ELSEVIER

Thermochimica Acta 339 (1999) 55–67

thermochimica acta

www.elsevier.com/locate/tca

Comparative thermoanalytical investigation of the cross-linking behaviour of three different paraffin waxes in the presence of potassium persulphate

A.S. Luyt[a,*], K. Ishripersadh[b], D.N. Timm[b]

[a]Department of Chemistry, University of the North (Qwa-Qwa), Private Bag X13, Phuthaditjhaba, 9866 South Africa
[b]Department of Chemistry, ML Sultan Technikon, PO Box 1334, Durban, 4000 South Africa

Received 11 January 1999; accepted 21 June 1999

Abstract

The cross-linking of three different paraffin waxes – a hard oxidised wax, a medium wax, and a hard wax with narrow molar mass distribution – in the presence of potassium persulphate (PPS) was investigated thermoanalytically. DSC and TG curves for untreated waxes and waxes treated with different amounts of PPS were obtained and the observations were compared with gel content data obtained through gravimetric analysis. Although initial indications were that cross-linking did occur, reheat curves of wax/PPS mixtures as well as gel content data showed that no cross-linking occurred. It was, however, found that PPS most probably decomposed into $KHSO_4$ and that this decomposition gave rise to functionalisation of the waxes.

Keywords: Wax; Cross-linking; Differential scanning calorimetry; Thermogravimetry

1. Introduction

Waxes, being long-chain hydrocarbons, may occur naturally as animal, vegetable and mineral wax or may be synthesised [1,4]. Most of these waxes can be cross-linked, but very little is known on the cross-linkability of the different waxes and the influence of cross-linking on their physical and mechanical properties.

Potassium persulphate (PPS), also known as potassium peroxodisulphate, is principally used as an initiator for olefin polymerisation in aqueous systems [2]. It is also used for etching and curing of grouts for soil stabilisation. The dry solid decomposes thermally to oxygen and potassium pyrosulphate [3] and hydrolyses in acid to potassium peroxymonosulphate and hydrogen peroxide. In recent (unpublished) experiments it was also used as initiator in the curing of polymer membranes in an aqueous medium.

Luyt et al. [3] investigated the possible curing of a hard paraffin wax in the presence of PPS thermoanalytically. They tried to establish the cross-linkability and extent of cross-linking through FTIR analyses and wax solubility. Although these results positively indicated that cross-linking may have occurred in the presence of PPS, the results of this study will prove beyond any doubt that PPS does not initiate wax cross-linking.

In this study, we investigated the cross-linkability of three different waxes in the presence of PPS. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to study possible cross-linking processes, while gravimetric analysis of

---

*Corresponding author. Fax: +27-58-713-0152

PII: S0040-6031(99)00178-1

gel content was used to establish whether cross-linking actually occurred.

2. Materials and methods

The materials used were three types of paraffin waxes (waxes 1–3) supplied by Schümann-Sasol in South Africa. Wax 1 is a typical hard oxidised Fischer-Tropsch wax that exhibits some properties of microcrystalline waxes [5,6]. This wax consists of long-chain acids, esters, alcohols, ketones and some unreacted paraffins (alkanes). It is also an emulsifiable wax which has good solvent–retention properties that allows it to be applied in polishes and coatings. Some of its characteristics are listed in Table 1. Wax 2 is a paraffinic Fischer-Tropsch wax with an average molecular formula of $C_{23}H_{48}$ [5,6]. This medium melting point wax has chains that are about 84% unbranched and is used mostly in candle moulding and polishes. Some characteristics of this wax are seen in Table 2. Wax 3 is a high molecular mass Fischer-Tropsch wax with a narrow carbon number distribution ranging from C_{38}–C_{93} [5,6]. It is chemically inert and is free of aromatics. Table 3 shows some of its properties.

PPS, obtained from BDH Laboratory Supplies in Poole, England is supposed to decompose at a temperature below 100°C [7]. The grade used was BDH AnalaR.

The differential scanning calorimeter was a Mettler DSC20 with a Mettler TC11 thermal analysis processor. The thermogravimetric analyser was a Mettler TG50 thermobalance connected to a Mettler TC10A thermal analysis processor. For both DSC and TG analyses the heating rate was $10°\mathrm{C\,min^{-1}}$ and the nitrogen flow through the cell was $85\ \mathrm{ml\,min^{-1}}$. The average sample size was 10–15 mg.

The amount of gel produced as a result of cross-linking was determined by extraction in a mixture of toluene and water, since uncured wax will dissolve in toluene and unreacted PPS/$KHSO_4$ will dissolve in water. Wax samples, initially mixed with, respectively, 10%, 30% and 50% of curing agent, were cured thermally from 30°C to 215°C in the DSC in a nitrogen

Table 1
Properties of wax 1

Property	Value
Average molecular mass	660
Boiling point	239°C
Congealing point	80°C minimum
Softening point	100°C
Physical appearance	Off-white waxy beads

Reactivity data
Reactions: reacts at high temperatures with oxidising agents
Thermal decomposition: occurs at ±250°C forming hydrocarbon gases
Air and water: no reaction

Table 2
Properties of wax 2

Property	Value
Average molecular mass	440
Congealing point	65–70°C
Physical appearance	Off-white waxy beads

Reactivity data
Reactions: reacts at high temperatures with oxidising agents
Thermal decomposition: occurs at ±250°C forming hydrocarbon gases
Air and water: no reaction

Table 3
Properties of wax 3

Property	Value
Average molecular mass	1300
Congealing point	102–108°C
Physical appearance	Hard white waxy beads
Reactivity data	
Reactions: reacts at high temperatures with oxidising agents	
Thermal decomposition: occurs at ±250°C forming hydrocarbon gases	
Air and water: no reaction	

atmosphere. The cured samples were weighed and inserted into a pre-weighed wire mesh (38 μm). The samples were inserted in a Soxhlet apparatus and heated for 6 h. The extracted samples were removed from the Soxhlet apparatus and vacuum dried overnight before weighing. The gel content was calculated as follows [8]:

$$\text{Step 1}: \ \%\text{Extract} = (\text{mass loss during extraction/sample mass}) \times 100 = [(W3 - W2)/W1)] \times 100,$$

where $W1$ is the mass of the sample, $W2$ mass of the mesh pouch, sample and pan after extraction, and $W3$ is the mass of the mesh pouch, sample and pan before extraction

$$\text{Step 2}: \ \%\text{Gel} = 100 - \%\text{Extract}.$$

3. Results and discussion

The thermal events observed during the heating of pure potassium persulphate (PPS) are seen in Fig. 1.

