperature scans in air demonstrate that the ideal temperature range for our study is between 130 and 220°C.

The resulting curve is quite complex: we identify a first peak at 200°C relative to the polymerisation process [9] and a second peak at 290°C corresponding to the degradation of low molecular mass substances deriving from the heating of linseed oil. Above 300°C we observe exclusively degradation processes, as demonstrated by preliminary thermogravimetric analyses.

By performing the scans first under nitrogen and then under oxygen atmosphere we confirm that the first peak (at 200°C) is associated to the polymerisation reaction. In fact, in the first case the peak in the DSC curve disappears, whereas in the second case, it significantly increases.

Temperatures between 130 and 150°C were selected for the isothermal kinetic study: above this temperature the reaction is very fast and cannot be completely detected by DSC since the initial phases are covered by the settling of the instrument.

From the curve of pure linseed oil at 130 and 150°C it has to be noted that the polymerisation reaction is significantly accelerated by the temperature increase. As a consequence, the maximum is shifted towards lower time values. Figure 1 represents graphically the conversion values calculated for the different curves.

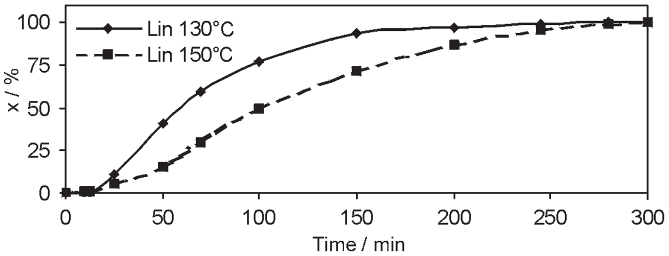

Fig. 1 Conversion values calculated from the DSC curves of pure linseed oil at 130 and 150°C

On the basis of this evidence, we conclude that we are able to study the polymerisation reaction correctly through differential scanning calorimetry. Furthermore, this technique is sufficiently sensitive to estimate different kinetic rates.

The same values for the linseed oil/minium mixture at 150°C are shown in Fig. 2. A remarkable acceleration in the kinetics due the catalytic action of the pigment is observed: while in pure linseed oil the conversion after 50 min is 41%, in the linseed oil/pigment mixture the conversion is 44% after 30 min.

The kinetic results are elaborated to quantify the conversion curves. An exponential function with two constant parameters similar to that of Avrami and Evans for kinetic phenomena is employed:

$$x = 1 - \exp[-kt^n] \quad (2)$$

where k is the rate constant and n is an index associated to the transformation's mechanism.

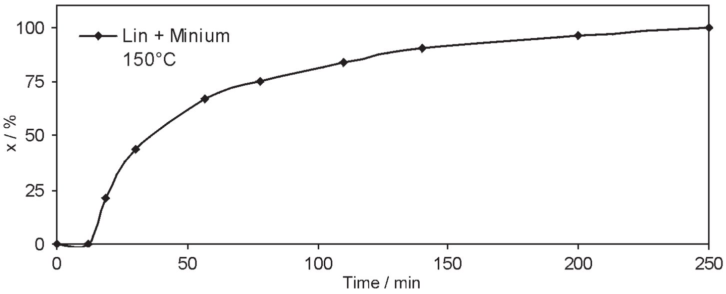

Fig. 2 Conversion values calculated from the DSC curve of linseed oil/minium mixture at 150°C

It is well known that the Avrami–Evans equation [10–12] was originally proposed for the description of the growth rate of the oxide islands on the metal surfaces; subsequently was extensively employed in the studies of the crystallization kinetics of polymers [13] but the physical meaning of the two constants was discussed. In our case it is proposed as an empirical equation containing two adjustable parameters in order to fit the experimental values of the conversion.

By linearising the above equation:

$$\log[-\ln(1-x)] = \log k + n\log t \quad (3)$$

we can easily obtain k and n, respectively from the intercept on the x axis and from the slope of the curve obtained by representing log[–ln(1–x)] *vs*. log$t$ (Fig. 3).

