Comparison of Two Curing Agents in Thermal Crosslinking. I. Hard Paraffin Wax

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ABSTRACT: The dynamic crosslinking of hard paraffin wax in the presence of dicumyl peroxide and potassium persulfate are investigated with differential scanning calorimetry, thermogravimetric analysis, infrared spectroscopy, and solubility analysis. The results indicate the occurrence of crosslinking, but there is an obvious difference in the respective crosslinking mechanisms in the presence of the two crosslinking agents. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1551–1559, 1998

Key words: hard paraffin wax; dicumyl peroxide; potassium persulfate; crosslinking

INTRODUCTION

Hard paraffin waxes are saturated hydrocarbons synthesized from petroleum through the Fischer–Tropsch process. These waxes are hard, have a high melting point and low viscosity, and are white in color with exceptional opacity. They consist of straight chain hydrocarbons in the range C28–C90 and have melting points of $\sim$ 90°C. They have densities of $\sim$ 0.94 g cm^{-3} at 25°C and they decompose thermally at 250°C.[1] Although these waxes have much shorter chains than the equivalent polymer, polyethylene, they may be regarded as polymers in the sense that they have long chains which may arrange and be crosslinked in similar ways to those of, for example, polyethylene.

When crosslinked in the presence of dicumyl peroxide (DP), the following changes are observed for these waxes: (1) the congealing point of crosslinked wax decreases with increasing peroxide/wax ratio; (2) elasticity increases; (3) beyond 50 : 50 wt/wt peroxide/wax ratio an insoluble, infusible, hard, brittle gel is obtained; (4) the crosslinked product is yellow in color; and (5) infrared (IR) spectra of crosslinked waxes differ from those of the starting materials, showing considerable absorption in the trans-internal olefin region, weak absorption in the saturated and in the aromatic carbonyl regions, and very weak absorption in the saturated open chain ketone region.[2]

In a related study,[3] the DP crosslinking of mineral oil and polyethylene was investigated. Various decomposition reactions in the mineral oil were studied by IR analysis, and the degree of crosslinking of polyethylene was determined by percent volume swelling, by fraction of solvent extractables, and from high-temperature Young's modulus determinations. It was found[4] that free radicals form rapidly in polyethylene in the presence of DP at high temperatures. This enables fast curing of polyethylene under these conditions. Baskett[5] found that the dicumyloxy decomposes to acetophenone and a methyl radical, with
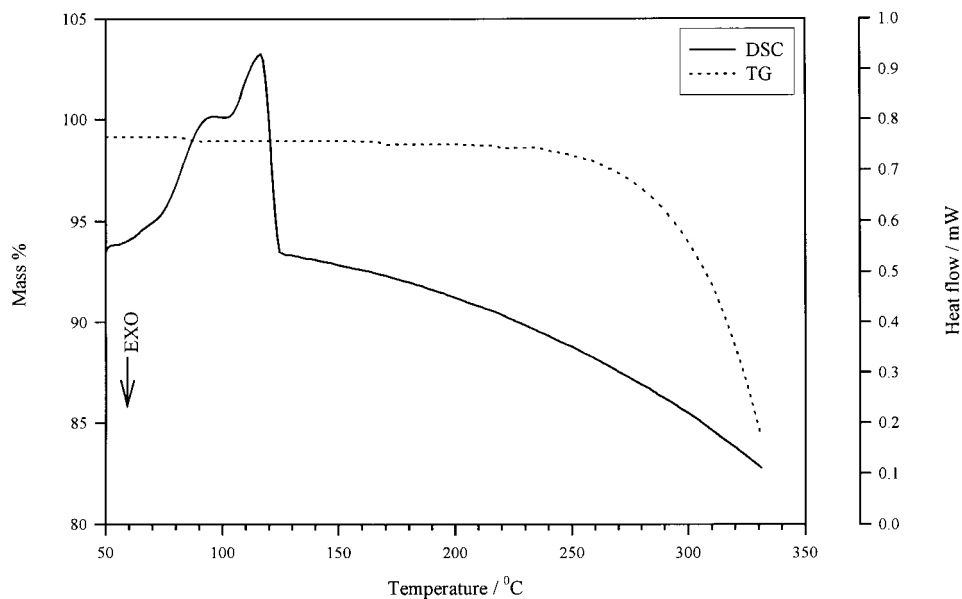
Figure 1 DSC and TG curves of pure H2 wax.

the formation of the latter favored by increasing temperature.

The present article discusses the thermal crosslinking of a hard paraffin wax in the presence of DP and potassium persulphate (PPS). Several possible peroxides were considered. Diacyl peroxides have a low crosslinking efficiency and combine with oxygenated groups, with subsequent oxidation.[6] A number of dialkyl peroxides, as well as tertiary butyl perbenzoate, have high crosslinking efficiencies, but only ditertiary butyl peroxide and DP are capable of curing compounds containing reinforcing fillers.[7] However, only DP is a solid and relatively nonvolatile. Based on unpublished observations that PPS acted as a good crosslinking agent in polymer membranes, we decided to investigate its curing capabilities.