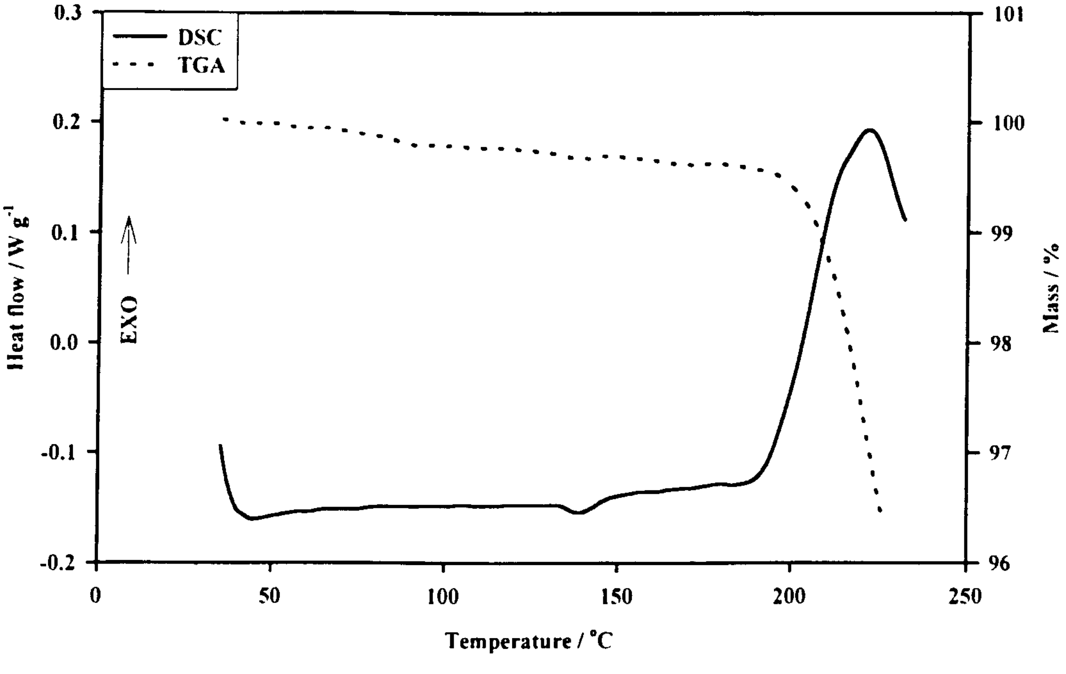

Fig. 1. DSC and TG curves for potassium persulphate (PPS).

The DSC curve shows an immediate change in heat capacity at the start temperature, followed by a weak endotherm at about 140°C and a strong exotherm between 200°C and 250°C. The immediate reaction occurring at about 30°C and the weak endotherm are reproducible, but cannot be explained because of a lack of available information on the thermal decomposition mechanism of PPS. The exotherm between 200°C and 250°C probably is the decomposition of PPS into K_2SO_4, which is the decomposition product according to literature [3]. The decomposition temperature is, however, much higher than the acceptable literature value [7]. Thermogravimetric analysis of PPS shows a small mass loss starting at about 200°C which is the same than the start temperature of the decomposition exotherm in the DSC curve. It was, however, not possible to draw a correlation between the observed mass loss and that expected for the decomposition reaction mentioned above.

Fig. 2 represents the DSC curves of the untreated wax and 10%, 30% and 50% m/m mixtures of potassium persulphate (PPS) with the wax. Melting of the untreated wax is seen as a broad endotherm in the temperature range 50–100°C. The presence of PPS, however, changes the melting characteristics of the wax, as seen in the shapes of the wax melting endotherms and the positions of their maxima. In all the three treated samples the melting endotherms form sharper peaks with maxima at about 100°C. For these samples, the exotherms between 185°C and 240°C are similar to that observed for pure, unmixed PPS (Fig. 1), but the peak maxima are at somewhat lower temperatures. The decomposition exotherms also increase in size with increasing PPS content, but this decomposition of PPS does not give rise to cross-linking of the wax, as will be seen later in the discussion.

Reheating the PPS treated wax samples showed an interesting phenomenon (Figs. 3–5). There are slight changes in the shapes of the wax melting endotherms and the positions of their maxima, but the total areas remained approximately the same than those of the wax melting endotherms in the first heat. Two endotherms, the first considerably weaker than the second, are also observed at about 180°C and 200°C. The only explanation for this observation was that the peaks represented phase changes and/or melting of the decomposition product(s) of PPS. To verify whether

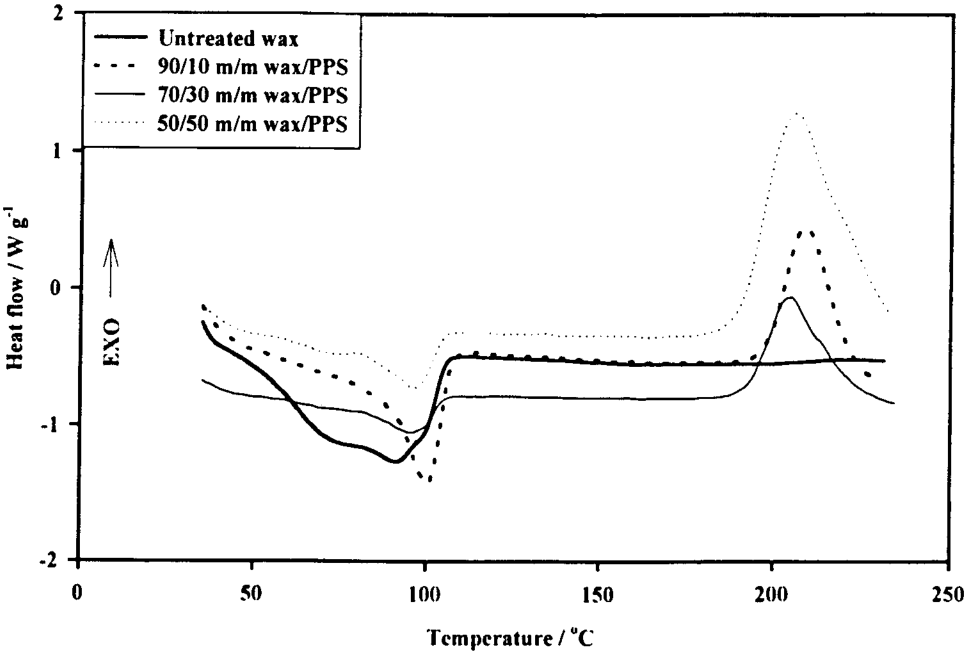

Fig. 2. DSC curves of untreated wax 1 as well as samples mixed with different amounts of PPS.

