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USE OF CYCLIC DIFFERENTIAL SCANNING CALORIMETRY

Experiments to investigate the formation of an 'activated cellulose' species during cotton (cellulose) fabric pyrolysis in air and the influence of flame retarded treatments thereon

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Formation of an activated cellulose (Cellulose*) species

$$\text{CELLULOSE} \xrightarrow[\text{air}]{\text{heat}} \text{CELLULOSE}^*$$

is the designated first stage of cellulose degradation in air [1]. Little is known about either the process or the nature of CELLULOSE*. The transition, designated T_2, is observed as an exotherm around 300°C as the sample temperature is raised. No corresponding endotherm is observed on cooling. The process is therefore not reversible but is repeatable as subsequent reheating results in the exotherm being observed again. The exotherm is also found to be oxygen dependant. The effect of all the flame retardant treatments studied was to reduce T_2 compared to the value for the untreated cotton.

Keywords: actived cellulose, DSC, flame retardation, pyrolysis

Introduction

One quarter of all fires reported annually are attributable to textiles being the first material ignited in such conflagrations. However these fires are then responsible for over one half of the consequent deaths due to fires [2]. This disproportionate fatality rate emphasises the importance of the development of successful flame retardant systems for textile materials. Cotton fabrics, which have a major share of the textile market, are the concern of the current studies. A comprehen-

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sive knowledge of the pyrolysis mechanism of cotton (cellulose) fabrics is needed to provide information on which to base development of durable flame retardant systems for cotton fabrics. Current flame retardant systems commonly applied to cotton fabrics function in the condensed and/or vapour phase depending on their chemical structure [3, 4]. Phosphorus and nitrogen containing retardants such as Proban (Albright & Wilson), a phosphonium salt-urea polycondensate, function in the condensed phase by lowering the temperature at which pyrolysis and, consequently, char formation occurs, thus limiting the production of flammable volatiles. Halogen containing flame retardants, now becoming 'ecologically undesirable' as a result of the Montreal Protocol, function in the vapour phase by inhibiting the flame chemistry.

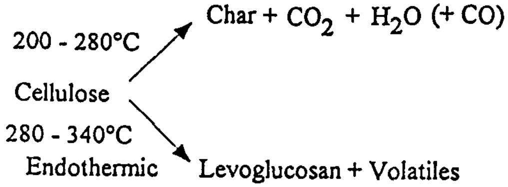

Fig. 1(a) Mechanism proposed for cellulose pyrolysis by Kilzer and Broido [5]

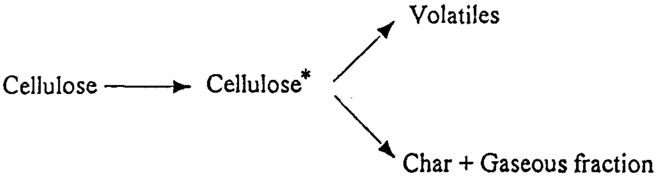

Fig. 1(b) Mechanism proposed for cellulose pyrolysis by Bradbury *et al* [6]

Kilzer and Broido [5] first proposed a decomposition mechanism for cellulose as shown in Fig. 1(a). This mechanism was later modified by Bradbury *et al.* in 1979 [6] who first proposed a precursor step involving the formation of an activated cellulose species as shown in Fig. 1(b). This initial step involving the formation of the CELLULOSE* species arose from flowing nitrogen experiments with cellulose powder under isothermal conditions.

Subsequent DTA and EGA studies in these laboratories [7] identified a low temperature peak in the 300°C region which was designated T_2 and ascribed to the formation of the 'ACTIVATED CELLULOSE' state previously proposed by Bradbury *et al.* [6]. This has led to a more detailed scheme for cellulose pyrolysis indicating the influence of flame retardant treatment, as shown in Fig. 2.

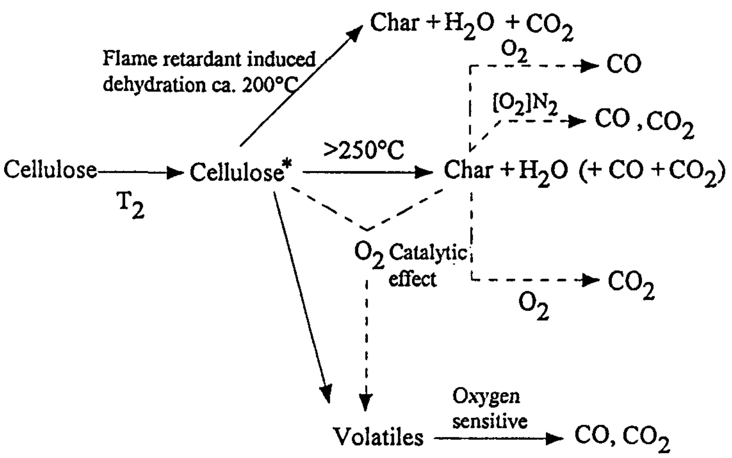

Fig. 2 Mechanism for pyrolysis of cellulose by Price, Horrocks and Akalin [7], [O] represents oxygen available from the initially charred cellulose