EXPERIMENTAL

Commercial H2 hard wax was obtained from Sasolchem, Johannesburg, South Africa, while chemically pure DP and PPS were obtained from Merck, Johannesburg, South Africa.

The wax was mixed in 80/20 m/m and 60/40 m/m ratios with the respective curing agents, and ground to form a homogeneous mixture. Crosslinking processes were followed thermoanalytically by heating 5 to 10 mg of the different samples in a Perkin–Elmer DSC7 and TGA7. The samples were

heated at $10°C \, min^{-1}$ from 40 to $340°C$ in a nitrogen flow of $20 \, cm^3/min^{-1}$.

The pure as well as crosslinked samples were characterized through Fourier Transform IR (FTIR) spectroscopy (Nicolet Impact 410 FTIR). The resolution on the FTIR was $4 \, cm^{-1}$ and the scan range $4,000–600 \, cm^{-1}$. The solubilities of the different samples, after being heated to $340°C$ in the differential scanning calorimetry (DSC), were tested in various organic solvents by stirring the sample in an excess solvent and, if necessary, heating the solvent until the sample dissolved.

RESULTS AND DISCUSSION

DP as Crosslinking Agent

Figure 1 shows the DSC and thermogravimetric analysis (TGA) curves for pure H2 wax. The DSC curve shows a double endothermic peak in the temperature range 50–125°C. The main peak at 105°C is preceded by a strong peak shoulder at 90°C (onset temperatures 70 and 90°C, respectively). The wax melting point is specified[1] as 90°C and therefore this is the melting endotherm for the wax, also because there is no mass loss accompanying it (see TGA curve). Above 150°C the baseline gradually changes in the exothermic direction. This is accompanied by a very small mass loss followed by a major mass loss starting
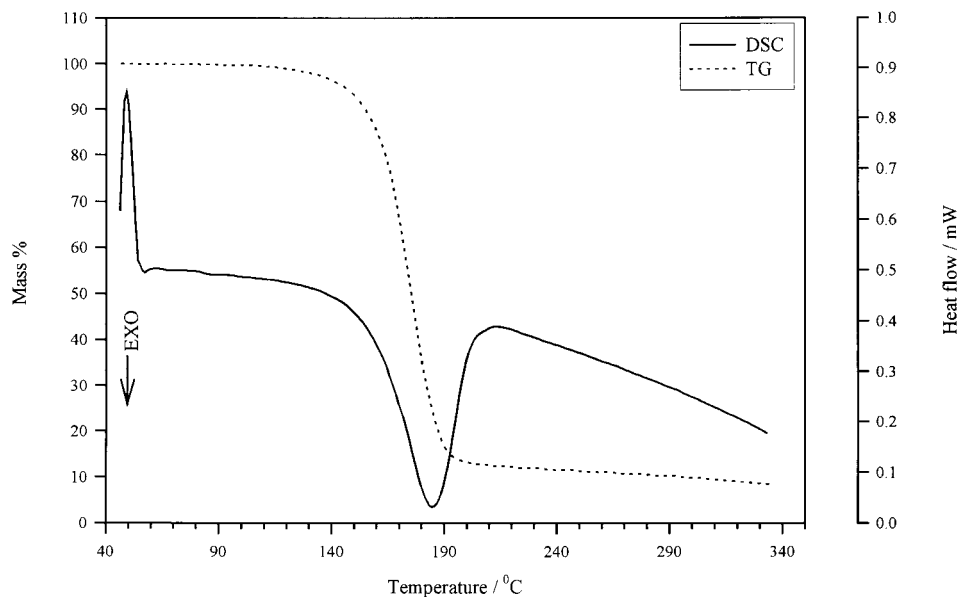
Figure 2 DSC and TG curves of pure DP.

at about 225°C (see TGA curve). This must be due to wax degradation, because the exotherm is broad and is accompanied by a mass loss.[8]

