

FTIR evolved gas analysis of the decomposition products of cellulose diacetate¹

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Abstract

Evolved gas analysis of unplasticised cellulose diacetate flake and plasticised cellulose diacetate film (Clarifoil) was carried out as part of an assessment of the potential hazard that could occur as a result of overheating these materials during processing. In order to perform this work, a simple apparatus for heating a sample and introducing the evolved gases into a FTIR gas flow cell was constructed. These measurements were supplemented by thermogravimetry as part of separate experiments. Studies of the infrared spectra and thermogravimetric data showed that both materials degrade above 250°C generating carbon monoxide, carbon dioxide and acetic acid. In addition, Clarifoil releases a significant amount of plasticiser (diethyl phthalate) between 100 and 250°C. Since its flash point is 160°C, the potential fire hazard of this material needs to be taken into account during any processing operation which could reach this temperature.

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1. Introduction

The thermal stability and degradation products of many materials is of paramount importance to their processing and handling. In particular, the production of plasticised cellulose diacetate film (Clarifoil) necessarily involves the creation of waste which could be shredded and thus recycled into the process stream. During this operation there is, however, the danger that the machinery could become clogged with material causing overheating and a subsequent fire risk. Whilst the thermal stability and decomposition kinetics of cellulose diacetate have been established by thermogravimetry (TG) [1], the precise nature of its degradation products has only been a speculation based on the chemical composition of the starting material. Without knowledge of the nature of the volatiles produced on heating it is impossible to assess the hazard that they could present in the event of an accident.

Numerous procedures have been developed specifically for the identification of volatile decomposition products generated during the thermal degradation of industrial materials [2-5]. The combination of TG and Fourier transform infrared evolved gas analysis (TG-(FTIR)EGA) is a powerful and versatile method of characterising the thermal degradation and decomposition pathways of many substances. Since the system requires the simultaneous use of two instrument systems, the authors have found the implementation of routine TG-(FTIR)EGA studies unattractive in terms of its deployment within a busy industrial analytical laboratory. In order to overcome this difficulty, an alternative strategy was investigated whereby TG and EGA were carried out as separate experiments.

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2. Experimental

Samples of raw cellulose diacetate flake and plasticised solvent cast 50 μm film (Clarifoil), were obtained from Courtaulds Acetate, Spondon, UK.

Thermogravimetry was performed using a TA Instruments model 951 TGA interfaced to a 9900 Computer/Thermal Analyzer. The thermobalance was calibrated for weight and temperature response according to the deflection caused by standard milligramme masses and the melting temperature of pure indium wire respectively. A sample of each material was heated from ambient to 600°C in a platinum boat at 10°C/min. All measurements were made under air (flow rate: 50 ml/min).

Evolved gas analysis was carried out independently from thermogravimetry by employing a simple tube furnace constructed from a 25 mm diameter test-tube lying horizontally on an electrical hotplate. A 40 mg sample of each material, in an aluminium foil tray, was placed in the tube and air (flow rate: 50 ml/min) was passed over the sample by means of a Dreschel head fitted to the end of the test-tube. A digital thermocouple placed just above the specimen was used to monitor its temperature whilst it was heated. Ballistic heating (as opposed to the programmed temperature ramp available with the thermobalance) of the sample was achieved by simply setting the temperature control of the hot plate to maximum. The evolved gases were then passed through a heated FTIR gas flow cell fitted to a Nicolet 740 FTIR spectrometer and spectra collected every 5.8 seconds (16 scans). Plots of sample temperature against the number of spectra collected (equivalent to time) for each EGA experiment (Fig. 1) showed that the temperature program was reproducible and permitted comparison of TG data with EGA results.

3. Results & Discussion

Plots of weight (%) and rate of weight loss (%/°C) against temperature for both unplasticised and plasticised material are shown in Figs 2 and 3. Three distinct weight loss processes can be observed for cellulose diacetate: 3% weight loss from ambient to 200°C (probably due to the loss of moisture within the sample), 82% weight loss from 250 to 400°C followed by complete oxidation of the residue from 400 to 600°C. The plasticised film exhibits an additional loss of material in the region between 100 to 250°C. This accounts for 14% of the original sample weight and is presumably due to evolution of plasticiser. A small residue also remains at 600°C amounting to about 1% of the original material.

