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FLAMMABILITY CHARACTERIZED BY FLASH-IGNITION TEMPERATURES

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The effects of the experimental conditions (sample size, heating rate, static and dynamic atmosphere) were studied on the value of the flash-ignition temperature (T_i) obtained with a modified derivatograph able to measure T_i simultaneously with the TG, DTG, DTA and T curves. The effects of various parameters are discussed and the optimum conditions determined. T_i for bleached cotton fibre was found to be 270 ± 1 °C.

For characterization of the combustion properties of materials, various parameters are employed. These are the ease of ignition, rate of flame propagation, amount of heat evolved in combustion, etc. One of the most important parameters is the ease of ignition, which can be expressed numerically by the value of the limited oxygen index (LOI) [1] and the time or temperature of ignition. It is well known that different techniques are available for the measurement of ignition temperature [2, 3].

Thermal analysis has recently become an important quality and research control method in the study of flammability and flame retardation processes [4–6].

We have developed a spark-producing attachment for a derivatograph which permits ignition temperature (T_i) detection and TG, DTG, DTA and T scans simultaneously [7, 8]. A derivatoghraph can be applied for measurement of the above properties. This has to search for the optimum experimental conditions and to evaluate the extent of factors influencing the results obtained by means of complex thermal analysis. The objective of this study is to examine the effects of the experimental conditions on T_i. The effects of sample size, heating rate, atmosphere, and rate of air flow are systematically studied. The correlation between TG and DTG signals and T_i values is examined.

Experimental

Materials: Bleached cotton fibre with an average degree of polymerization (DP) 1200 was used as model compound.

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Methods: The measurements were carried out with a modified Q 1500 derivatograph [7, 8] which was able to measure the flash ignition temperatures of materials. T_i is defined as the lowest initial temperature of air passing around the specimen at which a sufficient amount of combustible gas is evolved to be ignited by an external ignition source. In our case, a pilot spark is built into the furnace space of the instrument and the ignition point of the gases evolved is indicated with and additional thermocouple. Different amounts of sample, e.g. 50–650 mg, were accomodated in a medium size ceramic crucible. Heating was at a rate of 10, 5, 2.5 or 1.25 deg min^{-1}, from room temperature to 600°. The measurements were performed in static and dynamic air atmospheres, at a flow rate of 0–30 dm^3/h.

Effects of experimental conditions

Sample size

In order to establish the effect of the sample size on the value of T_i, various amounts of samples in the range 40–650 mg were studied at four different heating rates. It turned out that a T_i peak appeared only when more than 50 mg of sample was used. The upper limit was 650 mg due to the capacity of the crucible. The variation of T_i with sample amount is shown in Figs 1–4. It is seen that T_i was influenced by the amount of samples. Nevertheless, in a certain interval T_i was independent of the sample size.The lower limit of this interval was 350 mg. The smaller the sample size, the higher T_i at a heating rate of 10 or 5 deg min^{-1}. In the discussed interval, T_i increased by abount 20 or 40 deg. At the lowest heating rate, the constant interval was 350–500 mg. At a heating rate of 2.5 deg·min^{-1}, the points on the T_i *vs.* sample size curve were between the former ones. When the sample amount was higher than 350 mg, T_i did not depend on the sample size. This is important from a practical point of view, for this is the lowest T_i value and hence can be considered the most dangerous fire situation. Further, this is the reason for the use of 400 mg of sample.

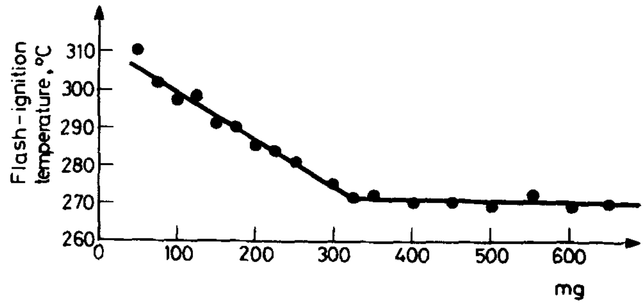

Fig. 1 Flash-ignition temperature *vs.* sample size in static air. Heating rate: 10 deg/min