This paper reports the use of cyclic differential scanning calorimetry together with weight loss measurements to investigate the initial formation of the 'ACTIVATED CELLULOSE' species in an attempt to more fully understand the transition. Differential scanning calorimetry is more sensitive than differential thermal analysis and gives better quantitative data.

Experimental

Since the DSC is controlled by a computer it could be set to heat up to a certain temperature, the peak associated with the CELLULOSE → CELLULOSE* transition identified, the sample cooled down to room temperature and then reheated to just past the peak temperature. Thus it was possible to oscillate over the peak temperature.

Equipment

DSC studies were preformed on a Mettler DSC 30 (with liquid nitrogen cooling capabilities) and a TC10A microprocessor control unit. Fabric samples (10 mg) were placd in an aluminium capsule perforated with two holes and subjected to the same 5 deg·min^{-1} temperature rise, as had been used in all previous DTA studies in these laboratories [7]. This rate allowed any changes in the sample to occur slowly and clearly. After each run the sample was weighed. Experiments were performed in static air and under flowing nitrogen, the flow rate being 500 ml·min^{-1}. The sensitivity of the Mettler was set at 80 mW full scale deflection.

Materials

Using a paper hole puncher, fabric samples of approximately 10 mg in weight were produced. Five different flame retardants were studied at their commercial levels of application. Three retardants, namely phosphonium salt-urea-ammonia cured polycondensate (Proban CC, Albright & Wilson), a phosphonopropionamide (Pyrovatex, Ciba-Geigy) and ammonium polyphosphate (Amgard TR, Albright & Wilson) function in the condensed phase. Ammonium phosphate-ammonium bromide (Amgard CD, Albright & Wilson) and the antimony (III) oxide-aliphatic bromide (Flacavon H14/587, Schill & Seilacher) are examples of vapour phase active flame retardants. Full details have been published elsewhere [7]. The remaining fabrics studied were the untreated cotton and 50/50 and 70/30 polyester/cotton blends.

Procedure

The fabric samples were sealed in aluminium capsules perforated with two holes and then placed on the thermocouple sensor. Three runs were performed with each fabric, firstly a trace up to 360°C was produced, to identify the transition by correlating the appearance of the CELLULOSE $\rightarrow$ CELLULOSE* transition with previous DTA studies. Once identified a second sample was prepared and then heated to just past the transition temperature or, if the peak merged with another peak e.g. a peak corresponding to CO_2 evolution [4], then up to the merging point. Then the sample was allowed to cool down to room temperature weighed and then heated back up to the peak temperature and then cooled back to room temperature, plotting a trace as the sample was cooled. This enabled a check of the reversibility of the CELLULOSE $\rightarrow$ CELLULOSE* transition. Finally a fresh sample was heated up to the onset of the transition temperature then weighed.

Using the DSC microprocessor control enabled the exact heating and cooling over the transition temperature peak. Interpretation of DSC traces can become very complex during thermal decomposition as the decrease in sample weight causes an exothermic shift of the baseline, at the same time endothermic bond rupture is occurring, as a result, only the net effect is observed. Therefore it is vital to correlate information gathered with that from other studies and techniques and not to rely soley on the information gathered by DSC.

Results and discussion

The information obtained in these experiments is collated in Table 1.