Gram-Schmidt reconstructs based on vector analysis of the acquired interferograms allows plots of the total evolved gases detected by the spectrometer to be generated (Fig. 4). The detector signal has been plotted as a function of sample temperature and qualitatively approximates to the derivative weight loss curves recorded during the TG experiments performed under more controlled conditions. A recent paper by Berbenni et al. gives a good discussion of the effect of heating rate and gas purge on the FTIR spectral response [6].

Figures 5 and 6 show chemigrams generated from the integrated absorbance over specific frequency ranges intended to show the concentration of a particular species present in the accumulated spectra; for example, plotting the integrated absorbance in the region 2222-2021 cm^{-1} permits the concentration of carbon monoxide to be monitored during the course of the experiment (solid lines). The window chosen should ideally include only

vibrational modes peculiar to the volatile under investigation. In some cases the infrared bands chosen may overlap with those of other species present thus confusing the analysis. This was the case for water, although it was apparent from the real-time display of acquired spectra on the instrument that water was being evolved. Chemigrams specific to acetic acid were generated using the -OH absorbance in the region 3633-3502 cm^{-1} (dashed lines).

It was not possible to define a frequency window specific to diethyl phthalate (DEP) due to overlap with bands attributable to the other evolved gases. An alternative approach was therefore adopted in order to monitor the evolution of the plasticiser. Using additional basis vectors at data points 123, 126 and 162 allowed a Gram-Schmidt Plus reconstruct to be generated (Fig. 7) which shows the evolution of gases without the contribution of CO, CO₂ and acetic acid. This deconvolution procedure creates a reconstruct for DEP directly from the modified Gram-Schmidt vector analysis.

With the additional information afforded by the EGA experiment it is now possible to confirm the degradation pathway of these materials. The initial weight loss of the unplasticised sample is due to moisture in the material, combined with residual free acetic acid (the specimen smelt slightly of vinegar). Above 250°C cellulose diacetate eliminates acetic acid, CO and CO₂ (and water) to form a carbonaceous residue which oxidises completely on further heating.

Clarifoil follows the same decomposition route as unplasticised material and that loss of plasticiser is well separated from the main degradation of the polymer. Although the flash point of DEP is 160°C compared with 40°C for that of acetic acid [7], DEP is liberated at a much lower temperature (and probably in greater quantity) thus presenting a greater environmental problem. Considerable caution, should therefore be exercised to ensure that waste film is not exposed to a situation where plasticiser vapour might build up.

4. Conclusions

This study demonstrates the utility of evolved gas analysis in determining the degradation pathway of raw and plasticised cellulose diacetate and how this information can be applied to evaluate the potential hazards of exposing these materials to adverse temperatures. In particular, plasticised cellulose diacetate film may liberate diethyl phthalate when exposed to temperatures > 100°C.