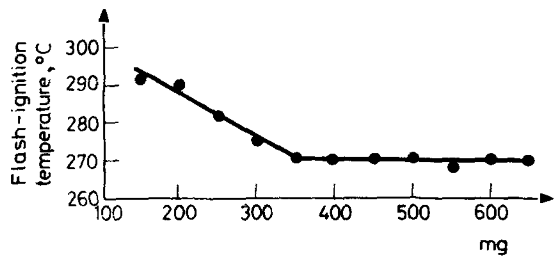

Fig. 2 Flash-ignition temperature *vs.* sample size in static air. Heating rate: 5 deg/min

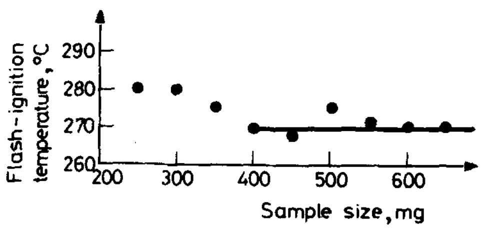

Fig. 3 Flash-ignition temperature *vs.* sample size in static air. Heating rate: 2.5 deg/min

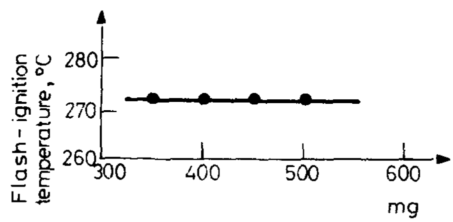

Fig. 4 Flash-ignition temperature *vs.* sample size in static air. Heating rate: 1.25 deg/min

Heating rate

The effect of the heating rate was studied in static air atmosphere with different amount of samples, e.g. 400, 450 and 500 mg. Figure 5 shows the plot of *vs.* heating rate. It is evident that T_i depended slightly on the heating rate under the present experimental conditions. For subsequent measurements, a 10 deg·min^{-1} heating rate was selected.

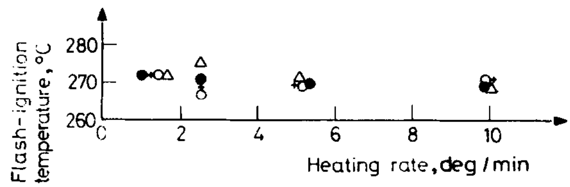

Fig. 5 Flash-ignition temperature *vs.* heating rate in static air. + 400 mg, ○ 450 mg, △ 500 mg, ● 600 mg.

Air flow

To study the effect of dynamic circumstances, 400 mg sample and a heating rate of 10 deg·min^{-1} were chosen. The air was supplied from a compressed air bottle connected to a flowmeter, the rate of air flow being regulated in the range 0–30 dm^3/h. The results obtained are depicted in Fig. 6. In an air flow, T_i was a few degrees higher that under static conditions. This may be attributed to the fact that the air introduced into the furnace diluted the concentration of flammable gases and the ignition was hindered. In other words, more sample had to be decomposed to produce the critical concentration for ignition, and this required a higher temperature (4–5 deg). The T_i peak became uncertain at a flow rate of 25 dm^3/h and there was no signal at a higher rate of flow. These results indicate that the ignition can be better controlled under static conditions, when the T_i values are reliable and reproducible.

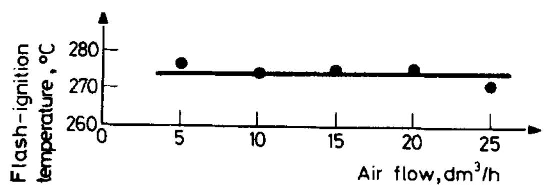

Fig. 6 Flash ignition temperature *vs.* air flow. Heating rate: 10 deg/min. Sample size: 400 mg.

Correlation between T_i and quantity of products

In principle one may expect a correlation between T_i and the quantity of evolved flammable gases, besides the heating rate and sample size. For informatory purposes the weight loss was plotted against the weight loss taking place up to T_i (Fig. 7). It is interesting that the weight loss was strongly influenced by the heating rate. It can be seen that for a 400 mg sample, T_i is 270 ±1°. However, with increase of the heating rate, the quantity of products decreased. For example when the heating rate was increased from 1.25 to 10 deg·min^{-1} (multiplied by 8), the quantity of evolved gases decreased from 80 to 20 mg (i.e. one-quarter). It is obvious that the most dangerous situation develops in practice at a high heating rate, because the concentration needed for ignition is then produced on the decomposition of 18–20 mg cotton fibre. In the weight interval 400–650 mg, the corresponding quantity is 3.5–5.0% of the initial weight. At the same time, at the lowest heating rate the quantity of flammable gases evolved is 70–80 mg, i.e. 18–20%. In the latter case, due to the low heating rate, the system is not far from equilibrium conditions.