The DSC and TGA curves for pure DP are represented in Figure 2. The DSC curve shows a melting endotherm for DP at about 40°C (in line with the melting range of 37–40°C provided by the suppliers), followed by a strong, broad exotherm between 150 and 200°C. This exotherm is accompanied by a major mass loss of about 90% of the initial mass. Because the analysis was performed in an inert atmosphere, this mass loss can be explained only as a decomposition of DP into volatile products. Figures 3 and 4 represent the DSC and TGA curves of wax samples heated in the presence of DP. The DSC curves show two melting endotherms for DP and H2 wax. The respective sizes of these melting endotherms correspond to the H2 wax/DP ratios of the samples analyzed. The third peak, a strong, broad exo-
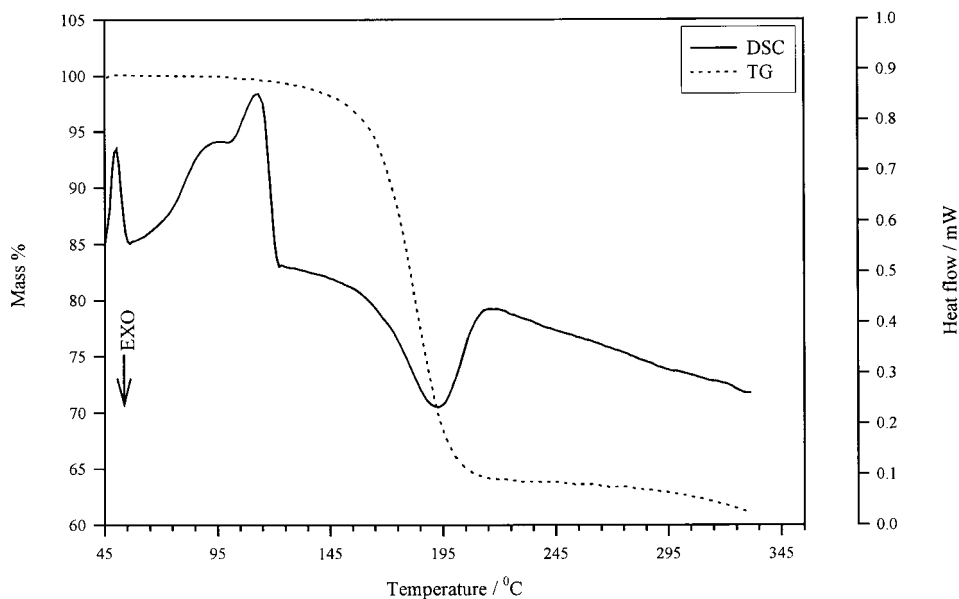

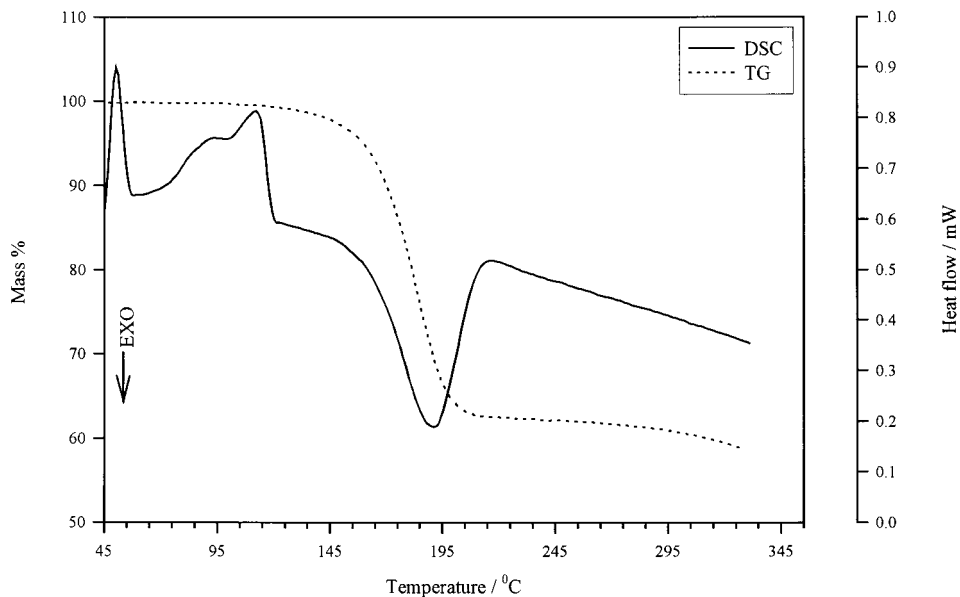**Figure 3** DSC and TG curves of an 80/20 m/m mixture of H2 wax and DP.

Figure 4 DSC and TG curves of a 60/40 m/m mixture of H2 wax and DP.

therm, is in the same temperature range as the decomposition peak for DP. It is also accompanied by a major mass loss of approximately 40%, compared with the 90% mass loss in pure DP (see TGA curves). It is, however, interesting to note that with double the amount of DP in the sample, the mass loss is approximately the same (see Fig. 4) as that of the first mixture (see Fig. 3). This exotherm may be the result of DP decomposition only, or of a combination of DP decomposition and wax crosslinking.[8] The latter is possible if the mechanism proposed by Brink and Dressler[2] is assumed to be correct, because the decomposition products of DP will then initiate crosslinking. All these exotherms are irreversible.

In addition to the above observations, the reaction enthalpy was found to increase linearly with increasing curing agent content (see Table I and Fig. 5). This may be due to the formation of more crosslinks, or to the degradation and evaporation of the larger amount of DP, or to a combination of both.