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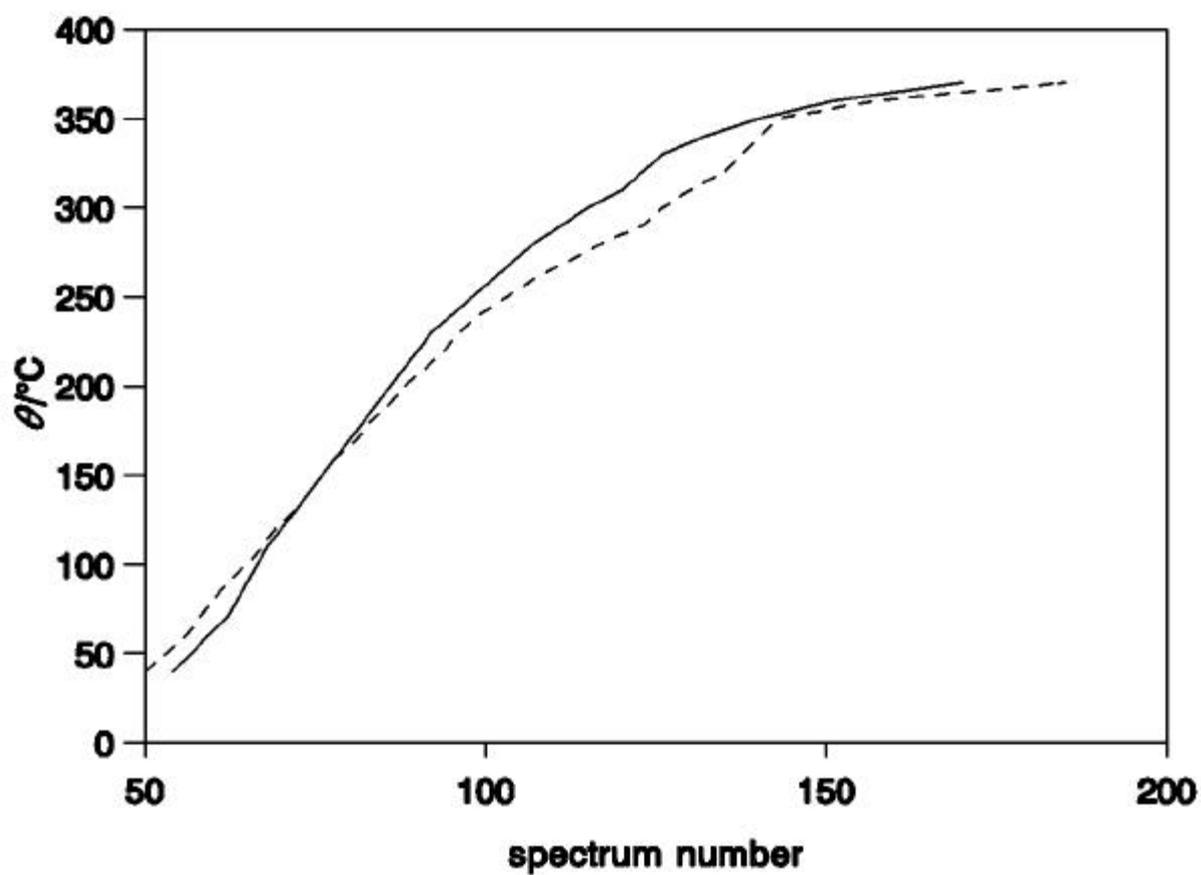


Fig. 1. Heating profiles during evolved gas experiments for cellulose diacetate (solid line) and Clarifoil (dashed line).

