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Comparative thermoanalytical investigation of the cross-linking behaviour of three different paraffin waxes in the presence of dicumyl peroxide

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Abstract

The cross-linking of three different paraffin waxes – a hard oxidized wax, a medium wax, and a hard wax with narrow molar mass distribution – in the presence of dicumyl peroxide (DCP) was investigated thermoanalytically. DSC and TG curves for untreated waxes and waxes treated with different amounts of DCP were obtained and the observations were compared with gel content data obtained through gravimetric analysis. It was found that all three waxes cross-linked in the presence of DCP, with the extent of cross-linking increasing with increasing DCP : wax ratio. It was also clear that the higher melting fractions of the different waxes preferably cross-linked. From the gel content data it seems as if the oxidized and higher molar mass waxes tend to cross-link at a faster rate. © 1999 Elsevier Science B.V. All rights reserved.

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 synthesized [1]. 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.

Brink and Dressler [2] cross-linked a hard Fischer–Tropsch wax using dicumyl peroxide (DCP) as the cross-linking agent. The cross-linking process was accomplished by stirring the two substances at 135°C in a nitrogen atmosphere. They reported that the congealing points, gel permeation chromatography, infrared spectroscopy and tensile testing proved that the product had been cross-linked and that the elasticity had increased when compared to the starting material. However, the cross-link intensity depended upon the amount of DCP used. An excess of 1.1 mol of DCP per mole of wax gave insoluble and infusible hard, brittle gels. The other drawback observed was the side reactions that occurred during the cross-linking process. A cross-linking mechanism was proposed and the efficiency of DCP as a cross-linking agent established.

Luyt et al. [3] investigated the same system thermoanalytically. They tried to establish the cross-linkability and extent of cross-linking through FTIR analyses and wax solubility. The FTIR spectra showed that an increasing DCP : wax ratio gave rise to a higher extent of cross-linking, while a decrease in solubility of the wax samples was observed with increasing DCP : wax ratio.

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In this study we compare the cross-linkability of three different waxes in the presence of DCP. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to study the cross-linking process, while the extent of cross-linking was determined through gravimetric analysis of the gel content.

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 oxidized Fischer–Tropsch wax that exhibits some properties of microcrystalline waxes [4,5]. 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 $C_{23}H_{48}$ [4,5]. 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} [4,5]. It is chemically inert and is free of aromatics. Table 3 shows some of its properties.

Dicumyl peroxide was selected because it is a strong oxidizing agent which may be used as a polymerization catalyst or vulcanization agent [6]. DCP, also known as bis(α,α-dimethylbenzyl)peroxide, has a melting point of 37–40°C and was obtained from Merck-Schuchardt.

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 oxidizing 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 oxidizing 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 oxidizing agents
Thermal decomposition: occurs at ±250°C forming hydrocarbon gases
Air and water: no reaction

The differential scanning calorimeter was a Mettler DSC20 with a Mettler TC11 thermal analysis processor. The thermogravimetric analyzer was a Mettler TG50 thermobalance connected to a Mettler TC10A thermal analysis processor. For both DSC and TG analyses the heating rate was 10°C/min and the nitrogen flow through the cell was 85 ml/min. The average sample size was 10–15 mg.

The amount of gel produced as a result of cross-linking was determined by extracting the uncured wax with toluene. 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 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 [7]:

$$\textit{Step}\ 1: \quad \%\ \text{Extract} = (\text{mass loss during extraction/sample mass})100 = [(W_3 - W_2)/W_1)]100,$$

where W_1 is the mass of the sample, W_2 the mass of the mesh pouch, sample and pan after extraction and W_3 is the mass of mesh pouch, sample and pan before extraction.

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

3. Results and discussion

Fig. 1 represents the DSC and TG curves of DCP. The endotherm at approximately 38°C shows the melting of DCP and is in good agreement with the literature value of 37–40°C. The decomposition of the DCP is reflected by the exotherms between 140°C and 200°C. The peak shoulder suggests that the decomposition occurs in more than one step. However, this is not evident in the TG curve. The mass loss between 140°C and 180°C indicates that the decomposition occurred in one step.

Fig. 2 represents the DSC curves of the untreated wax and 10%, 30% and 50% m/m mixtures of DCP with the wax. In the DSC curve of the untreated wax, the endotherm starting at approximately 50°C reflects the melting of the wax. There are slight changes in the shape of this endotherm when DCP is mixed into the samples. The DSC curves of wax mixed with different amounts of DCP show low-temperature endotherms increasing in size, which reflects the melting of increasing amounts of DCP in the samples. The DCP melting endotherm in the 10% mixed wax is not clearly defined as the concentration of the DCP is too small. The exotherms between 150°C and 200°C increase in size with increasing DCP content and reflect the expected decomposition of the DCP followed by the cross-linking of the wax. These peaks are, however, not well resolved indicating the interrelation of DCP decomposition and wax cross-linking.