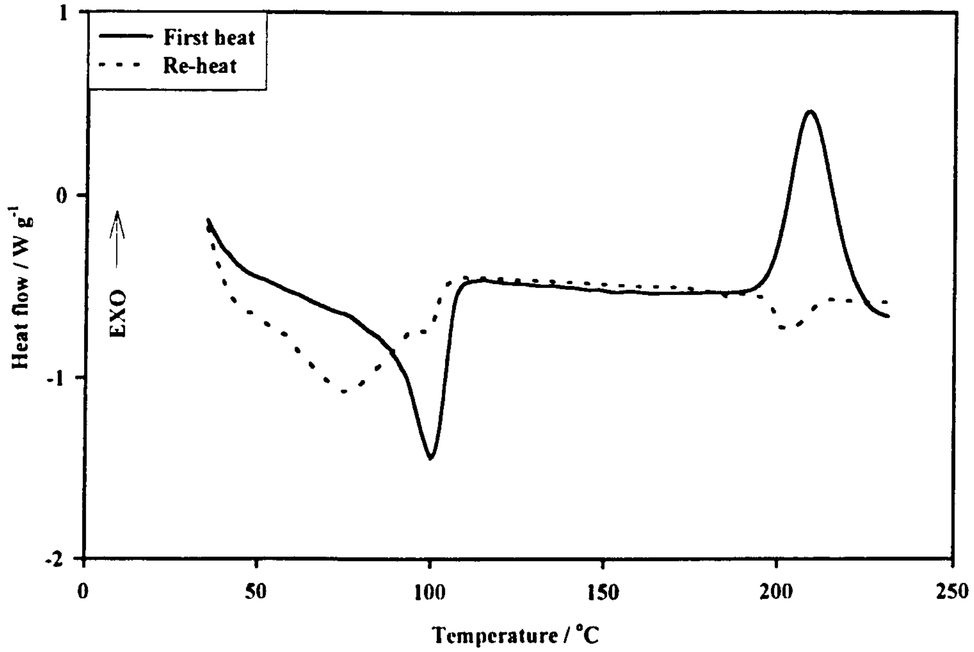

Fig. 3. Heat and reheat curves of 90/10 m/m wax 1/PPS.

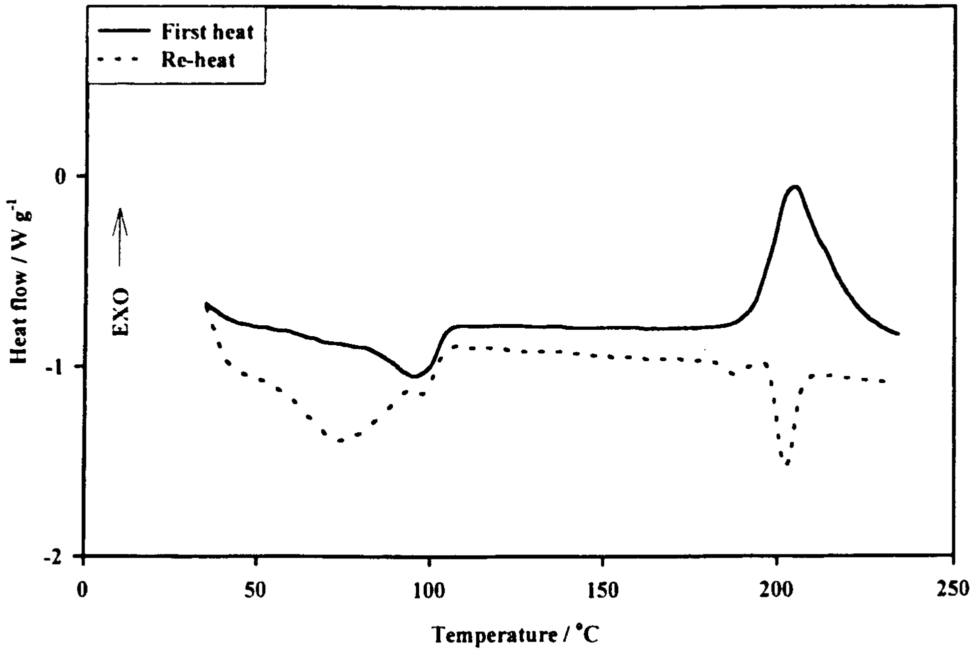

Fig. 4. Heat and reheat curves of 70/30 m/m wax 1/PPS.

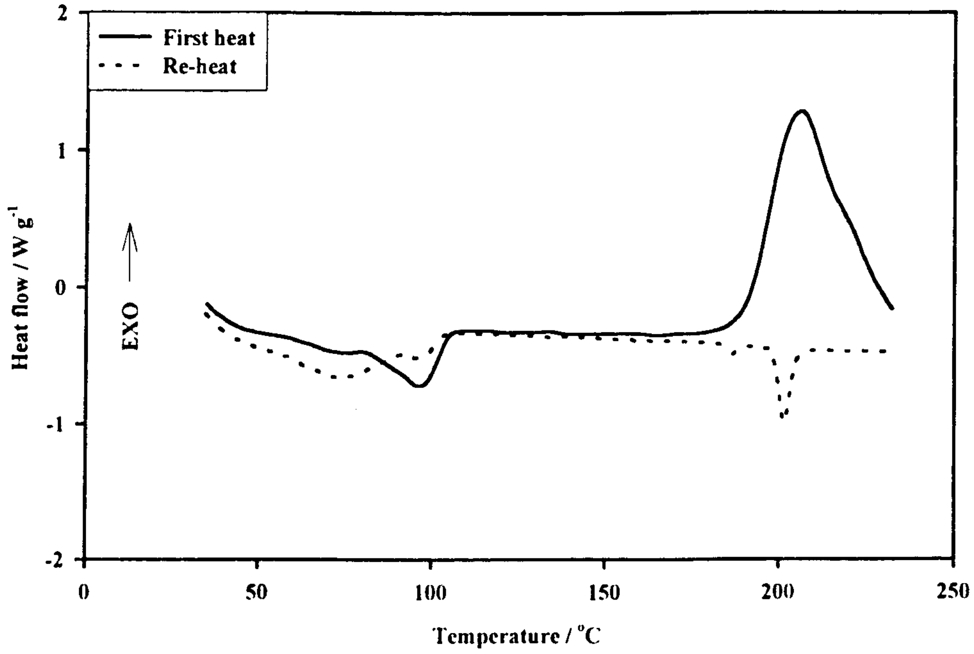

Fig. 5. Heat and reheat curves of 50/50 m/m wax 1/PPS.