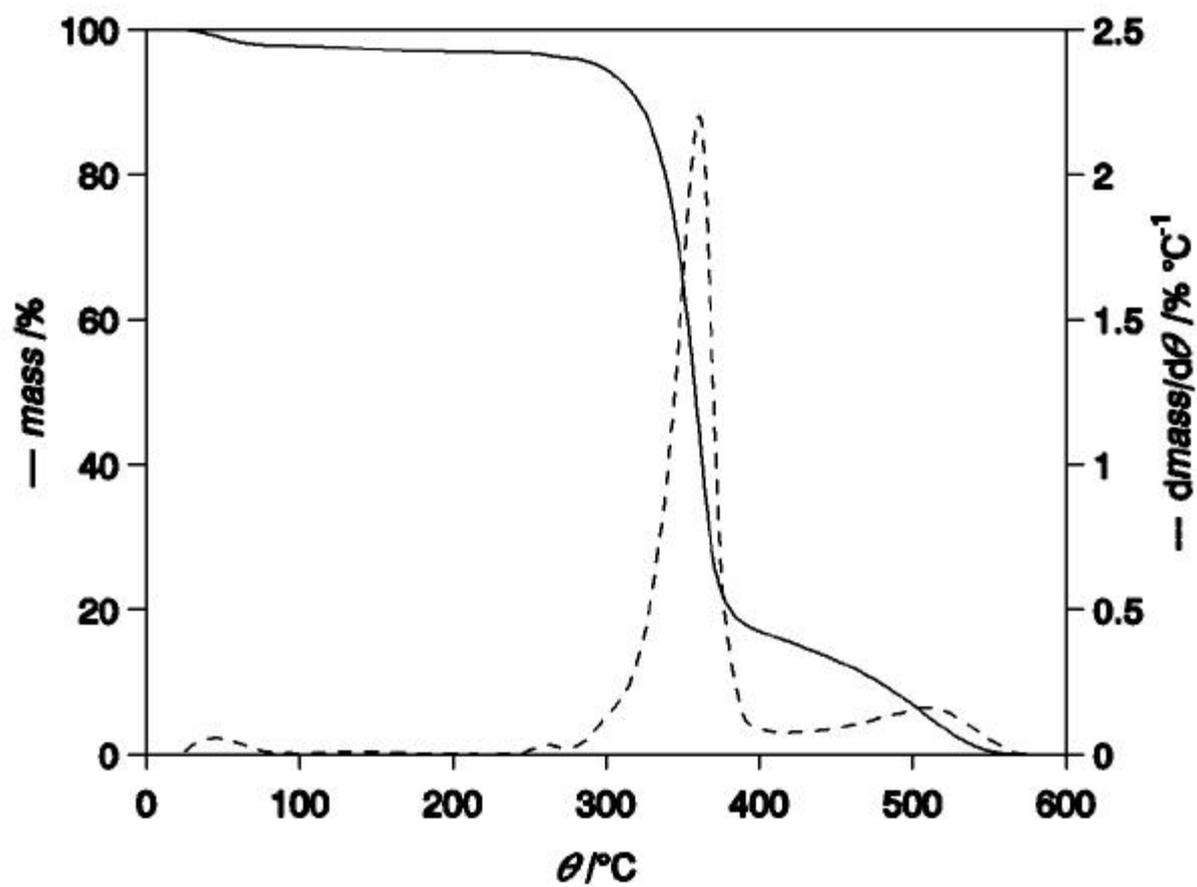


Fig. 2. TG (solid line) and derivative TG (dashed line) curves for cellulose diacetate in air (heating rate: $10^\circ\text{C min}^{-1}$).