Samples of wax 1, reheated after initial heating and cooling, show smaller wax melting endotherms, while the DCP melting endotherms and the exotherms are

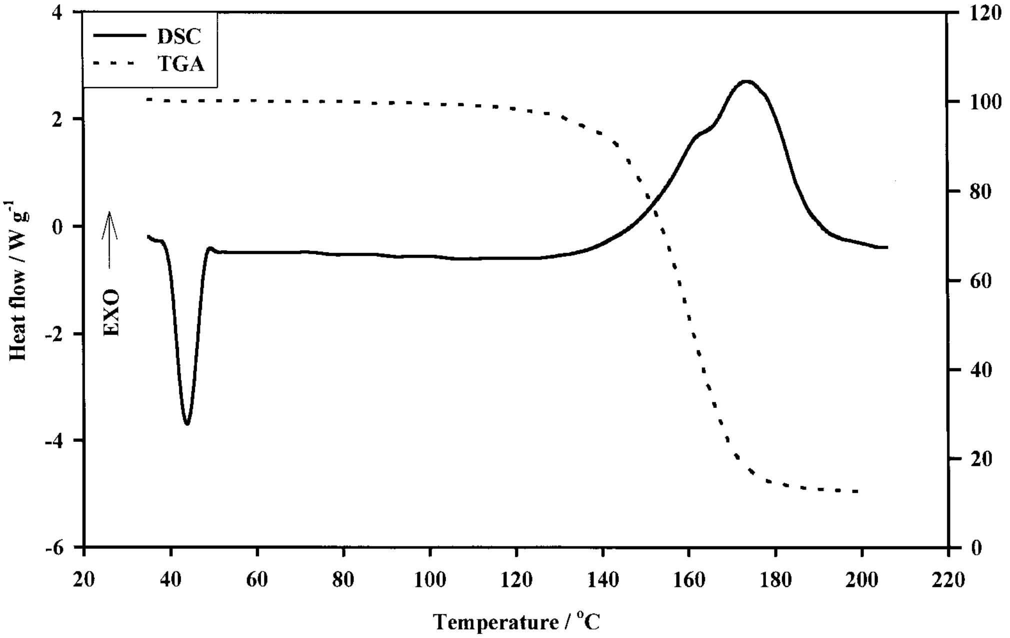

Fig. 1. DSC and TG curves for DCP.

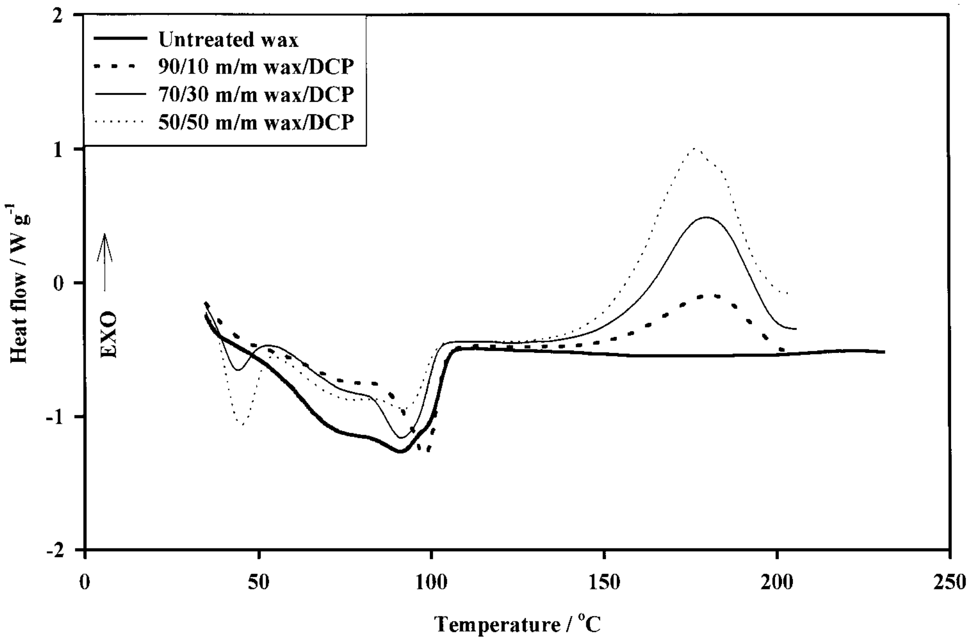

Fig. 2. DSC curves of untreated wax 1 as well as samples mixed with different amounts of DCP.

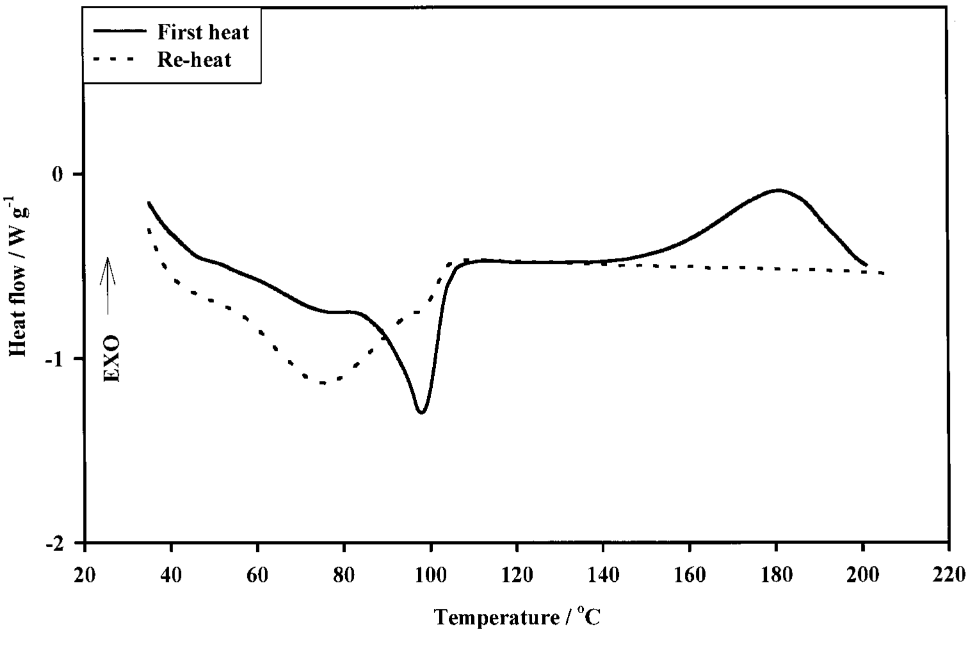

Fig. 3. Heat and reheat curves of 90/10 m/m wax 1/DCP.