Table 1 T_2 peak temperatures and percentage weight losses in both static air and flowing nitrogen

Sample	In static air			In flowing nitrogen		
		Weight loss / %			Weight loss / %	
	T_2 / °C	$RT \to T'$	$T' \to T''$	T_2 / °C	$RT \to T'$	$T' \to T''$
Untreated cotton	330	7	21	–	–	–
Proban	290	7.3	24.7	290	10.3	31.2
Pyrovatex	300	7.4	32.6	320*	1.7	47.8
Amgard CD	280*	5.4	44.5	250*	5	35.9
Amgard TR	270*	5.1	44.9	265*	4	24
Flacavon 50/50	318	7.9	21.8	255^+	4.8	16
Untreated 50/50	330	4.8	30	–	–	–
Untreated 70/30	330	4.6	16.9	–	–	–

+endotherm; *both CO and CO_2 evolved around T_2 temperature; RT room temperature; T' onset temperature of T_2 peak; T'' end temperature of T_2 peak

Static air experiments

The T_2 peak was observed for all fabrics in static air (Table 1) at around 300°C. These peaks were found to be repeatable but not reversible. This was indicated by the observations that as subsequent reheating resulted in the exotherm being observed again, but no corresponding endotherm was evident upon cooling. With each repetition the peak height diminished and the peak width broadened. In general it was found that the fabrics treated with flame retardants gave rise to a peak below 300°C whereas T_2 for untreated cotton and the 50/50 and 70/30 polyester cotton blends was around 330°C. A weight loss of approximately 7%, due to the loss of water in most cases (seen as a gentle endotherm from RT → 100°C in Figs 3, 4), was noted for the first heating cycle up to the onset temperature of the T_2 peak. This effect was absent on reheating. A significant weight loss is also noted over the T_2 Peak temperature inferring that a chemical reaction is occurring.

Flowing nitrogen experiments

Under flowing nitrogen totally different traces are observed. No T_2 peak was observed for the untreated cotton and cotton blends. T_2 was not repeatable for those fabrics which did show a T_2 peak. When present the temperature at which

T_2 appeared was little different to that in air. The initial small endotherm (RT → 100°C), ascribed to the loss of water, is still present on all traces and absent on reheating. The shape of the T_2 peak (Fig. 5) is sharper than it is in static air (Fig. 4) but not repeatable. These observations suggest that the CELLULOSE → CELLULOSE* transition requires the presence of oxygen. An inter-