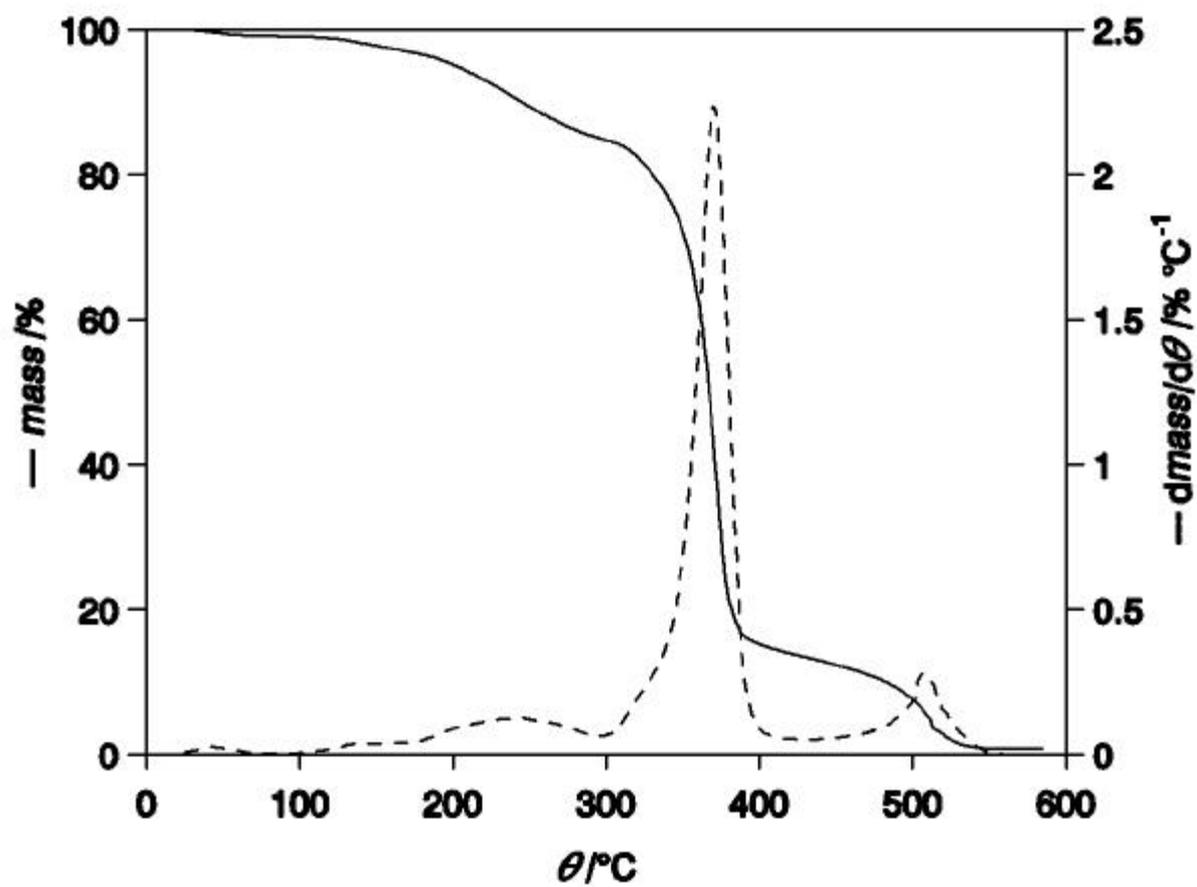


Fig. 3. TG (solid line) and derivative TG (dashed line) curves for Clarifoil in air (heating rate: 10°C min⁻¹).