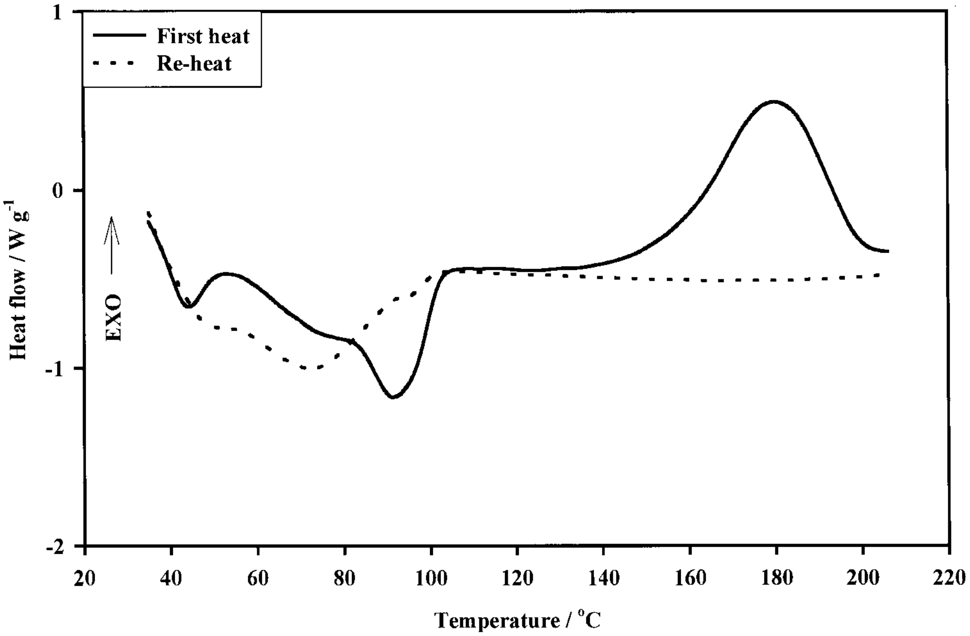

Fig. 4. Heat and reheat curves of 70/30 m/m wax 1/DCP.

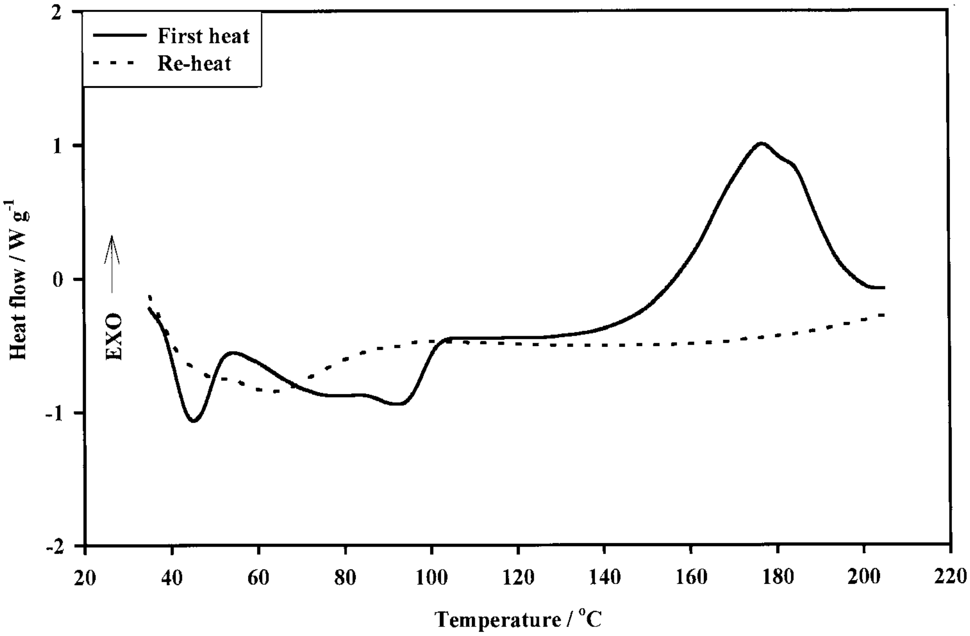

Fig. 5. Heat and reheat curves of 50/50 m/m wax 1/DCP.