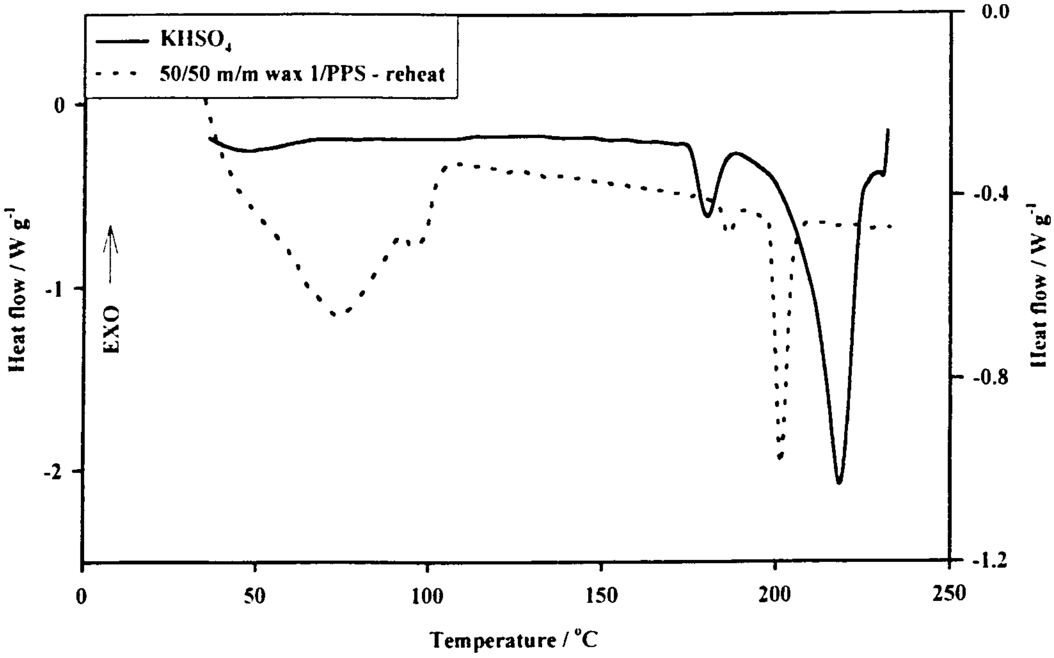

Fig. 6. Comparative DSC curves for $KHSO_4$ and reheat of a wax/PPS mixture.

this was true, DSC analyses were done on pure samples of different possible PPS decomposition products. Comparison of the two DSC curves in Fig. 6 proves that $KHSO_4$ is, within reasonable doubt, the decomposition product of PPS when heated in a wax mixture. None of the other compounds gave DSC curves that looked nearly the same than the reheat curves discussed above. A possible explanation for this phenomenon is that the decomposing PPS extracts hydrogen from the wax chain, and in the process, functionalises the wax with sulphur and oxygen containing groups. FTIR spectra, not presented here, show the development of vibration bands in the 1000–1250 cm^{-1} region.

The TG curves of the untreated wax and 10%, 30% and 50% m/m mixtures of PPS with the wax are seen in Fig. 7. Here the untreated wax shows only a small mass loss towards the end of the curve and gradually increasing mass losses, starting at approximately 150°C, are observed for the mixtures containing increasing amounts of PPS.

DSC thermal events of untreated and PPS treated wax 2 are seen in Fig. 8. Untreated wax 2 melts in the temperature range 40–80°C. The melting endotherms of the wax in the treated samples have different shapes to that of the untreated sample, indicating that the added PPS influenced the structure and melting behaviour of the wax. The peak intensities also decrease with increasing amount of PPS as a result of the smaller wax fractions in the respective samples. Exotherms, similar to the decomposition exotherm observed for pure PPS (Fig. 1), can be seen in the temperature range 200–230°C. The increase in peak intensity relates to the increased PPS fractions in the samples. There is also a slight shift to lower temperatures with increased amount of PPS. We shall also show later that, although cross-linking was initially thought to occur, the decomposition of PPS did not initiate wax cross-linking.

Comparison of the heating and reheating DSC curves of treated waxes are shown in Figs. 9–11. The melting endotherm of the wax in the sample did not decrease in size after heating it in the presence of PPS, indicating the absence of any cross-linking in this process. The two higher temperature endotherms in the reheat curves indicate, as discussed earlier, that PPS probably decomposed to $KHSO_4$, functionalising the wax in the process.

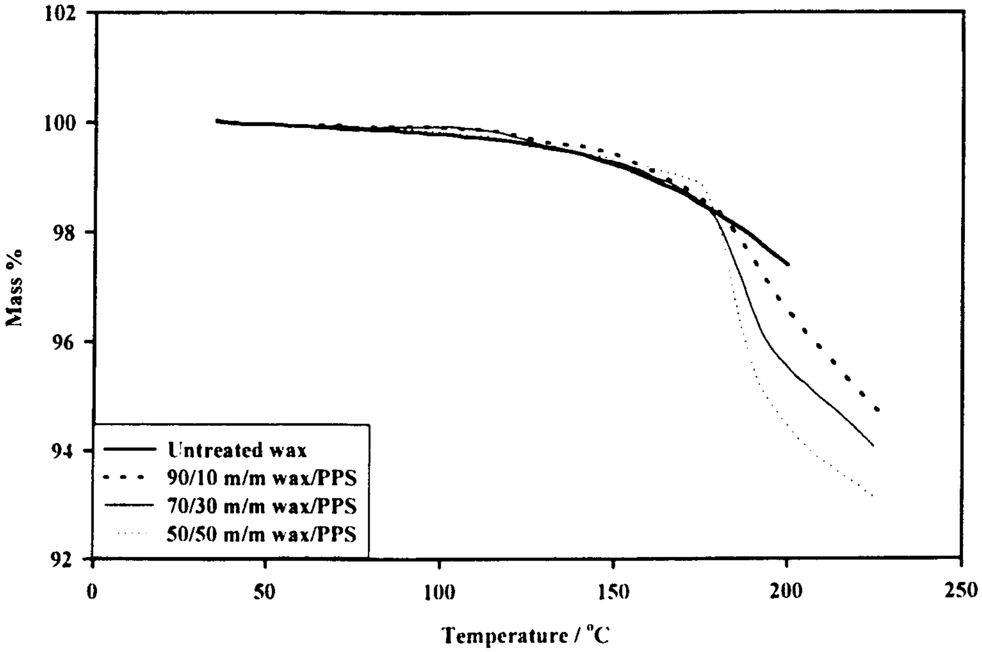

Fig. 7. TG curves of untreated wax 1 as well as samples mixed with different amounts of PPS.

