

# Thermoanalytical investigation of the cross-linkability of a hard paraffin wax in the presence of benzoyl peroxide

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## Abstract

The cross-linkability of a hard paraffin wax in the presence of relatively small amounts of benzoyl peroxide was investigated thermoanalytically. Differential scanning calorimetry results, supported by thermogravimetric data, indicated the possible cross-linking of higher molar mass fractions of the wax. These observations were, however, not supported by infrared and gel content data. Infrared data showed some degradation, while gel content analyses showed that, if cross-linking had occurred, no three-dimensional space network was formed. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Thermal analysis; Cross-linking; Wax; Benzoyl peroxide

## 1. Introduction

It was generally accepted that with saturated hydrocarbons, cross-linking can occur only via alkyl radicals which are formed by peroxide initiators or radiation. Cross-linking of waxes received little attention, but Brink and Dressler [1] found that the extent of cross-linking depends on the amount of cross-linking agent used. They also found that when the hard paraffin wax was cross-linked in the presence of dicumyl peroxide (DP), the congealing point of the cross-linked wax decreased with the increasing peroxide/wax (m/m) ratio, the elasticity increased and beyond 50/50 m/m peroxide/wax ratio, an insoluble, infusible, hard, brittle gel was obtained. It was also found that there is an obvious difference in the respective cross-linking mechanisms in the presence of dicumyl peroxide and potassium persulphate [2].

Luyt and Ishripersadh [3] found that the cross-linking efficiency of different waxes increases with amount of peroxide up to 50% by mass. They did, however, conclude that potassium persulphate does not initiate cross-linking [4].

In another study, it was found that the cross-linking process involves the formation of three-dimensional structures (gels) causing substantial changes in the material properties [5]. Cross-linking initiated by thermal decomposition of peroxides results in a decrease in the crystalline portion. This decrease is not extensive and corresponds to the gel content. For example, the crystalline portion in low density polyethylene (LDPE) was found to drop from the original value of 41% down to 36.5% after cross-linking [6].

In a structural investigation of chemically cross-linked low density polyethylene it was found that the gel fraction is high and shows no extremes, and that it increases slightly with considerable increase in the peroxide content. It was pointed out that the propor-

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tionality between gel content and concentration of peroxide does not exist at large concentrations [7]. This is probably because if the branching rate is not carefully controlled, the polymers could become branched beyond the gel point which can lead to formation of a gel phase in the reactor and loss of polymer physical properties in end use applications.

The number of cross-links formed in a polymer may be derived from the amount of decomposed peroxide and from the cross-linking efficiency. If the reaction conditions are chosen so that about five half-lives of peroxide decomposition is reached, the amount of undecomposed peroxide (about 3% of its original concentration) may be ignored [8]. Only small amounts of peroxide produces a high level of cross-linking in high molecular weight polymers if cross-linking proceeds in the melt [6,8]. It was further found that tetrafunctional chain coupling of polymers is one important process for introducing long chain branching in order to modify flow behavior and for forming cross-linked networks. Reactor modeling for polymers branched beyond the gel point is a difficult problem because of the divergence of the moments of the molecular weight distribution to infinity [9].

Some more work was done on the cross-linking of different waxes with the aim to introduce flexibility and to improve thermal stability [10,11]. The aim of this project was to investigate the extent of cross-linking (if any) of a hard paraffin wax in the presence of relatively low concentrations of benzoyl peroxide (BP).

## 2. Experimental

### 2.1. Instrumentation

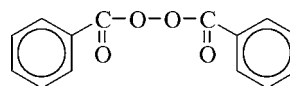
Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer thermogravimetric analyzer, heating from 40 to 400°C at a rate of 10°C min<sup>-1</sup> and kept at that temperature for 15 min under a nitrogen atmosphere. Sample size ranged between 5 and 10 mg.

Differential scanning calorimetry (DSC) was also carried out on a Perkin-Elmer DSC7 thermal analyzer in nitrogen atmosphere. Samples ranging between 5 and 10 mg were heated from 40 to 140°C, kept at 140°C for 15 min and reheated from 10 to 170°C at a rate of 10°C min<sup>-1</sup>.

Fourier-transform infrared (FT-IR) spectroscopy, with a photoacoustic cell, was used to characterize any differences in wax structure as a result of heating the wax in the presence of different amounts of peroxide. The resolution was 8 cm<sup>-1</sup> and the scan range 4000–400 cm<sup>-1</sup>.