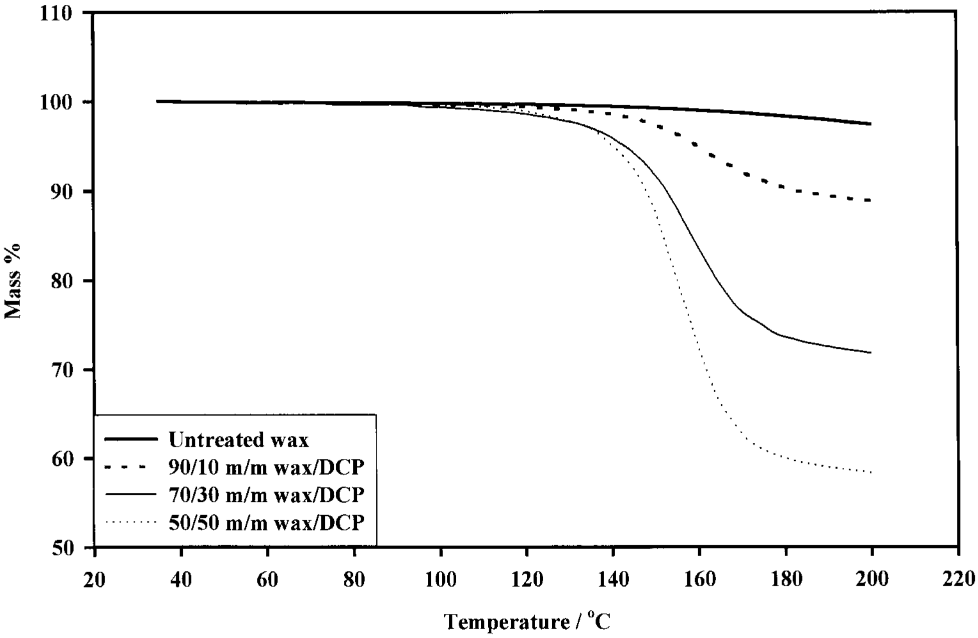

Fig. 6. TG curves of untreated wax 1 as well as samples mixed with different amounts of DCP.

absent (Figs. 3–5). The ratios of the sizes of the reheat wax melting endotherms to that of the initial wax melting endotherms are inversely proportional to the amount of DCP mixed into the wax, confirming increased cross-linking of the wax in the presence of increased amounts of DCP. The peak maxima on reheat also shift to lower temperatures, indicating that cross-linking occurred in the higher temperature fractions of the wax.

Fig. 6 represents the TG curves of the untreated wax and 10%, 30% and 50% m/m mixtures of DCP with the wax. The untreated wax shows only a small mass loss towards the end of the curve. A gradual mass loss is noted for the mixtures at approximately 160°C. The trend observed in these reactions is that as the amount of DCP increases, the mass loss increases showing that DCP decomposition products evaporate during and after cross-linking initiation.

The DSC curves of the untreated wax and the 10%, 30% and 50% m/m mixtures of DCP with the wax are shown in Fig. 7. The untreated wax shows a double melting endotherm between 40°C and 80°C. Because DCP melts at only a slightly lower temperature than wax 2, the treated waxes show broad melting endotherms between 30°C and 70°C, with the peak maxima shifting to lower temperatures as the amount of DCP increases. These endotherms are characteristic of an overlap between the melting events of substances with closely separated melting points. The decomposition/cross-linking exotherms between 150°C and 200°C are similar to what was observed for wax 1 and the explanation will be the same.

As was the case with wax 1, the DSC reheat curves of the cross-linked samples (Figs. 8–10) show increasingly smaller wax melting endotherms compared to the one observed during the first heating of the mixture. This is indicative of incomplete cross-linking of the wax, with increased extent of cross-linking in the presence of increased amounts of DCP. As with wax 1, there is also a shift of wax melting endotherms to lower temperatures, indicating preferable cross-linking of the higher melting fractions of the wax.

TGA results of the untreated and 10%, 30% and 50% m/m DCP mixed waxes are shown in Fig. 11. The TG curves show that the untreated wax has only a small mass loss of less than 5%, while the treated samples show mass losses of 9%, 32% and 49%, respectively, starting at about 160°C. These values are in accordance with the amounts of DCP initially mixed into the wax.

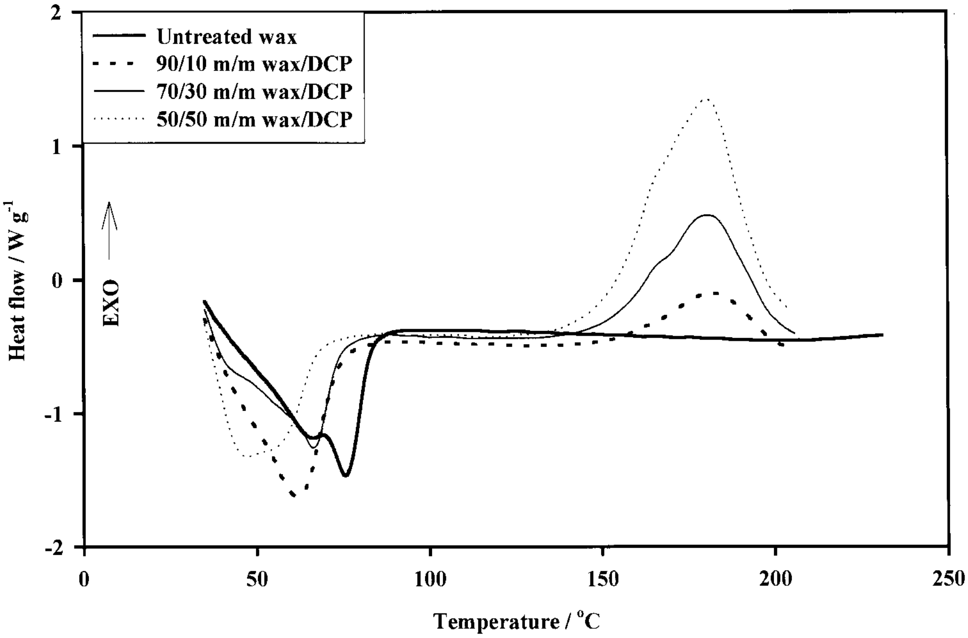

Fig. 7. DSC curves of untreated wax 2 as well as samples mixed with different amounts of DCP.