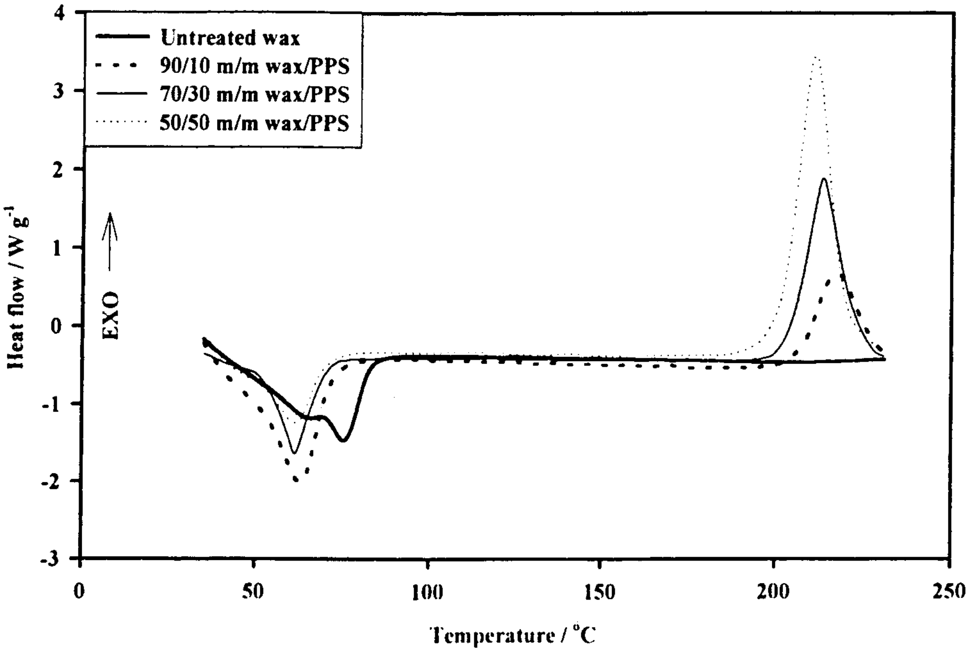

Fig. 8. DSC curves of untreated wax 2 as well as samples mixed with different amounts of PPS.

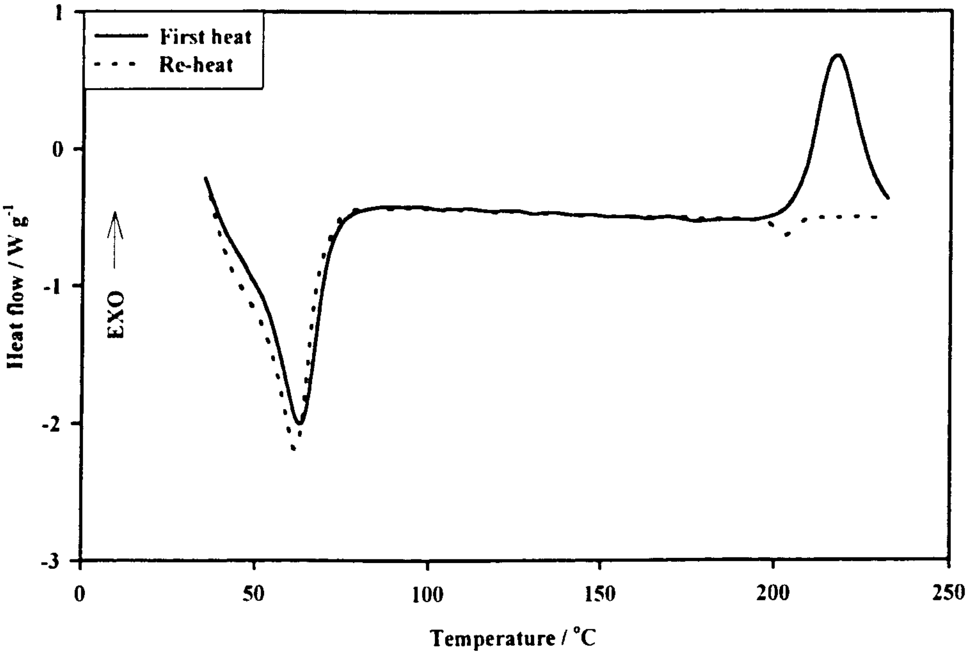

Fig. 9. Heat and reheat curves of 90/10 m/m wax 2/PPS.

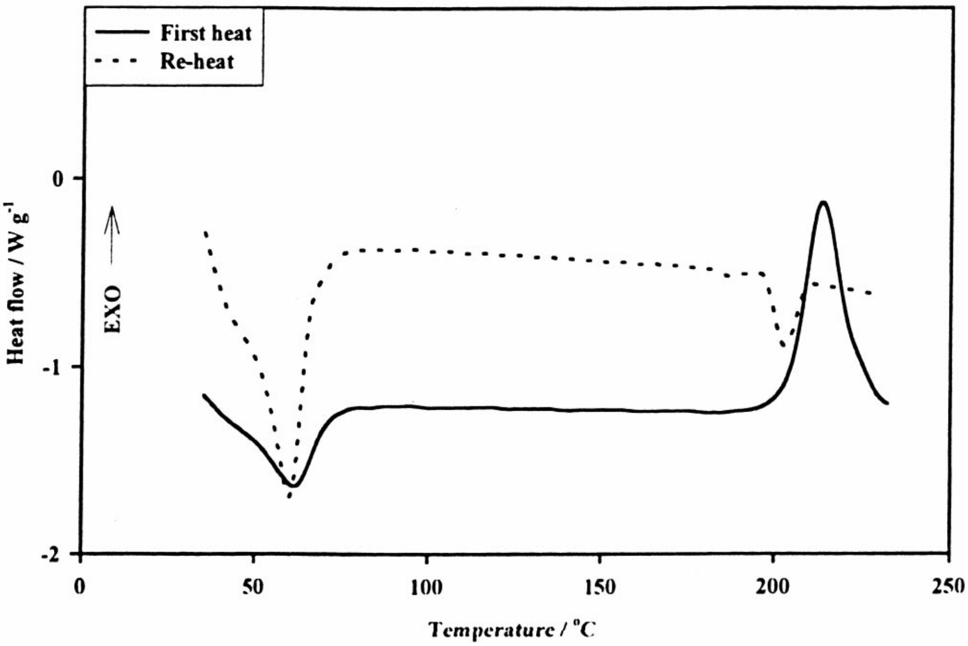

Fig. 10. Heat and reheat curves of 70/30 m/m wax 2/PPS.