It has been assumed that in the course of decomposition (under equilibrium conditions) the quantity of levoglycosan responsible for the flammability of cellulose is 20–25% [9]. Our result coincides with this observation.

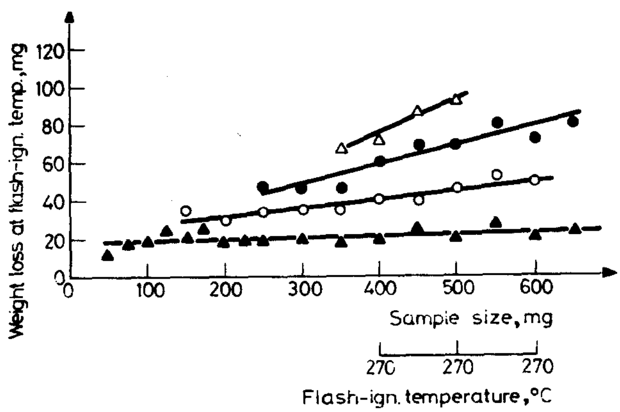

Fig. 7 Weight loss at flash-ignition temperature *vs.* sample size in static air. Heating rate: ▲ 10 deg/min, ○ 5 deg/min, ● 2.5 deg/min, △ 1.25 deg/min.

Reliability of T_i obtained by thermal method

Twenty parallel measurements were carried out on a modified derivatograph at a heating rate of 10 deg·min^{-1} in a static air atmosphere. The amount of sample was 400 mg. On the basis of the experimental results, the average T_i, the standard deviation, the range of deviation, and the reliability domain valid for the 95% confidence interval were calculated by a statistical method with the aid of a computer.
The results obtained were as follows:

$$T_i = 270°;\ s^{x^2} = 3.90,\ s^x = 1.97, \text{ range: 8 deg; reliability domain: } T_i + t_{n-1_\alpha} \cdot \frac{s^x}{\sqrt{n}} = 270 \pm 0.87 \sim 270 \pm 1°,$$

where

T_{i_2} = average ignition temperature in °C,

s^{x^2} = empirical variance

s^x = standard deviation,

t_{n-1_α} = Student statistical parameter,

n = number of measurements,

$1-\alpha$ = confidence interval

It can be concluded that the measurement technique described proved suitable for determination of the ignition temperature of cellulosic fibres.

Conclusion

The results concerning the bleached cotton specimens studied with a modified derivatograph able to measure flash-ignition temperatures can be summarized as follows:

i The measured flash-ignition temperature generally depends on the experimental conditions.
ii With increase of the amount of sample, T_i becomes constant at and above 350 mg, except at a heating rate of 1.25 deg min^{-1}
iii The heating rate has almost no effect on T_i when the sample amount is 350 mg or more.
With decrease of the heating rate, the interval becomes narrower.

iv T_i values obtained in a dynamic air atmosphere proved a few degrees higher than those under static conditions.

v From the TG curves, the minimum amount of sample decomposed was determined, and was found to be 18–20 mg at a heating rate of 10 deg min^{-1}.

vii Statistical methods were used to evaluate the reliability domain of the T_i values, which was found to be 270 ± 1°.

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Zusammenfassung – Es wurde der Einfluß experimenteller Bedingungen (Probengröße, Aufheizgeschwindigkeit, stehende und bewegte Atmosphäre) auf den Wert der Entzündungstemperatur (T_i) untersucht, welche mittels eines zur gleichzeitigen Messung von T_i sowie der TG, DTG, DTA und T-kurven modifizierten Derivatographen bestimmt wurde. Der Einfluß verschiedener Parameter wurde besprochen und Optimumbedingungen festgestellt. Für gebleichte Wolle wurde ein T_i-Wert von 270 ± 1 °C gemessen.

РЕЗЮМЕ — Изучено влияние экспериментальных условий (размер образца, скорость нагрева, статическая и динамическая атмосферы) на значение температуры вспышки-воспламенения (Ti), измеренной с помощью модифицированного дериватографа, позволяющего измерять T_i одновременно с ТГ, ДТГ, ДТА и T-кривыми. Обсуждено влияние различных параметров и определены оптимальные условия. Найдено, что для отбеленного хлопкового волокна температура T_i равна 270±1°.