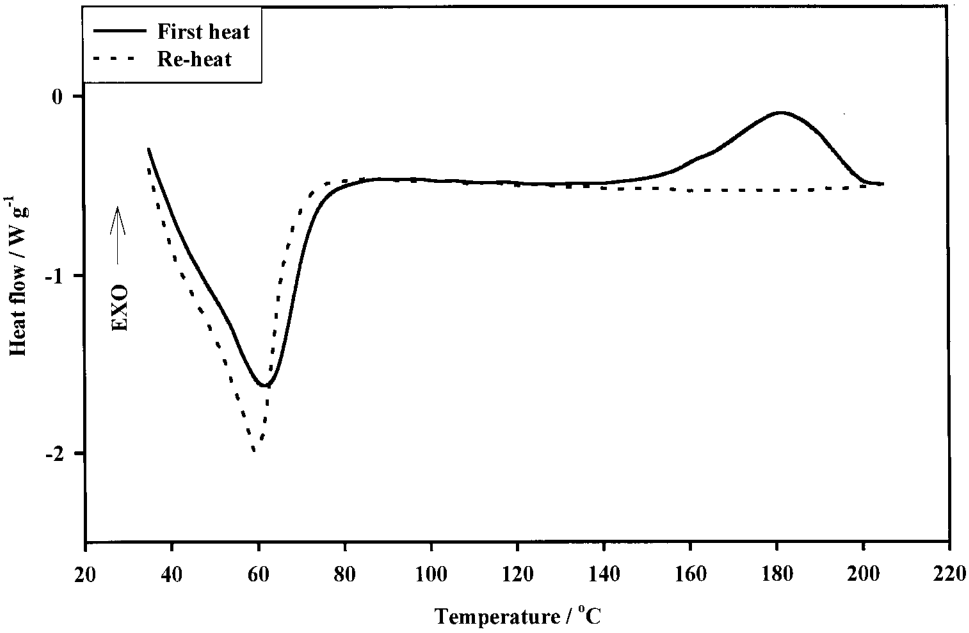

Fig. 8. Heat and reheat curves of 90/10 m/m wax 2/DCP.

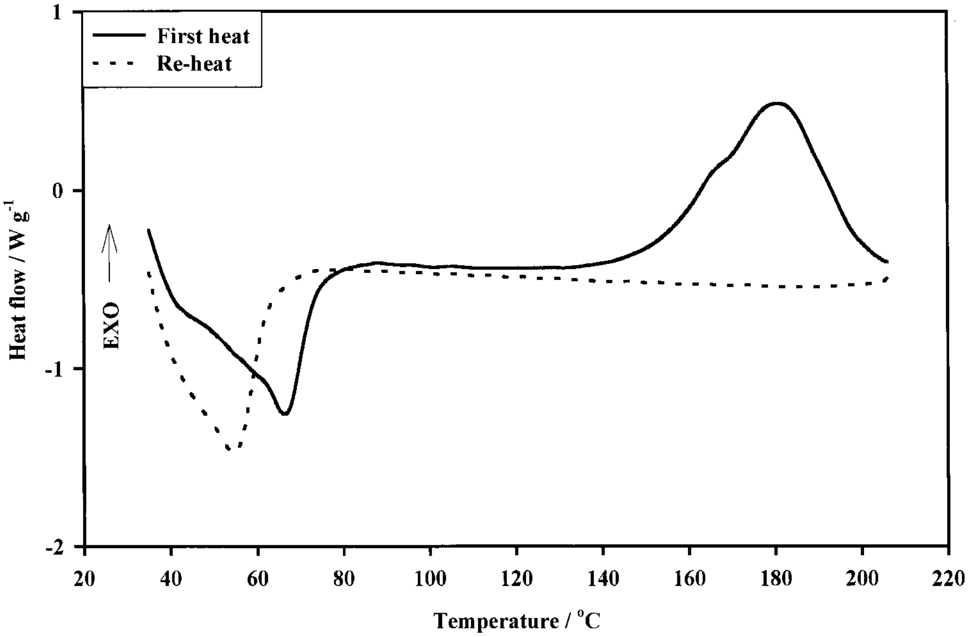

Fig. 9. Heat and reheat curves of 70/30 m/m wax 2/DCP.

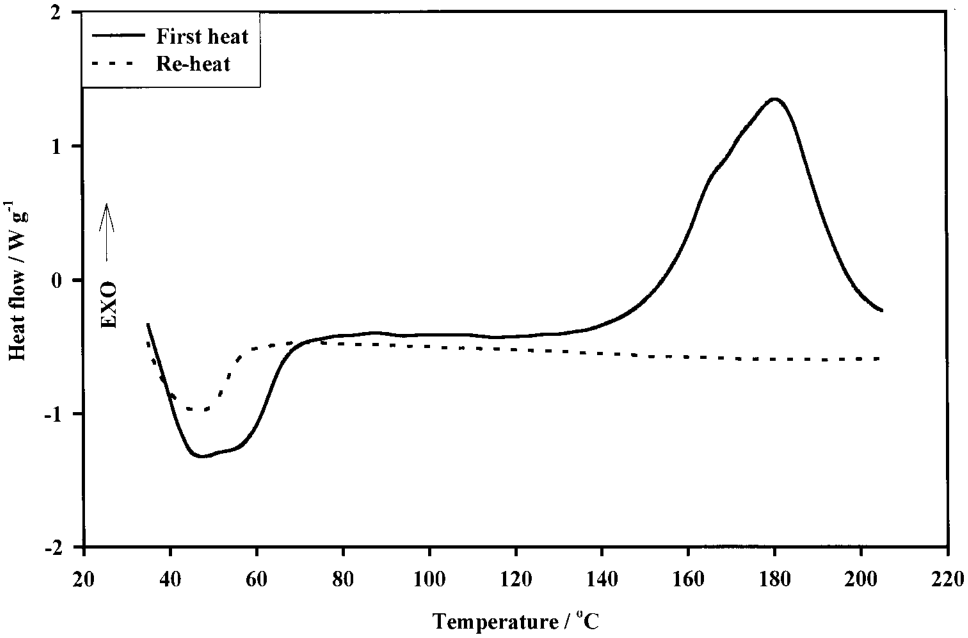

Fig. 10. Heat and reheat curves of 50/50 m/m wax 2/DCP.