It was also observed that the solubilities of the product obtained after heating to 340°C decreased with an increase in the curing agent content (see Table II). The solubility of the wax was qualitatively determined in various solvents, including dichloromethane, chloroform, chlorobenzene, benzene, tetrahydrofuran (THF), diethylether, xylene, and toluene. Only toluene was found to dissolve the hard wax at room temperature.

From Table II it is clear that at all temperatures the pure wax and pure DP are soluble. The solubility, however, decreased with increasing content of the crosslinking agent in the DP/wax mixture. This may be further proof that crosslinking did occur and that the crosslink density increases with increasing content of the crosslinking agent.[9]

Figure 6(a) gives the FTIR spectrum of pure H2 wax. The following vibrational peaks are relevant and changes in them will be discussed: the aliphatic C—H stretching vibration at 2750 cm^{-1},

Table I   Onset Temperatures, Peak Temperatures, and Enthalpy Values of the Exotherms in Figures 2–4

Sample (mass %)	Onset Temperature (°C)	Peak Temperature (°C)	ΔH (J g^{-1})
100% DP	147.0	173.1	461.4
80% H2 wax/20% DP	155.1	179.0	142.0
60% H2 wax/40% DP	151.3	177.3	229.3
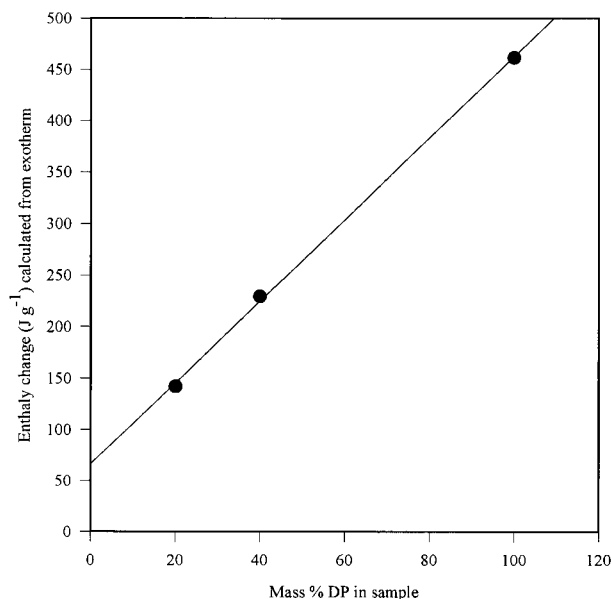
Figure 5 Enthalpy change as function of mass percent DP in sample.

Figure 6 FTIR spectra of (a) pure wax, (b) 80/20 m/m, and (c) 60/40 m/m wax/DP mixtures after being treated to 340°C.

the methylene group (—CH$_2$—) bending vibration at 1450 cm^{-1}, the methyl group (CH$_3$—) bending vibration at 1375 cm^{-1}, and the C—H out-of-plane bending vibration at 900–690 cm^{-1}. Upon heating in the presence of 20% DP [see Fig. 6(b)] there was a reduction in the intensity of the —CH$_2$— and CH$_3$— bending vibrations, which suggests that substitution of the hydrogen atom took place on the polymer backbone. The intensity of the C—H out-of-plane bending vibration also decreased drastically. There was also a development of the hydrogen-bonded OH stretching vibration of medium intensity at around 3500 to 3200 cm^{-1}. This may be due to moisture in the sample, but because the sample was properly dried before analysis, it may also be the result of intermediate alcohols or hydroperoxides formed during the course of crosslinking.[2] There was also a clear separation of the C—H stretching vibrations, with the aliphatic C—H stretching vibra-
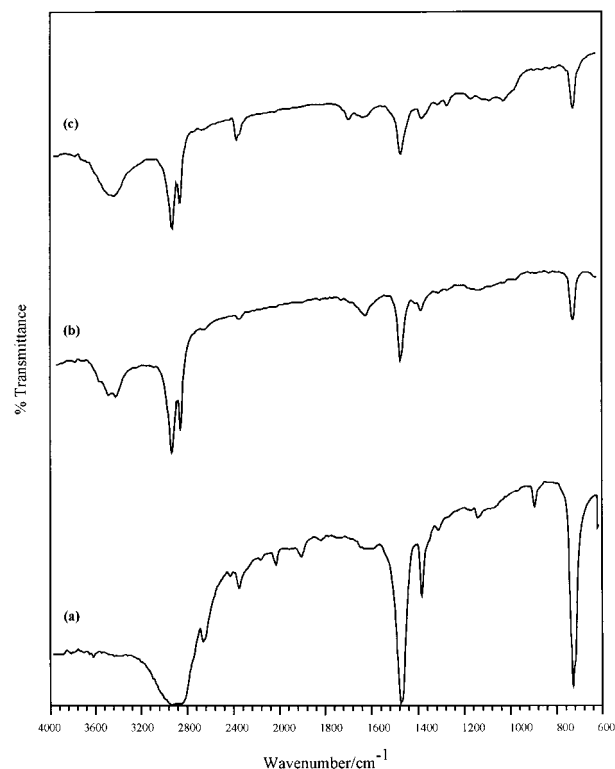
tion at around 2750 cm^{-1} and the aromatic C—H stretching vibration at 2900 to 3000 cm^{-1}. Heating in the presence of 40% DP [see Fig. 6(c)] gave a further reduction of the methylene (—CH$_2$—) and methyl (—CH$_3$—) bending vibrations. The hydrogen-bonded OH stretching vibration at 3500 to 3200 cm^{-1} became broad and intense. This also suggests that crosslinking increases with an increase in the content of the crosslinking agent. One aspect which is obvious in the sample heated in the presence of 40% DP [see Fig. 6(c)] is that the C—H out-of-plane bending vibration seems to have a lower intensity. This vibration is far more important than the in-plane bands because it re-