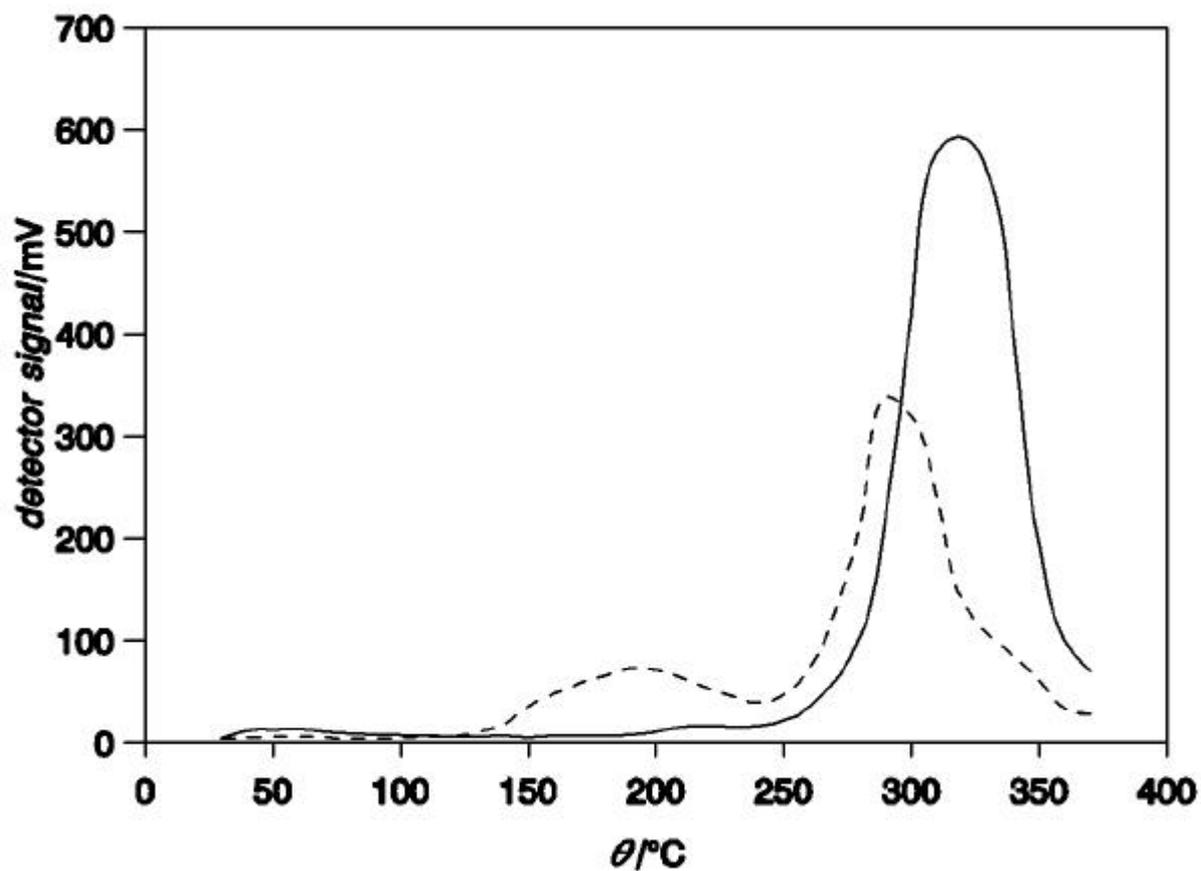


Fig. 4. Gram-Schmidt reconstructs of total integrated IR detector response of the evolved gases produced on heating cellulose diacetate (solid line) and Clarifoil (dashed line) in air according to the temperature programs in Fig. 1.