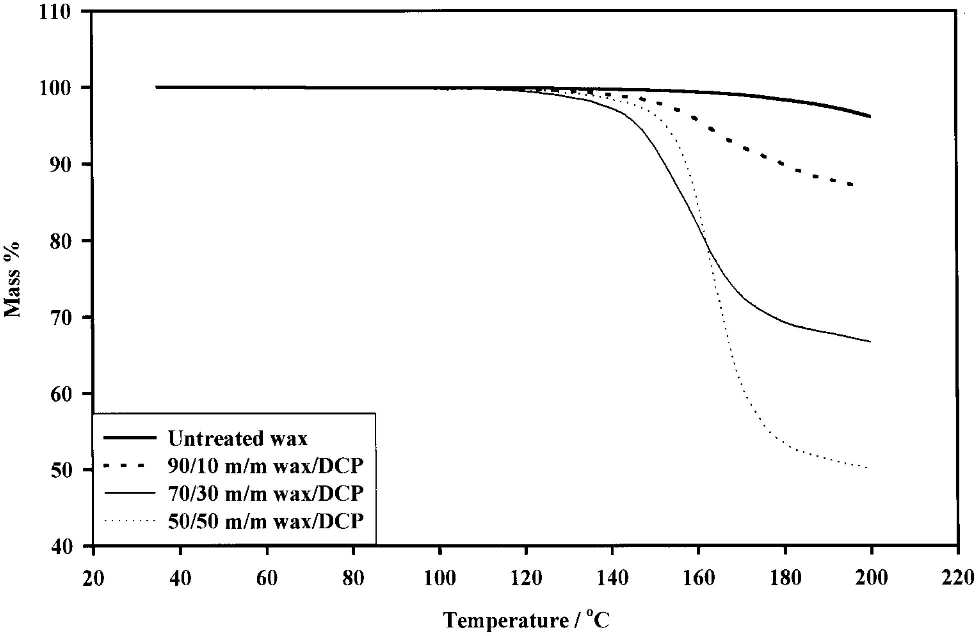

Fig. 11. TG curves of untreated wax 2 as well as samples mixed with different amounts of DCP.

The melting endotherms of wax 3 in the different samples can be seen in the temperature range 90–120°C (Fig. 12). There are some differences in the shapes and sizes of these melting endotherms, indicating (i) the differences in amount of wax in the different samples and (ii) influence of curing agent on the wax structure. The DCP melting endotherms appear in the temperature range 40–50°C and the increased peak intensities are evident of the increased fraction of DCP in the samples. As with the previous two waxes, broad strong exotherms are observed in the temperature range 150–200°C, indicating decomposition of DCP and cross-linking of the wax. The sizes of the peaks are in line with the amounts of DCP mixed into the different wax samples. The 50/50 m/m wax/DCP sample clearly shows two peak maxima in this exotherm, which may be indicative of DCP decomposition immediately followed by wax cross-linking.

In the case of wax 3 the reheating of the treated samples (Figs. 13–15) also serves as a proof that cross-linking did occur. The initial heat curves show the (i) melting endotherms for DCP at about 40°C, (ii) the wax melting endotherms between 100°C and 120°C, and (iii) the reaction exotherms between 150°C and 200°C. The reheat curves, however, only show wax melting endotherms which are clearly smaller than the initial melting endotherms and shifted to slightly lower temperatures. This indicates that certain fractions of the wax must have been cross-linked.

The TG analyses for this combination of wax 3 and cross-linking agent do not differ much from what was observed and discussed for the previous two waxes (Fig. 16). The wax only shows an extremely small mass loss over the temperature range, while the mass losses observed for the treated samples are in line with the values expected when all the DCP mixed into the samples decomposes and evaporates.

The gel contents of the different samples were determined and the values are summarized in Table 4. For all three waxes there is a general increase in gel content with increasing amount of DCP mixed into the wax. There are small differences in the gel content values for untreated waxes and waxes cured in the presence of 10% DCP. Higher DCP concentrations, however, give rise to increasingly higher gel content values indicating more effective cross-linking of the respective waxes. It is interesting to see that the

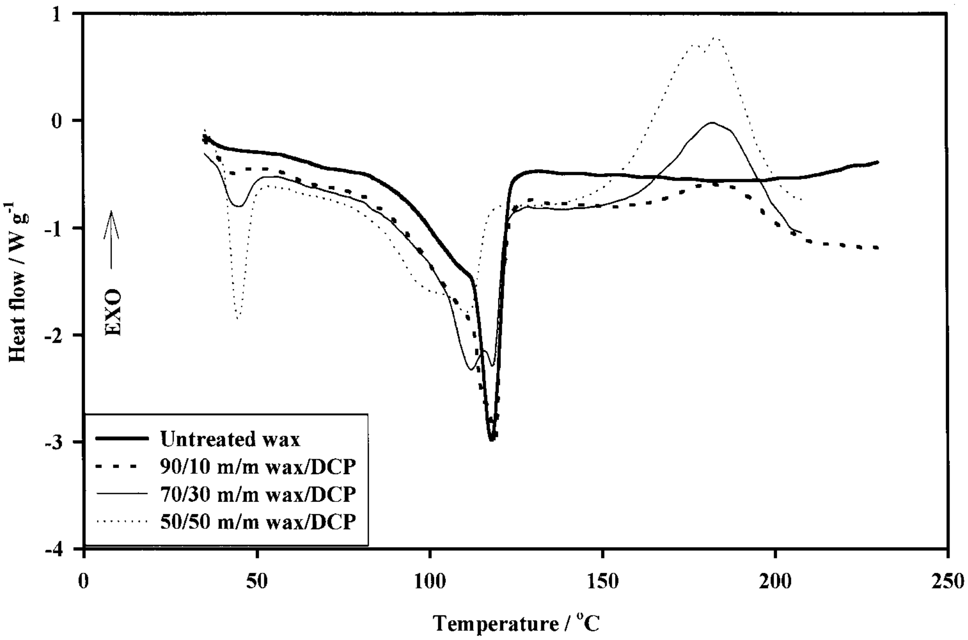

Fig. 12. DSC curves of untreated wax 3 as well as samples mixed with different amounts of DCP.