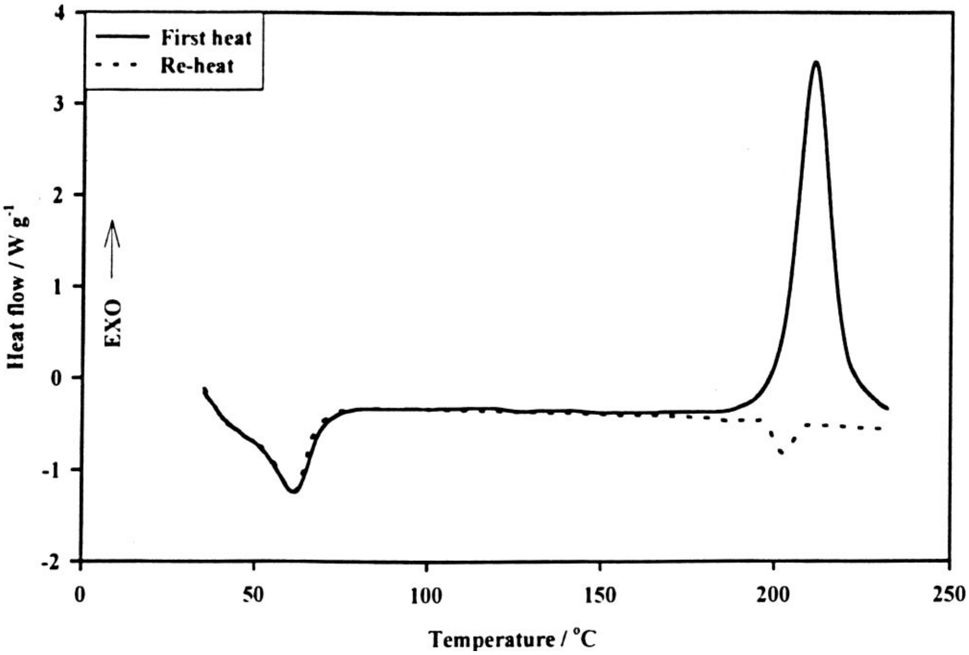

Fig. 11. Heat and reheat curves of 50/50 m/m wax 2/PPS.

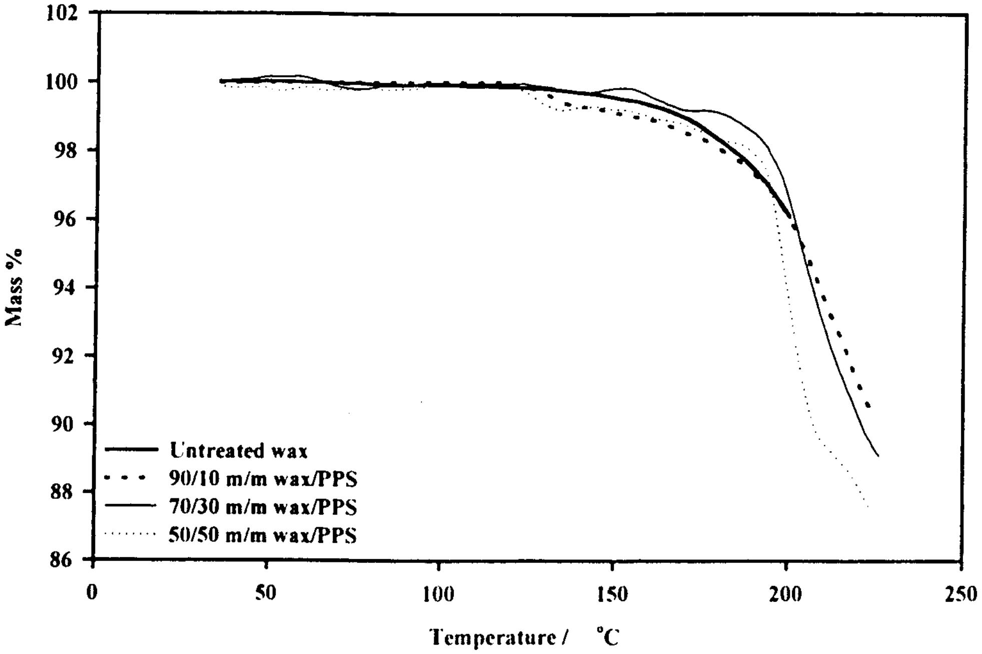

Fig. 12. TG curves of untreated wax 2 as well as samples mixed with different amounts of PPS

Thermogravimetric analysis of treated and untreated samples of wax 2 can be seen in Fig. 12. The untreated as well as treated samples show equivalent amounts of mass loss, indicating that the mass loss in this case is primarily due to wax degradation. Since we know that PPS decomposes to a certain extent, the small difference in total mass loss at 230°C is probably due to evaporation of volatile PPS decomposition products.

The DSC curves in Fig. 13 show wax melting endotherms between 95°C and 125°C for all the samples. Contrary to the DSC analyses previously discussed, the melting peaks for the untreated and PPS treated samples have a similar shape, indicating that the history built into the initial wax structure was not disturbed by the presence of PPS. The respective peak sizes are also related to the fraction of wax present in each sample. The exotherms between 200°C and 230°C for the treated samples are for the decomposition of PPS and their respective heights are directly proportional to the amount of PPS initially mixed into the sample. As in the case of wax 2, these exotherms also shift to a slightly lower temperature with increasing PPS : wax ratio.

Comparison of the reheat curves with the initial heat curves (Figs. 14–16) shows essentially no decrease in size for the wax melting endotherms on reheating the samples. There are, however, slight changes in the shapes and positions of these endotherms compared to the endotherms during first heat. This again points to the absence of any cross-linking reaction in the presence of PPS, but functionalisation of the wax probably caused the change in shapes and positions of the wax melting endotherms. As was the case with the previous two waxes, the reheat curves display two weak endotherms between 180°C and 210°C, typical of the phase transition and melting endotherms for $KHSO_4$.