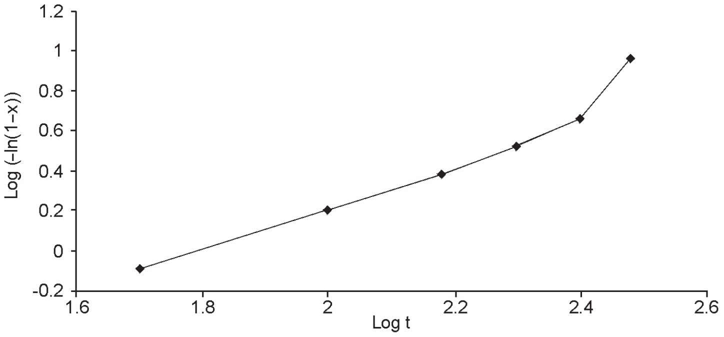

Fig. 3 Application of Avrami–Evans equation to linseed oil/minium mixture

The curve has a linear profile with the exception of the results relative to high polymerisation times. In these cases the error treshold is higher because the dependence on the choice of the base line in the curve cannot be ignored.

By relating the values of k and n with the time at which the maximum in the curve is recorded (Table 1) we obtain regular profiles for both the examined systems, as shown in

Figs 4 and 5. Particularly we observe that the rate constant rapidly decreases with the increase of the polymerisation time: this is true both for the polymerisation of pure linseed oil at the different temperatures and for linseed oil *vs*. the oil/pigment mixture. Furthermore, the value of n increases constantly but remains between 1 and 2: this indicates a first or second order reaction rate. Probably the latter refers to pure linseed oil at low temperatures.

Table 1 Relation of *k* and *n* *vs*. the time of the maximum in the DSC curve

System	*T*/°C	*t* of peak	*k*	*n*
Linseed oil+minium	140	17	$3.2\cdot10^{-2}$	0.9
Linseed oil+minium	150	18	$1.5\cdot10^{-2}$	1.0
Linseed oil+red earth	150	22	$7.0\cdot10^{-3}$	1.2
Linseed oil+Sn and Pb yellow	150	27	$2.5\cdot10^{-3}$	1.4
Linseed oil+chromium yellow	150	31	$1.6\cdot10^{-3}$	1.5
Linseed oil	150	33	$1.2\cdot10^{-3}$	1.5
Linseed oil	140	38	$6.5\cdot10^{-4}$	1.7
Linseed oil	135	48	$3.3\cdot10^{-4}$	1.7
Linseed oil	130	50	$2.5\cdot10^{-4}$	1.8

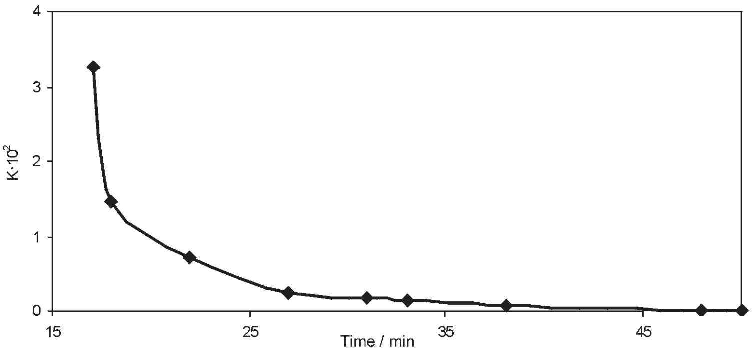

Fig. 4 Rate constant (*k*) as function of time

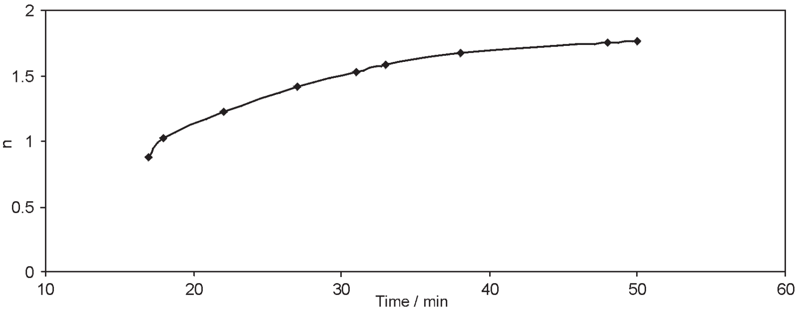

Fig. 5 Index (*n*) as function of time

Conclusions

The results described in the present work demonstrate that:

- The calorimetric technique enabled us to monitor the polymerisation process of linseed oil in the temperature range between 130 and 220°C;
- Reproducible values for isothermal analysis are obtained between 130 and 150°C;
- The results are quantitative and can be justified by kinetic equations;
- From the Avrami–Evans equation only qualitative information is obtained;
- All of the considered pigments accelerate the polymerisation reaction of linseed oil and have therefore a catalytic action.

This is the first attempt to quantify a phenomenon empirically known to painters. Further studies in order to obtain the kinetic equations of the catalytic effect herein described are in progress and will be reported in due course.

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