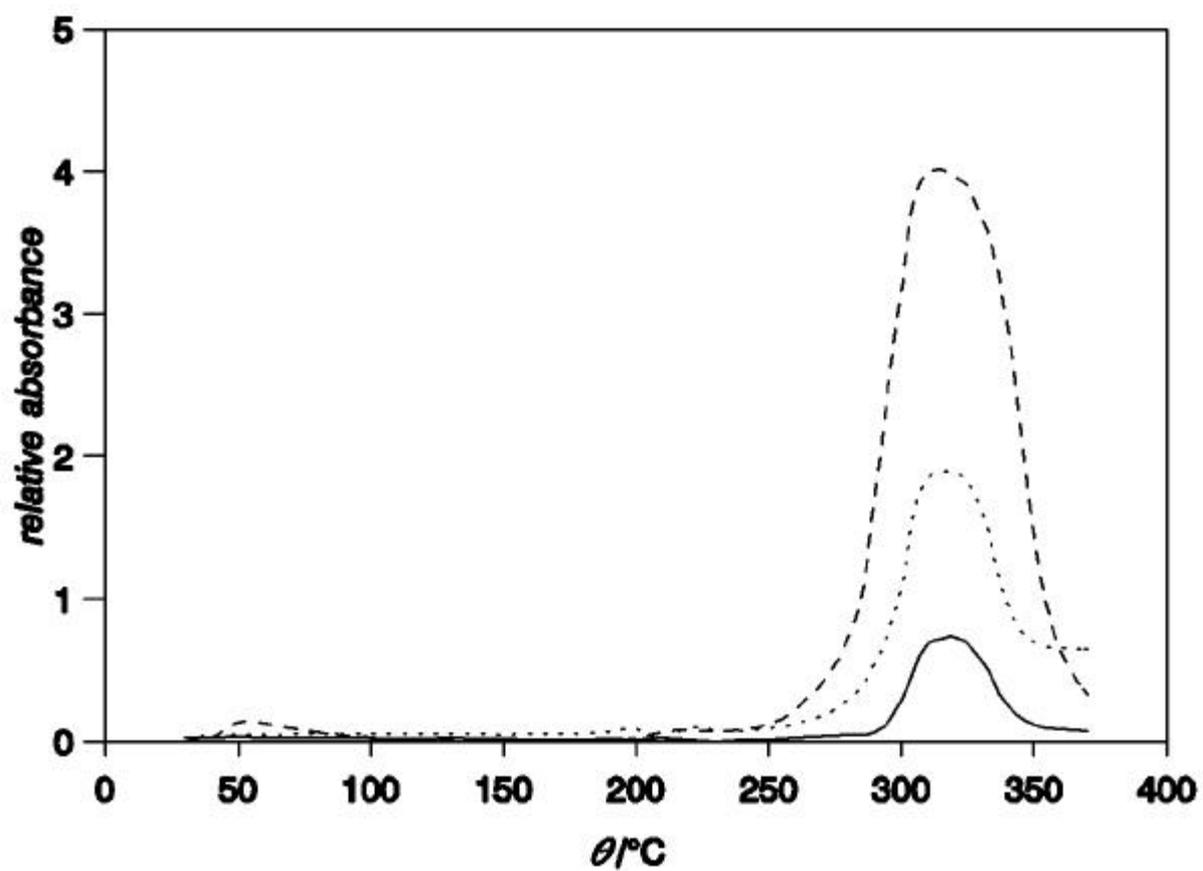


Fig. 5. Chemigrams showing the evolution of CO (solid line), CO₂ (dotted line) and acetic acid (dashed line) from cellulose diacetate.

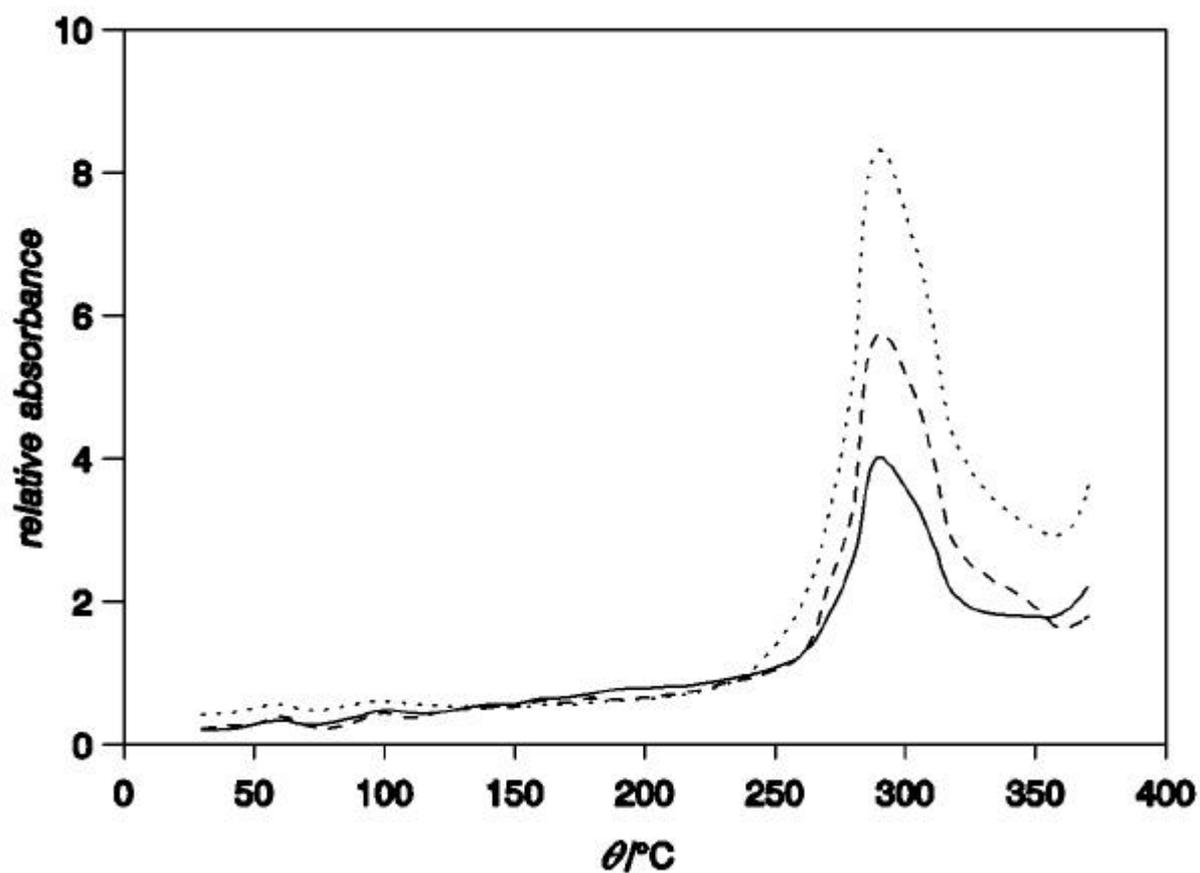


Fig. 6. Chemigrams showing the evolution of CO (solid line), CO₂ (dotted line) and acetic acid (dashed line) from Clarifoil.