The TGA curves (Fig. 17) follow essentially the same pattern observed for the previous waxes. The untreated wax shows an initial slight increase in mass, which may be attributed to moisture absorption. It did, however, show no significant mass loss up to the maximum temperature of analysis. The treated samples show small mass losses, starting at about 200°C. The extent of mass loss for the respective samples increases with increasing amounts of PPS mixed into the samples.

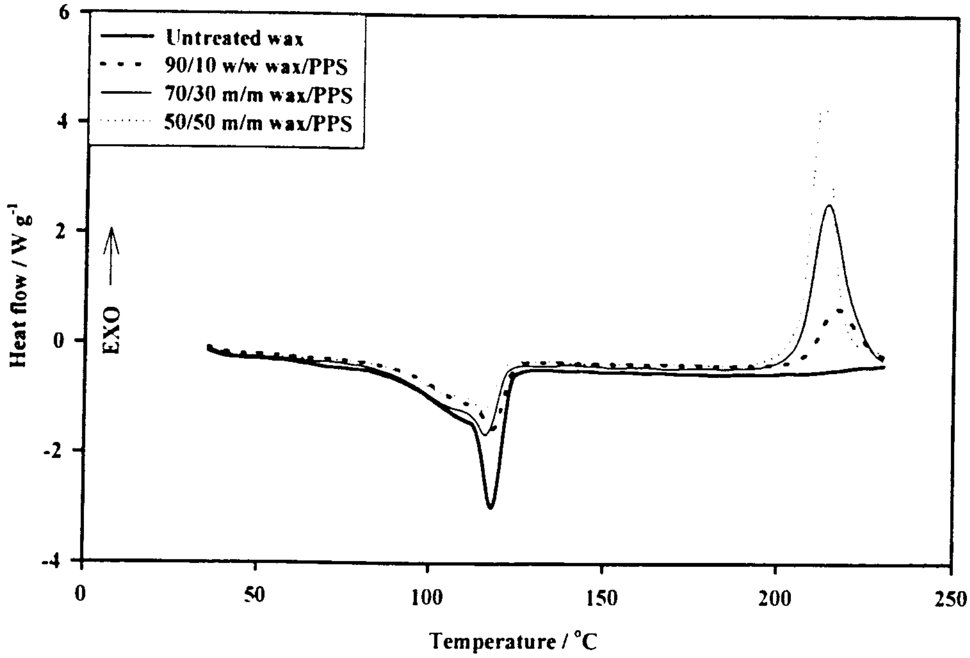

Fig. 13. DSC curves of untreated wax 3 as well as samples mixed with different amounts of PPS.

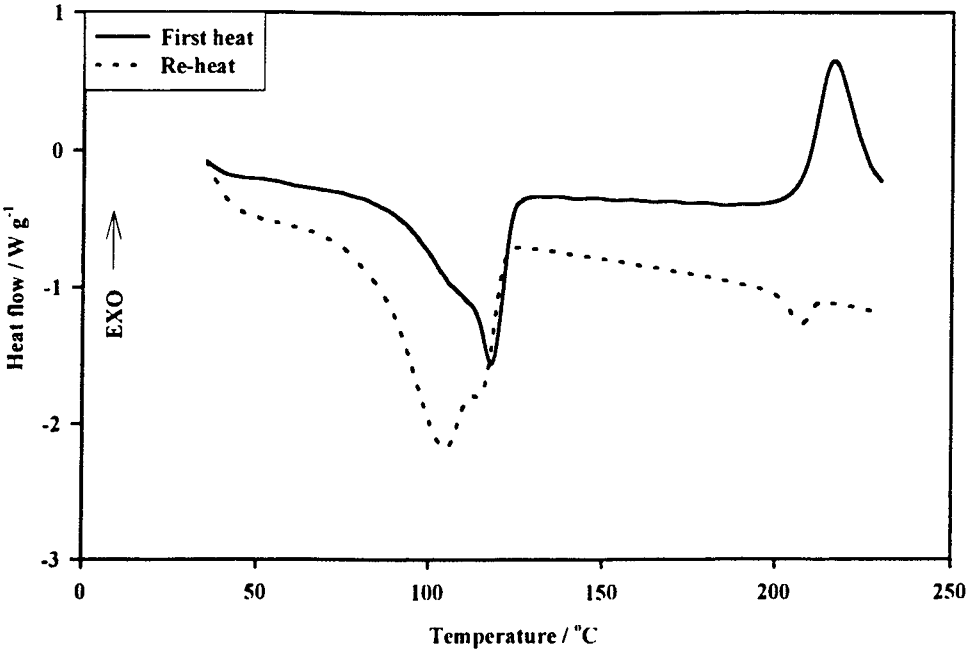

Fig. 14. Heat and reheat curves of 90/10 m/m wax 3/PPS.

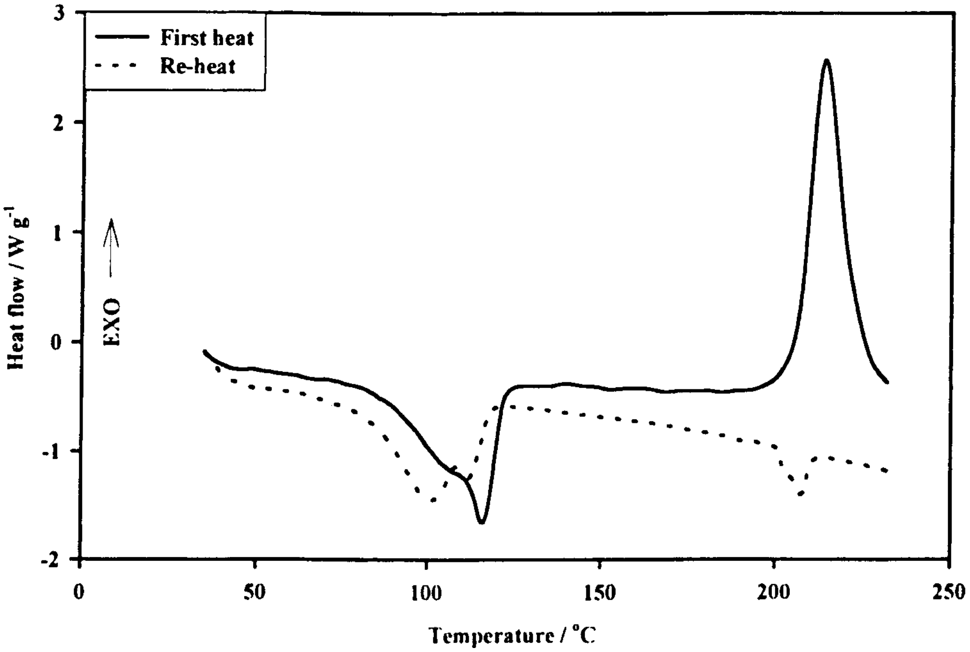

Fig. 15. Heat and reheat curves of 70/30 m/m wax 3/PPS.