### 2.2. Materials

A hard, brittle, straight hydrocarbon-chain paraffin wax was used. This was supplied by Schumann-Sasol and has a melting point of 90°C and decomposes at 250°C. BP was supplied by Sigma Aldrich. This has a formula weight of 242.23 g mol<sup>-1</sup>, a melting point of 105°C and the chemical structure shown below.



Chemical structure of BP

### 2.3. Methods

For cross-linking the wax was mixed in 100/0, 95/5, 90/10 and 85/15 m/m wax/peroxide ratios by grinding in a mortar with a pestle to form a homogenous mixture. The cross-linking process was followed thermoanalytically under the conditions described above.

Xylene extraction was used to determine the gel content, which is a three-dimensional network structure formed when there is effective cross-linking of the wax chains. Samples were pressed using a 10 t hot-melt press at 140°C for 15 min. They were then wrapped in fine stainless steel mesh and tied with a string. These samples were then placed in a round-bottomed flask containing xylene and refluxed for 12 h, changing xylene at 3 h intervals. After extraction of any uncross-linked wax, the wrapped samples were washed with chloroform and first dried at room temperature for 24 h and then at about 40°C in the oven for 4 h to evaporate all chloroform. The samples were then re-weighed and the gel content determined. This was done by calculating the percentage ratio of the mass of xylene-insoluble gel to that of the sample before extraction.

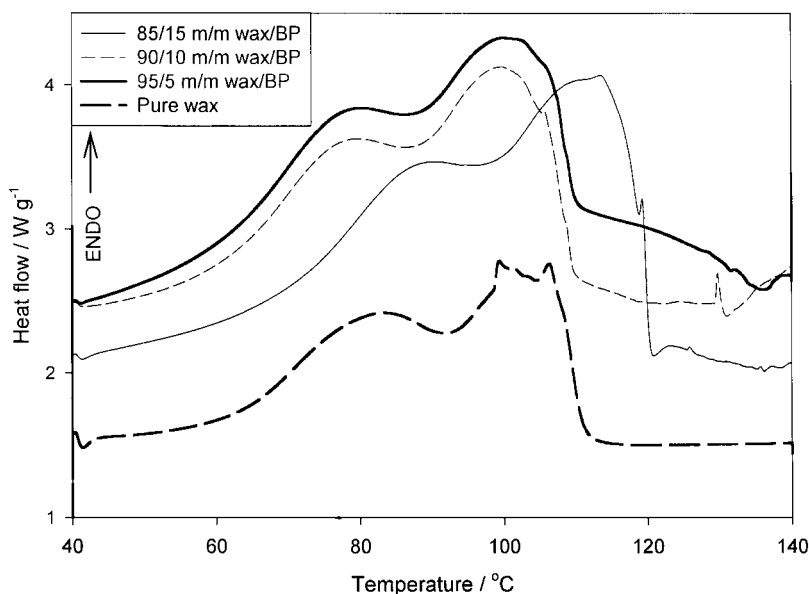


Fig. 1. DSC curves (first heat) of pure wax, 95/5, 90/10 and 85/15 m/m wax/BP.

### 3. Results and discussion

#### 3.1. DSC

Fig. 1 shows the (first heat) DSC curves for pure and treated wax samples. The curve for pure wax shows a triple endothermic event with the first peak at about 84°C. The second peak is the highest at about 99°C, and the third peak is close to the second peak at about 106°C. This endothermic event indicates wax melting, but the reason for the multiple peaks is not clear yet. The curve for the wax mixed with 5% (by mass) of BP shows a double endothermic event. The first peak is at about 78°C and the second peak at 102°C. The wax mixed with 10% BP shows a similar endothermic event. In this case the first peak is at about 78°C and the second peak at 98°C. For the wax mixed with 15% BP, the first peak is at about 87°C, and the second peak is at 113°C. The reproducibility of these results indicates that concentrations of BP higher than 10% retard the wax melting process. The onset temperature of melting and the melting enthalpy for the four samples are summarized in Table 1. These data show an initial decrease followed by an increase in onset temperature of melting, as well as a general increase in melting enthalpy, with increasing amount of peroxide

mixed into the wax. It seems as if the presence of BP in the wax matrix has an influence on the melting history of the wax, while increasing amounts of BP cause an increase in the onset temperature and enthalpy of melting of the wax samples.