Table II   Solubilities in Toluene of Pure Wax, Pure DP, and Their Mixtures, Heated to 340°C in DSC

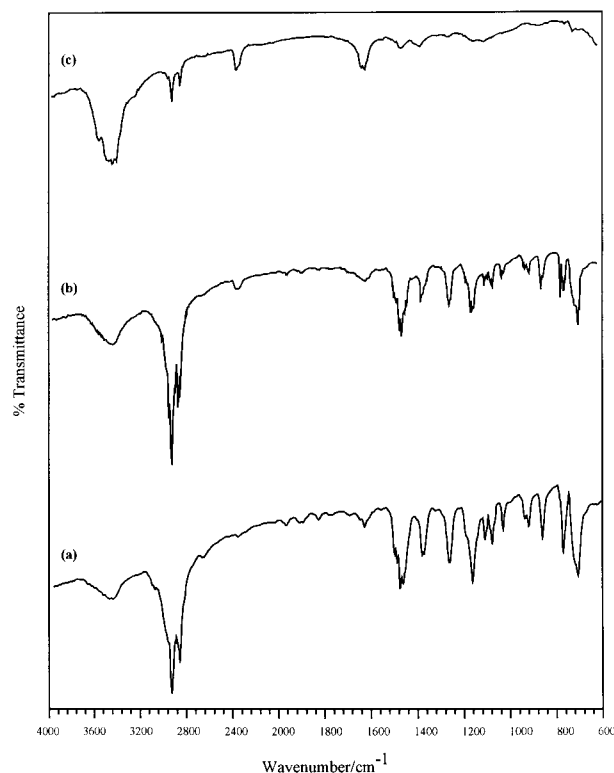| Sample (mass %)	Testing Temperature		
	30°C	45°C	60°C
100% H2 wax	Slightly soluble	Soluble	Soluble
100% DP	Soluble	Soluble	Soluble
80% H2 wax/20% DP	Slightly soluble	Slightly soluble	Slightly soluble
60% H2 wax/40% DP	Insoluble	Insoluble	Slightly soluble

Figure 7 FTIR spectra of 60/40 m/m wax/DP samples taken before, during, and after the crosslinking exotherm: (a) 153°C, (b) 192°C, and (c) 220°C.

sults from strong coupling with the adjacent hydrogen atom. The reduction of this vibration therefore supports the view that the adjacent hydrogen has been replaced by a crosslink.

Figure 7 shows the FTIR spectra of samples taken at temperatures before, during, and after the crosslinking exotherm. The spectrum of the sample taken before the crosslinking exotherm, at 153°C [Fig. 7(a)], shows that crosslinking may not be well defined at this stage. This is clearly indicated by the gradual change in the intensities of the aliphatic and aromatic CH stretching vibrations at 2750 and 2900 to 3000 cm^{-1}, respectively, which suggests the gradual substitution of the hydrogen atom on the polymer backbone by crosslinks. The hydrogen-bonded OH stretching vibration of medium intensity at 3500 to 3000 cm^{-1} is not well resolved at the first two stages, as compared with the last stage [Fig. 7(c)], which may point to the formation of intermediate alcohols or hydroperoxides in the crosslinking mechanism.

PPS as Crosslinking Agent

The DSC and TGA curves for pure PPS are shown in Figure 8. The baseline of the DSC curve shows a gradual change in the exothermic direction, followed by an intense, sharp exotherm starting at about 270°C, which may be due to degradation of PPS although it corresponds to a very small mass loss. The TGA curve shows a stepwise mass loss. In the first step the sample lost about 5% of its initial mass, followed by a major mass loss of about 17% and about 3% in the last step, which corresponds with the DSC degradation exotherm.