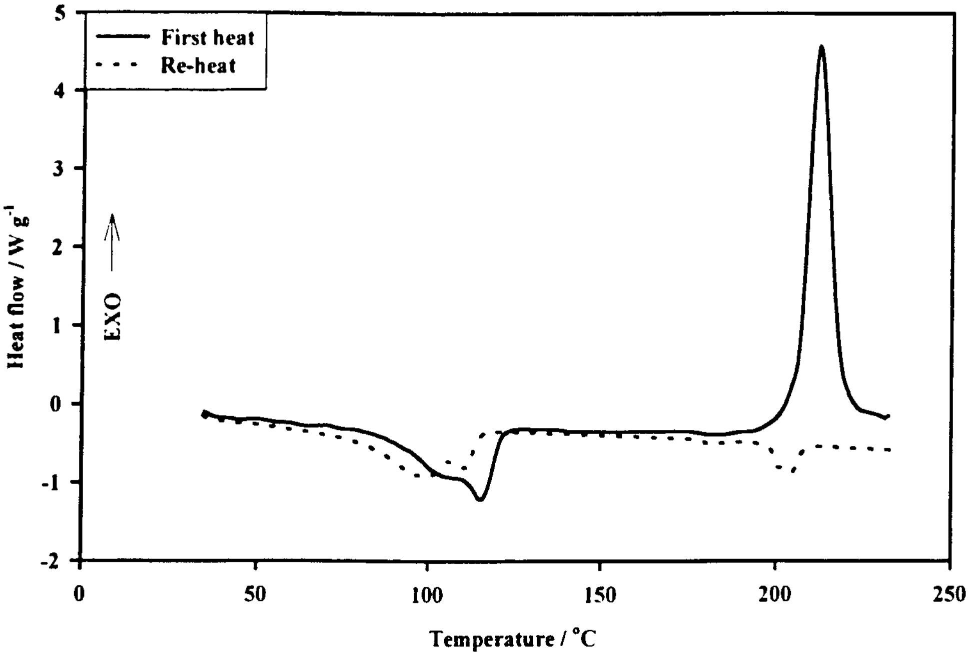

Fig. 16. Heat and reheat curves of 50/50 m/m wax 3/PPS.

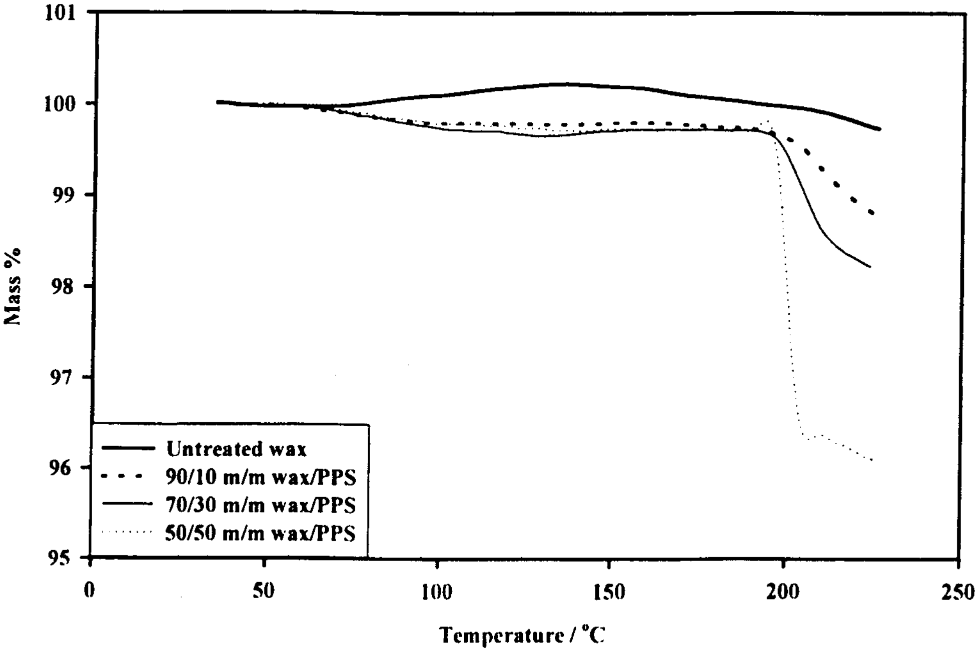

Fig. 17. TG curves of untreated wax 3 as well as samples mixed with different amounts of PPS.

The gel contents of the different samples were determined and the values are summarised in Table 4. For all the three waxes the gel content values for untreated and treated samples were constant and low within experimental error. This is a clear indication that no wax cross-linking occurred in the presence of potassium persulphate.

4. Conclusions

None of the investigated waxes cross-linked in the presence of potassium persulphate, as was evident from the DSC reheat curves of the treated samples and the lack of any gel formation in the presence of PPS. We did, however, establish that heating of PPS in the presence of a wax gave rise to the formation of $KHSO_4$ and that, in the process, functionalisation of the wax took place.

Table 4
Gel content values

Sample	%Gel content			
	Untreated wax	Wax + 10% PPS	Wax + 30% PPS	Wax + 50% PPS
Wax 1	4	6	6	6
Wax 2	12	12	14	14
Wax 3	1	1	3	3

Acknowledgements

ML Sultan Technikon, the University of the North (Qwa-Qwa), and the Foundation for Research Development in South Africa are thanked for their financial assistance.

References

[1] R.Z. Hamilton, Chemistry, Molecular Biology and Functions, 1st ed., Dundee, 1995.
[2] Encyclopedia of Chemical Technology, 3rd ed., vol. 18.
[3] A.S. Luyt, N.S. Nhlapo, H.C.M. Vosloo, Comparison of two curing agents in thermal cross-linking. I. Hard paraffin wax, J. Appl. Polym. Sci., accepted for publication.
[4] G.C. Gerrans, H.R. Corbett, Spectrum 28 (3) (1990).
[5] Sasolchem Technical Bulletin 1993.
[6] R.C. Weast (Ed.), CRC Handbook of Chemistry and Physics, 58th ed., CRC Press, FL, 1977.
[7] Annual Book of ASTM Standards, 1990, pp. 132–138.