Fig. 2 shows the reheat DSC curves for pure and treated wax samples. The curve for pure wax shows peak maxima at 84 and 105°C. Peak shoulders are visible at 98 and 102°C. The curve for wax treated with 5% (by mass) BP shows a triple endothermic event with the third peak emerging as a peak shoulder. The first peak is at 76°C, the second at 100°C and third at 106°C. The curve for wax treated with 10% (by mass) BP also shows a triple endothermic feature, but the shoulder developed into a peak. The peak temperatures are generally the same as that observed for the 95/5 m/m sample. The curve for the 85/15 m/m

Table 1  
Onset temperatures and enthalpies of the different samples (first heat)

	Wax/BP ratio (m/m)			
	100/0	95/5	90/10	85/15
Onset temperature (°C)	64.2	61.7	66.5	70.4
$\Delta H$ (J g <sup>-1</sup> )	226.6	305.1	327.7	409.4

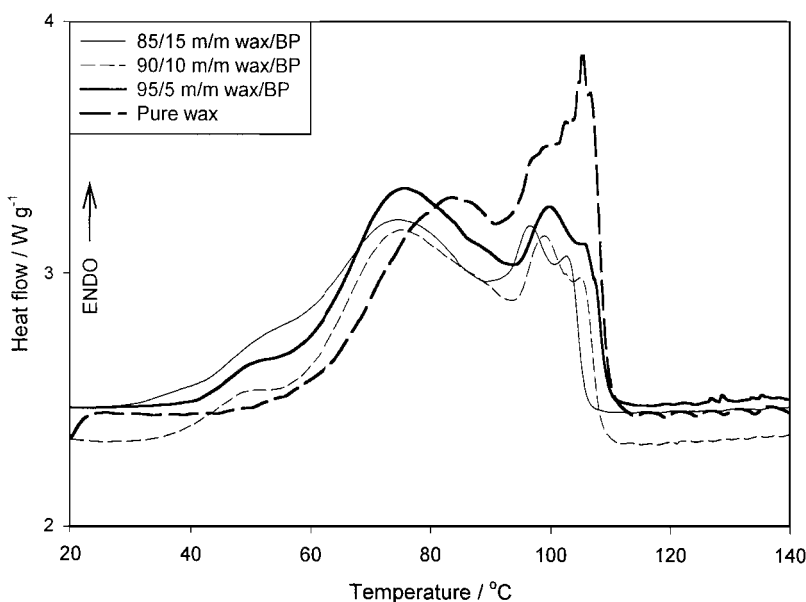


Fig. 2. DSC curves (reheat) of pure wax, 95/5, 90/10 and 85/15 m/m wax/BP.

sample shows that the different peaks in the melting endotherm appears at similar temperatures than for the previous samples, with the peak at about 105°C even more prominent. The data in Table 2 indicates a general decrease in peak area with decreasing wax/BP ratios, as well as a decrease in onset temperature with increasing peroxide content. The higher temperature parts of the melting peaks of the treated samples are generally weaker than the lower temperature part, whereas the opposite is true for the untreated sample. The decrease in peak area, which is indicative of a decrease in crystallinity, indicates an increase in extent of cross-linking with increasing peroxide

Table 2

Melting enthalpy, onset temperature and crystallinity of different samples obtained from DSC reheat curves<sup>a</sup>

	Wax/BP ratio (m/m)			
	100/0	95/5	90/10	85/15
$\Delta H$ (J g <sup>-1</sup> )	225.2	216.0	211.2	200.4
Onset temperature (°C)	64.2	56.5	55.4	49.0
Degree of crystallinity	0.78	0.75	0.73	0.70

<sup>a</sup> Degree of crystallinity ( $X_c$ )= $\Delta H/\Delta H^\circ$ , where  $\Delta H^\circ$  (PE)=288 J g<sup>-1</sup> for crystalline polyethylene [11] and it was assumed that wax, with a very similar structure, has the same enthalpy.

content. The comparatively larger decrease of the higher temperature part of the peak may indicate that cross-linking preferably occurs in the higher molar mass fraction of the wax, or that chain scission (degradation) has occurred in this part of the wax.

### 3.2. TGA

TGA curves for the treated samples show that cross-linked wax undergoes degradation and mass loss in one single step, starting at about 250°C (Fig. 3). Table 3 shows the onset temperatures and wt.% loss at three different temperatures for each of the samples.

From the TGA curves and the data in Table 3, it can be seen that there is no observable trend in the onset temperatures and wt.% loss at 300°C for samples with increasing amounts of peroxide. There is, however, a definite decrease in wt.% loss at higher temperatures with increasing peroxide content. This indicates thermal stabilization of the wax in the presence of increasing amounts of peroxide.