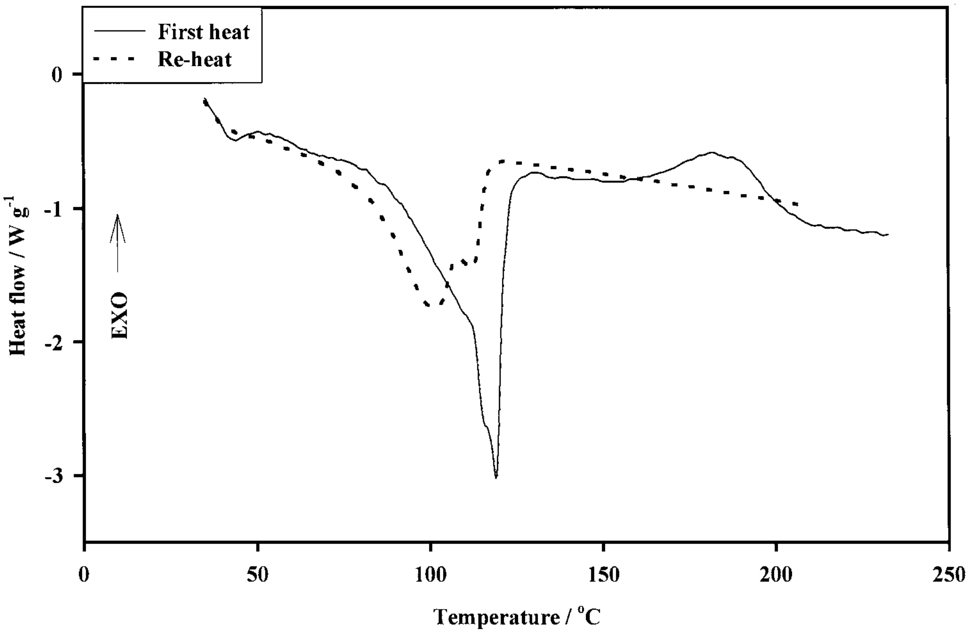

Fig. 13. Heat and reheat curves of 90/10 m/m wax 3/DCP.

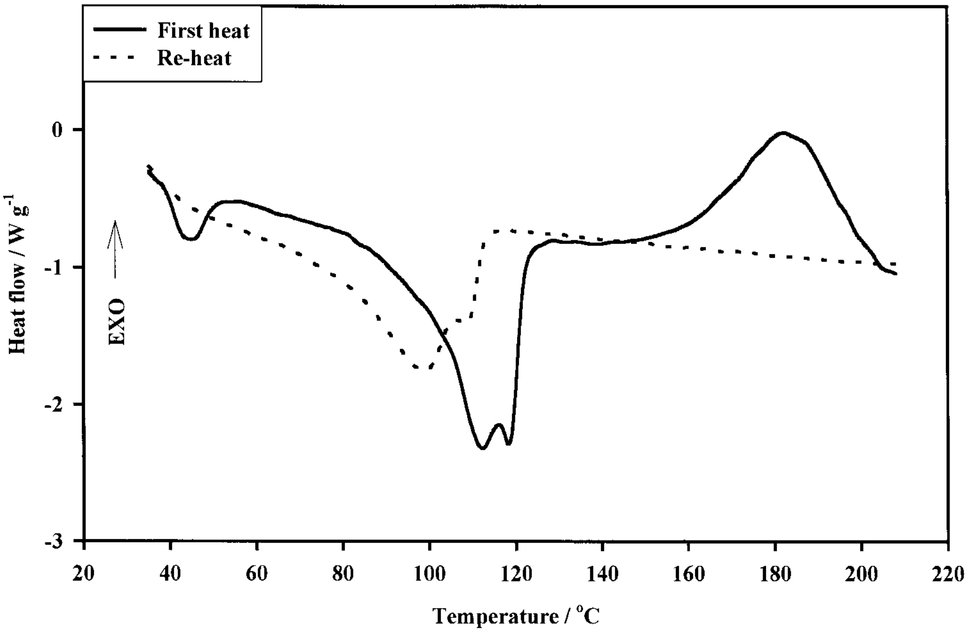

Fig. 14. Heat and reheat curves of 70/30 m/m wax 3/DCP.