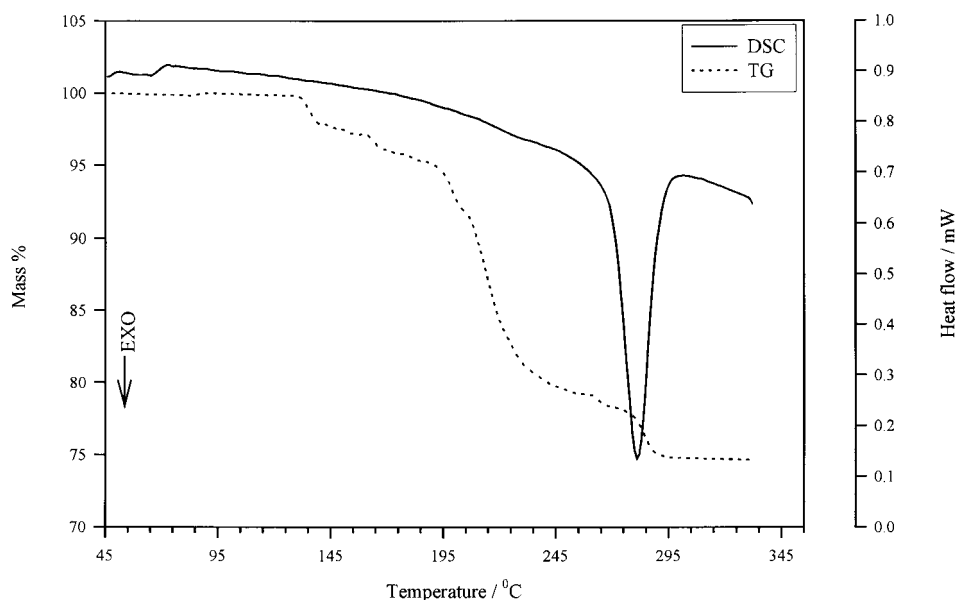Figures 9 and 10 represent the DSC and TGA curves of wax heated in the presence of different

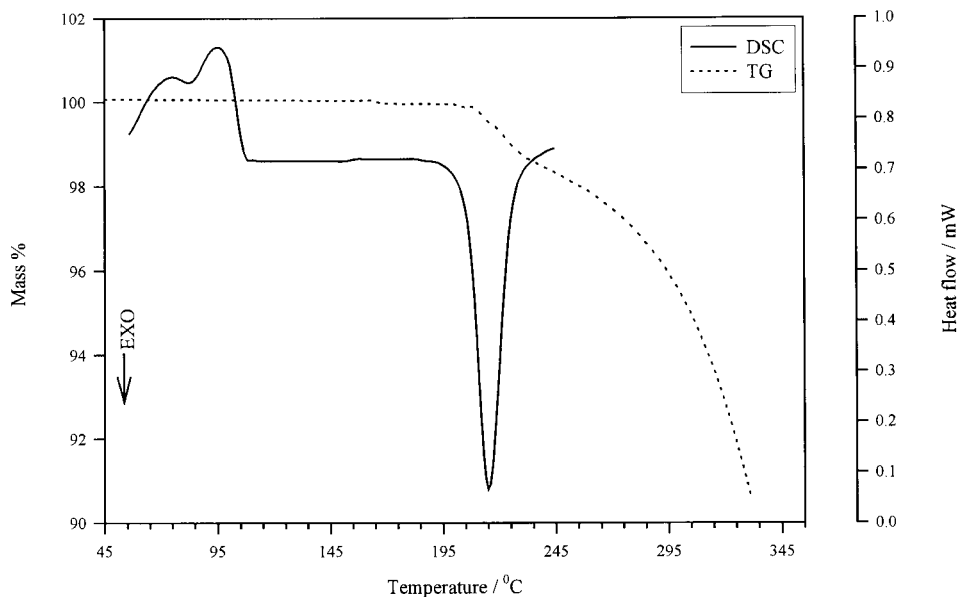**Figure 8** DSC and TG curves of pure PPS.

Figure 9 DSC and TG curves of an 80/20 m/m mixture of H2 wax and PPS.