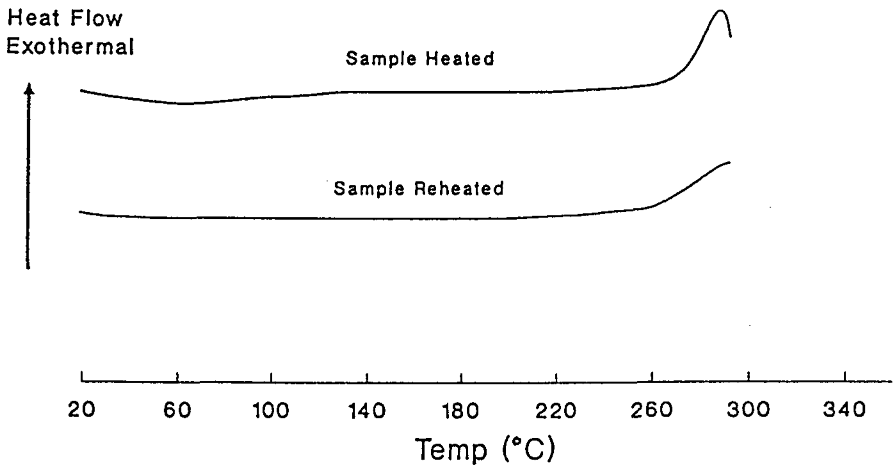

Fig. 3 DSC trace for proban treated cotton in static air

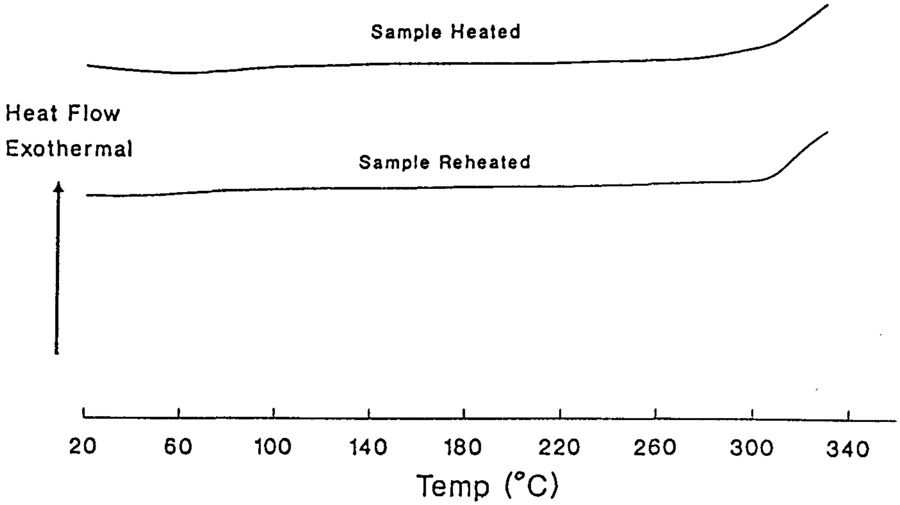

Fig. 4 DSC trace for untreated cotton in static air

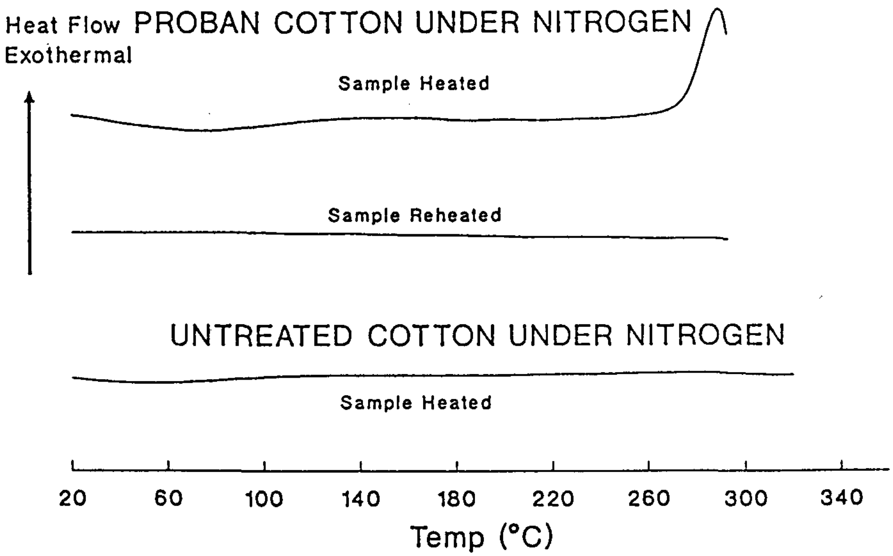

Fig. 5 DSC traces obtained under flowing nitrogen

esting observation is that the loss in weight over the T_2 peak is greater for Proban-treated cotton than it was in air.

Conclusion

The CELLULOSE → CELLULOSE* transition temperature T_2 was observed to be lowered by all flame retardants studied, the vapour phase flame retardants having the greatest lowering effect. However with Amgard TG and CD, carbon monoxide and carbon dioxide are evolved before the T_2 peak is seen and this interfered with the detection of T_2. The Proban-treated cotton clearly showed the T_2 peak before any CO and CO_2 evolution. The transition is repeatable with varied success dependant on the actual flame retardant but the transition is not reversible. Under nitrogen in the case of flame retardant treated samples the transition is not repeatable and it is not even seen with untreated cotton. The transition is therefore influenced by the flame retardant and also requires the presence of oxygen. The influence of weight of sample had no significant effect except that in the case of experiments with single fibres, rather than fabrics, much larger peaks were seen. It should be pointed out that most reported studies on cellulose [8] have used cellulose powder whereas this study only utilised commercially available fabric samples.

Further studies concerned with the activated cellulose species are being undertaken using electron spin resonance techniques. Since the slight endotherm observed indicates that water is being lost up to 300°C there is a distinct possibility that double bonds are being formed in the cellulose molecule. It has been postulated that peroxy radicals could be associated with T_2, as induction temperatures near 300°C are indicative of peroxy radical formation. ESR has been used by other workers to study the formation of free radicals in photo-irradiated cellulose and the subsequent radical decay [9, 10]. No attempt was made to identify the free radicals involved.

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Zusammenfassung — Die Bildung aktivierter Zellulose aus Zellulose in Gegenwart von Wärme und Luft ist der ermittelte erste Schritt des Abbaues in Luft [1]. Über Prozeß und Natur von aktivierter Zellulose ist nur wenig bekannt. Die mit T_2 gekennzeichnete Umwandlung ist bei 300°C exotherm, wenn die Probentemperatur steigt. Beim Abkühlen wird keine entsprechende endotherme Erscheinung beobachtet. Der Prozeß ist somit nicht reversibel, jedoch bei nachfolgendem Wiedererhitzen wiederholbar. Die exotherme Erscheinung ist weiterhin sauerstoffabhängig. Der Einfluß aller untersuchten flammenhemmenden Behandlungen besteht in einer Reduzierung von T_2, verglichen mit dem Wert von unbehandelter Baumwolle.