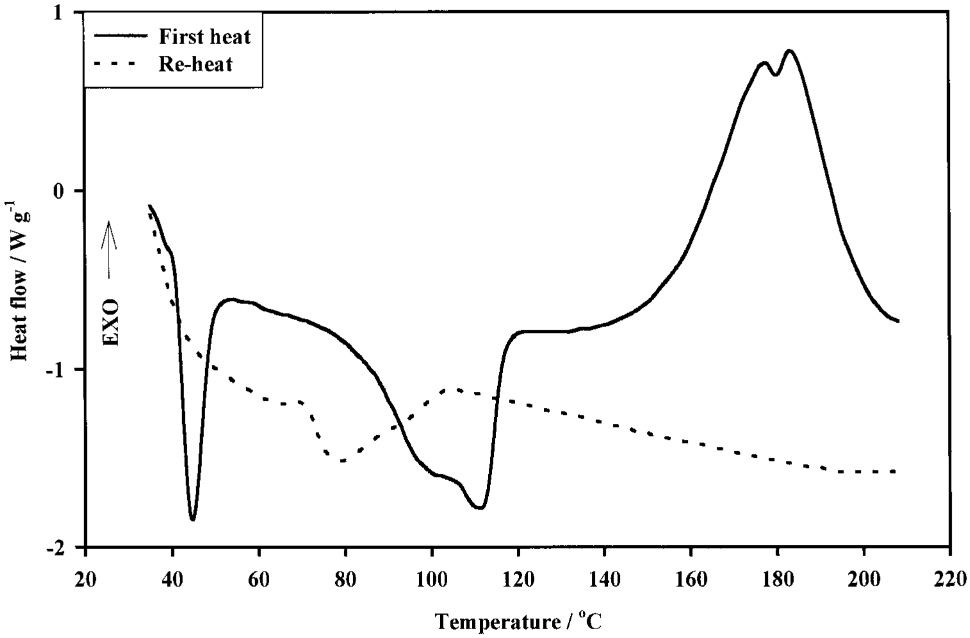

Fig. 15. Heat and reheat curves of 50/50 m/m wax 3/DCP.

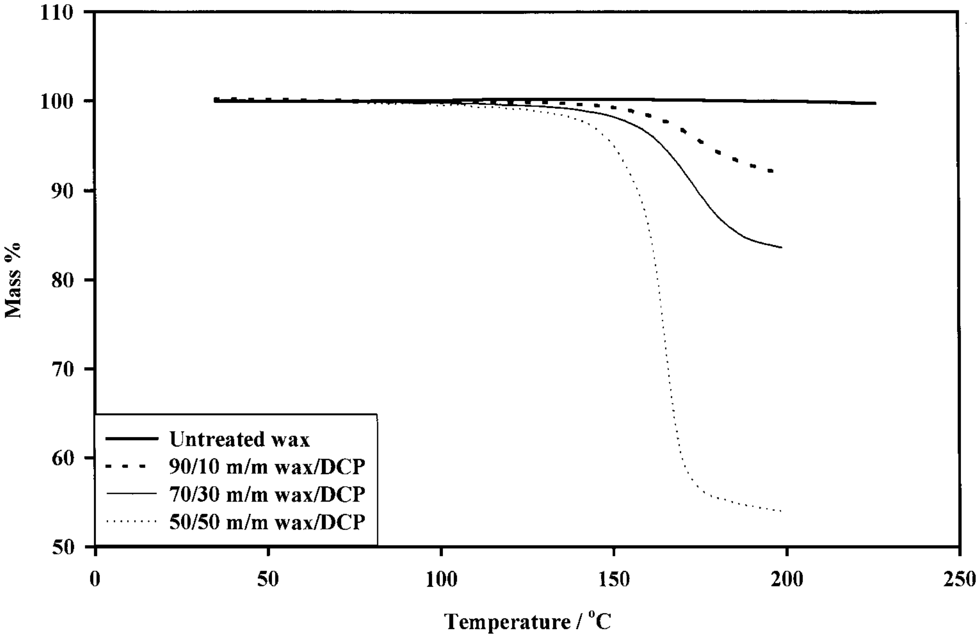

Fig. 16. TG curves of untreated wax 3 as well as samples mixed with different amounts of DCP.

maximum values for gel content increase in the order wax 1 > wax 3 > wax 2. According to the mechanism proposed by Brink and Dressler [2] the $PhC(CH_3)_2O\cdot$ and $CH_3\cdot$ free radicals, formed during the decomposition of DCP, attack the hydrocarbon chain removing hydrogen atoms. The unpaired electrons on two hydrocarbon free radical chains then combine to form a cross-link. We may reason that, in the case of an oxidized wax like wax 1, the hydrogen atoms in –OH groups are easier to remove than H-atoms in R–H, giving rise to a faster rate of cross-linking and eventually to a higher extent of cross-linking. Wax 3, which has a structure similar to that of wax 2, but with longer chains and a much narrower molar mass distribution, probably gives more efficient cross-linking because of more available sites per hydrocarbon chain.

Table 4
Gel content values

Sample	Percent of gel content			
	Untreated wax	Wax+10% DCP	Wax+30% DCP	Wax+50% DCP
Wax 1	6.1	10.0	33.3	70.2
Wax 2	11.2	13.9	30.5	47.5
Wax 3	1.1	23.1	36.6	66.8

4. Conclusions

All three investigated waxes cross-link in the presence of dicumyl peroxide and the decrease in the size of the wax melting endotherm as well as the increase in wax gel content, which are measures of the extent of cross-linking, are proportional to the wax : DCP ratio. It further seems as if certain fractions of the waxes preferably cross-link, because there are changes in shape and temperature shifts of the wax melting endotherms compared to wax melting before cross-linking. It also seems as if the presence of DCP in the wax matrix has an influence on the structural history of the wax, giving rise to wax melting endotherms of different shapes depending on the amount of DCP mixed into the wax.

Waxes 1 and 3 have much higher extent of cross-linking than wax 2, and it is believed that longer hydrocarbon chains and the presence of –OH groups favourably influence the rate of cross-linking of these waxes. In an extension of this study the cross-linking kinetics of the different waxes is investigated in order to verify whether this assumption is true.

Acknowledgements

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