amounts of PPS. The DSC curves show double melting endotherms for H2 wax in the temperature range 50–125°C. However, at about 215°C (onset temperature 205°C) the DSC curve shows an intense and irreversible exotherm which is accompanied by a small mass loss of less than 2%. This is probably due to decomposition of PPS and interaction with the wax, although the exotherm was observed at a much lower temperature (compared with that of pure PPS) and it was not preceded by a mass loss. The exotherm was followed by a larger mass loss of about 9% up to the final temperature of 340°C, which may be due to wax degradation or decomposition of excess PPS. It is further interesting to note that with double the amount of PPS in the sample, the mass loss accompanying the exotherm remained at about 2% (see Fig. 10), signifying that decomposition does not make the primary contribution to the exothermic event.
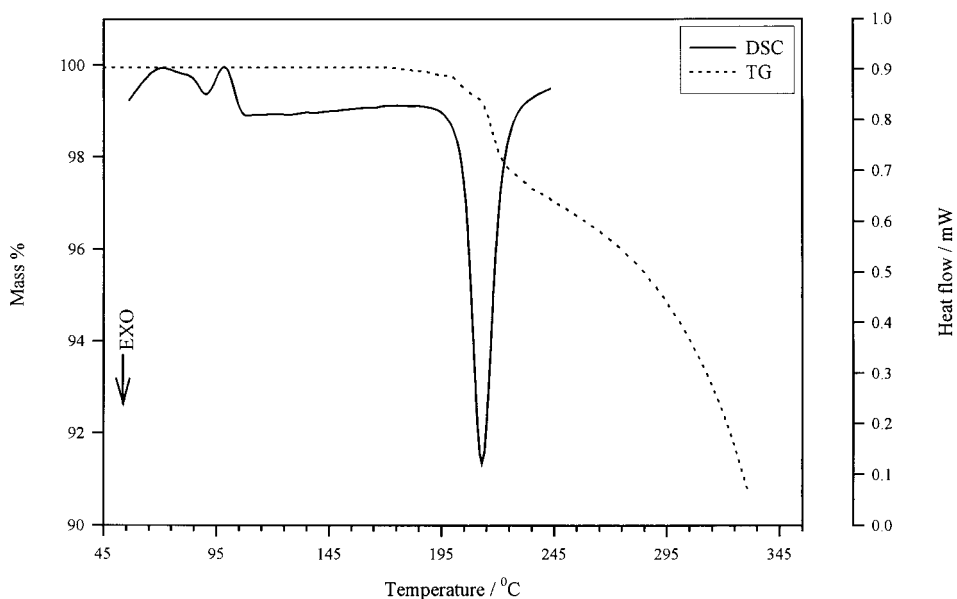

Figure 10 DSC and TG curves of a 60/40 m/m mixture of H2 wax and PPS.

Table III   Onset Temperatures, Peak Temperatures, and Enthalpy Values of the Exotherms in Figures 7–9

Sample (mass %)	Onset Temperature (°C)	Peak Temperature (°C)	ΔH (J g^{-1})
100% PPS	251.9	253.8	65.1
80% H2 wax/20% PPS	206.9	214.9	186.2
60% H2 wax/40% PPS	207.1	213.1	264.0

The corresponding reaction enthalpies for the exothermic reaction increased with an increase in crosslinking agent content (see Table III) and were much larger than that for the exotherm observed in pure PPS. This supports the assumption that the exotherm observed for the mixtures must be due primarily to crosslinking, also because the mass loss as a result of decomposition did not increase (see TGA curves).

Table IV qualitatively gives the solubilities of samples after heating to 340°C in DSC. The pure wax was insoluble in various solvents such as dichloromethane, chloroform, chlorobenzene, benzene, THF, diethylether, and xylene. In toluene, however, the pure wax was slightly soluble at 30°C, but dissolved completely at higher temperatures. Heating in the presence of PPS resulted in insoluble products at the lower temperatures, with the products becoming slightly soluble at 60°C. These observations also suggest that crosslinking occurred.

Figure 11(a) shows the FTIR spectrum of pure wax, discussed in the previous section (see Fig. 6). However, upon heating in the presence of about 20% PPS, a hydrogen-bonded OH stretching vibration of weak intensity emerged at around 3500 to 3200 cm^{-1}. This may be the result of hydroperoxides formed during the process. The intensity of the C—H out-of-plane bending vibration also decreased with an increase in crosslinking agent content. There was also a reduction in the intensity of the —CH$_2$— (methylene group) bending vibration at 1450 cm^{-1} and the CH$_3$— (methyl group) bending vibration at 1375 cm^{-1} [see Fig. 11(b,c)], which suggests the substitution of hydrogen atoms as a result of crosslinking. The emergence of a C=O stretching vibration at 1725 cm^{-1}, indicating the occurrence of oxidation, agrees with the possibility that the polymer backbone underwent some modification.

Figure 12 compares the FTIR spectra of samples taken before, during, and after the crosslinking exotherm at 198°C. The hydrogen-bonded OH stretching vibration at 3500 to 3200 cm^{-1} is one of the distinguishable features when comparing the three systems. It shows a smooth peak before, a double peak during, and a triple peak after the crosslinking exotherm. Other features are the disappearance of the strong S=O asymmetric stretch at 1300 cm^{-1} and the appearance of the strong S—O band at 1160 cm^{-1}. All these features point to interaction with the polymer backbone, which may result in crosslinking.

CONCLUSIONS

From the above discussion it is clear that both DP and PPS initiate crosslinking in a hard paraffin wax.