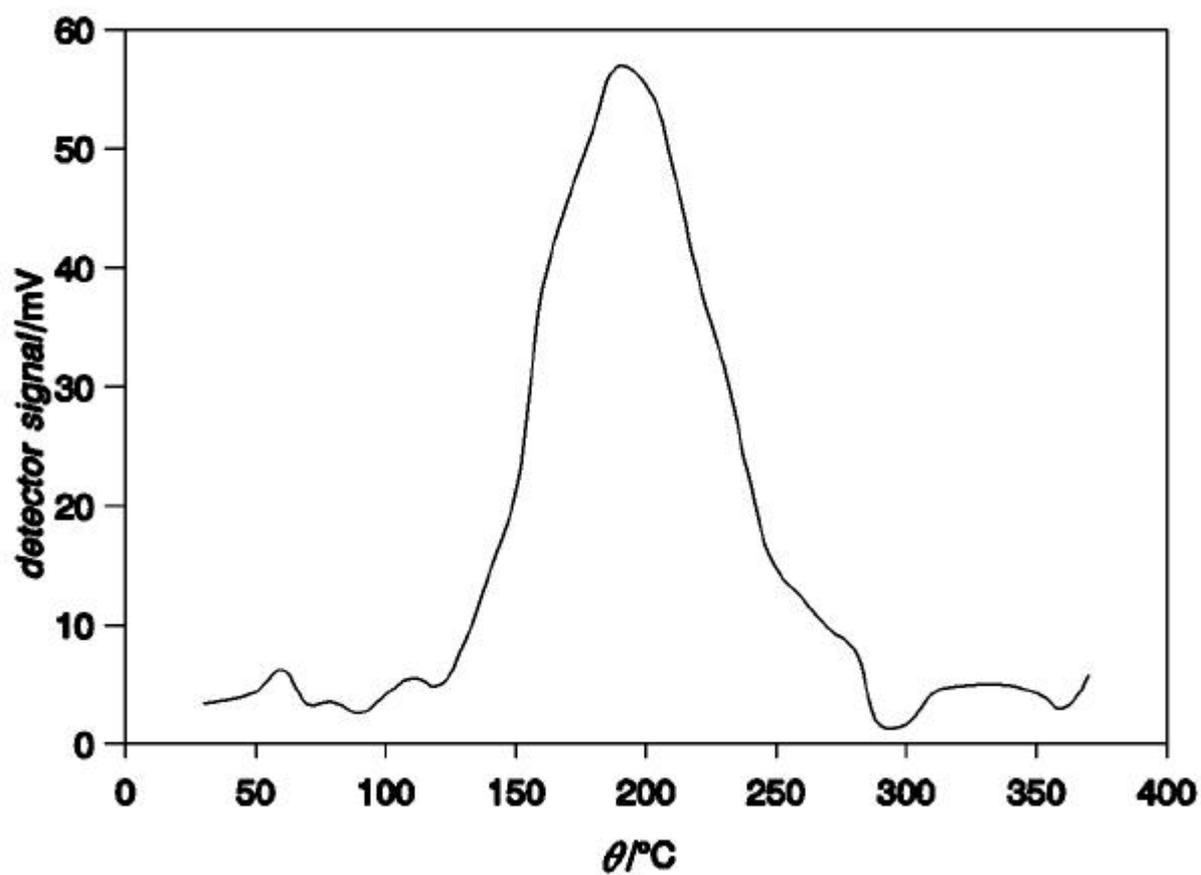


Fig. 7. Gram-Schmidt Plus reconstruct for Clarifoil illustrating the loss of plasticiser on heating.