### 3.3. FT-IR

Table 4 summarizes the only observed differences between the FT-IR spectra of the different samples

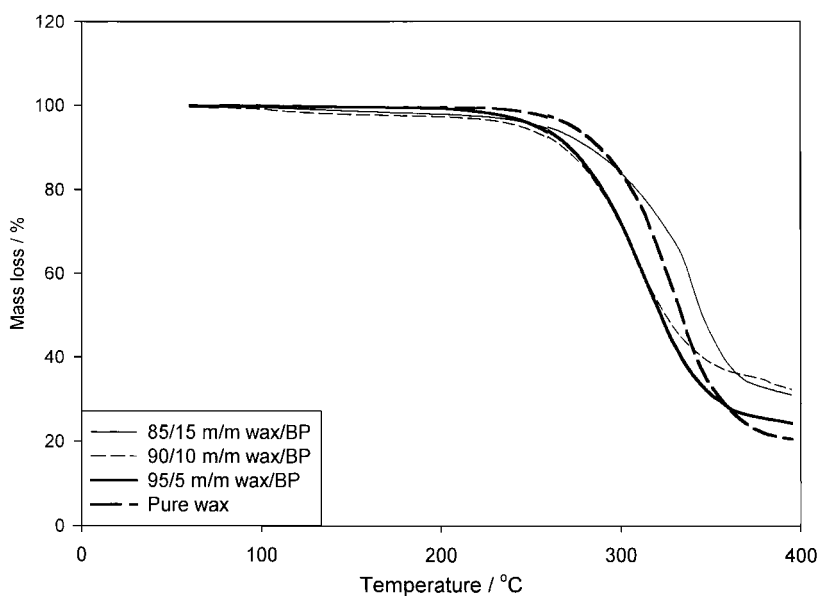


Fig. 3. TGA curves of pure wax, 95/5, 90/10 and 85/15 m/m wax/BP after treatment.

after being heated in the DSC. The doublet peak in the region  $730\text{--}760\text{ cm}^{-1}$  shows compounds containing at least four adjacent methylene groups, i.e.  $-(\text{CH}_2)_n-$ ,  $n > 4$ . This band is said to increase in intensity with increasing length of the chain [12]. These spectra show a decrease in percentage of transmittance in this

region from pure wax to 90/10 m/m wax/BP and a slight increase for 85/15 m/m wax/BP. This suggests that for treated samples, the chain lengths initially decrease, probably as a result of more degradation than cross-linking, while the increase in the case of 85/15 m/m wax/BP suggests a higher extent of cross-linking.

Table 3

Onset temperatures and wt.% loss at specific temperatures for the different samples

	Wax/BP ratio (m/m)			
	100/0	95/5	90/10	85/15
Onset temperature (°C)	293.2	270.5	269.3	310.8
Loss (wt.%) at				
$T=300^\circ\text{C}$	16	28	28	16
$T=350^\circ\text{C}$	67	69	62	54
$T=400^\circ\text{C}$	80	76	68	69

Table 4

FT-IR absorption in the region  $730\text{--}760\text{ cm}^{-1}$  absorption as a function of wax/peroxide m/m ratio

	Wax/BP ratio (m/m)			
	100/0	95/5	90/10	85/15
Transmittance (%)	81.3	79.4	78.8	79.8

### 3.4. Gel content

Xylene extraction of the treated samples showed that no gel was formed under these conditions. Although the DSC, TGA and FT-IR results indicated that some cross-linking occurred, it seems as if the cross-linking did not give rise to a three-dimensional space network. The partially cross-linked fractions were probably smaller than the size of the mesh, so that they were extracted together with the uncross-linked wax.

## 4. Conclusions

Contrary to the observations during the cross-linking of polyethylene [6,8], wax does not effectively cross-link in the presence of relatively small amounts of BP. Although it may be concluded from the DSC

data that cross-linking has occurred in the higher molar mass fractions of the wax, the FT-IR and gel content data does not support this observation. The TGA data, on the other hand, show that with increasing peroxide/wax ratios, a decreasing amount of wax decomposes at temperatures  $>350^{\circ}\text{C}$ , which supports the conclusion from the DSC data that cross-linking has occurred in the higher molar mass fractions of the wax. However, because no gel was found after xylene extraction of the samples, it may be concluded that only small cross-links (and not a three-dimensional space network) have formed.

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