In the presence of DP, a single broad exotherm was observed in the same temperature range as the decomposition exotherm for pure DP. FTIR indicated the possible formation of hydroperoxides, which are well-known crosslinking agents. The linear increase in the values of enthalpy

Table IV   Solubilities in Toluene of Pure Wax, Pure PPS, and Their Mixtures, Heated to 340°C in DSC

Sample (mass %)	Testing Temperature		
	30°C	45°C	60°C
100% H2 wax	Slightly soluble	Soluble	Soluble
100% PPS	Insoluble	Insoluble	Slightly soluble
80% H2 wax/20% PPS	Insoluble	Insoluble	Slightly soluble
60% H2 wax/40% PPS	Insoluble	Insoluble	Slightly soluble

change that are associated with the crosslinking exotherm, with the amount of DP in the sample, also supports the view that DP initiates crosslinking on decomposition. The decrease in solubility of crosslinked products further supports the conclusion that DP does initiate crosslinking in a hard paraffin wax.

In contrast, the presence of PPS gave a crosslinking exotherm at a much lower temperature than the decomposition exotherm for pure PPS. Here also, the FTIR (appearance of S—O band and hydrogen-bonded OH stretching vibration) and solubility analyses indicated the initiation of crosslinking.

Although it seems as if DP initiates crosslinking through its decomposition products, whereas PPS reacts with the wax while still in its original state, the exact crosslinking mechanisms have yet to be established. This, as well as the determination of the mechanical properties of the pure and crosslinked samples, form part of an ongoing study into the crosslinking of waxes and related substances.
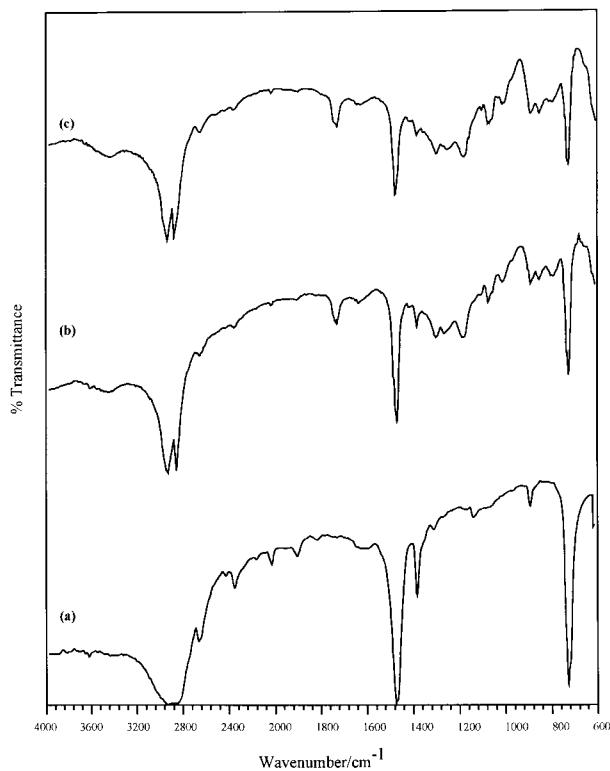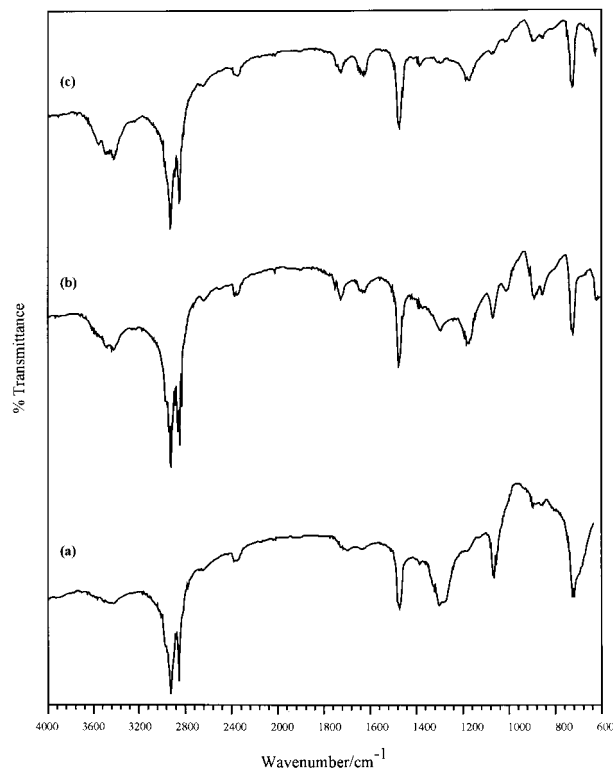

Figure 12 FTIR spectra of 60/40 m/m wax/PPS samples taken before, during, and after the crosslinking exotherm: (a) 198°C, (b) 222°C, and (c) 243°C.

Figure 11 FTIR spectra of (a) pure wax, (b) 80/20 m/m, and (c) 60/40 m/m wax/PPS mixtures after being heated to 340°C.

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