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Comparison of microstructural and physical properties of two petroleum waxes

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Abstract Microstructural and physical properties of two petroleum waxes, petrolatum and microcrystalline wax, were characterized in this work. Petroleum waxes are known to be hydrophobic and can be used in applications where a good moisture barrier is needed. In order to achieve a better understanding of different inherent properties of a wax, the two waxes in this work were characterized with infrared spectroscopy, confocal laser scanning microscopy, differential scanning calorimetry, rheology and X-ray diffraction. It was concluded from the results of infrared spectroscopy that the two waxes consisted only of saturated alkanes. Confocal laser scanning microscopy showed that the petrolatum sample had a more open microstructure with coarse crystals separated from each other than the microcrystalline wax, which appeared to have a more network-like crystalline structure consisting of somewhat finer crystals. Both waxes crystallized over a broad temperature range. Their crystallization characteristics were quite different, however, probably owing to a different oil content. According to modulated differential scanning calorimetry and rheological measurements the microcrystalline wax crystallized through a two-step process, whereas the petrolatum crystallized through only one step.

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Introduction

Petroleum waxes are very hydrophobic and coatings or films made of such waxes are known to be efficient water vapour barriers because of their hydrophobic character [1]. Petroleum waxes are separated from crude petroleum and can be divided into three types: paraffin waxes, microcrystalline waxes and petrolatums [2]. All three are complex mixtures of different alkanes, mainly of high molecular weight differing in composition and microstructure. Paraffin waxes consist mainly of straight-chain hydrocarbons, which form large crystals (macro-crystals), while microcrystalline waxes consist primarily of iso-alkanes and naphthene-containing alkanes and petrolatums are mixtures of microcrystalline waxes and oil [1]. Due to the large amount of branched and naphthenic hydrocarbons in microcrystalline waxes, they mainly form small irregular crystals during crystallization, so called micro-crystals. Paraffin waxes have a lower molecular weight than microcrystalline waxes. The average hydrocarbons in commercial paraffin waxes consist of 26–30 carbon atoms, while the average hydrocarbons in microcrystalline waxes consist of 41–50 carbon atoms [3].

Extensive work has been reported on phase transitions during melting and crystallization of *n*-alkanes, mixtures of *n*-alkanes and some petroleum waxes [4]. However, only a limited amount of research has been published on microcrystalline waxes and especially petrolatums. Differential scanning calorimetry (DSC) is a useful method for analysing melting, crystallization and other thermal transitions of different materials. The crystallization and melting behaviour, which could be obtained from DSC measurements, can also provide some information on a material's composition. *n*-Alkanes and their mixtures often show multiple phase transitions during melting and crystallization [5, 6]. For example, paraffin waxes often show one peak in DSC thermograms corresponding to a solid–solid transition just below a sharp peak corresponding to the melting, whereas microcrystalline waxes often show only one single broad peak and no separate solid–solid transitions [4].

The microstructure of these waxes, i.e. how the crystalline and the non-crystalline phases are distributed, is important for different physical properties of a wax. The constitution of the areas surrounding the crystals, where gases and moisture can be transported, is especially important for e.g. barrier properties [7]. Crystals are believed to be impermeable to oxygen and water vapour [7, 8]. Models have been proposed for how the crystalline and amorphous phases are distributed in a wax. Four models of the structure of paraffinic waxes have been suggested [9]. These models describe wax structures as (i) bundles or (ii) thin plates consisting of extended chains in an amorphous matrix, as (iii) thick plates with some defects, due to chain ends or branches, with an amorphous phase consisting of oil inclusions or as (iv) conglomerates of bundles or thin plates with poorly aligned chain ends. The amorphous phase can consist either of irregularly organized paraffinic chains or poorly aligned chain ends. Wax structures may be explained by these models or by combinations of them. The structure of hard waxes, such as paraffin wax, is often described as large crystalline plates with a mobile amorphous phase between the large plates, i.e. model (iii) mentioned above. The mobile amorphous phase mainly consists of iso-paraffins melting at lower temperatures and this mobile amorphous phase can become a solid amorphous phase during cooling [10]. This mobile amorphous zone can affect many properties of a wax. A microcrystalline wax that consists of more iso- or cycloalkanes than paraffin waxes is proposed to form smaller crystalline bundles or plates with an amorphous phase consisting of either dangling chain ends or low molecular weight alkanes, i.e. a combination of models (ii) and (iv) mentioned above.

The aim of this work was to characterize two petroleum waxes with regard to microstructure, mechanical properties and crystallization behaviour.

Materials and methods

Materials

Two petroleum waxes were characterized in this study, a white vaseline consisting of petrolatum (ACO Vaselin, ACO Hud AB, Sweden) and a microcrystalline wax (Microwax 1847, Kahl & Co, Germany). ACO Vaselin shows a creamy consistency at room temperature, while Microwax 1847, due to a lower oil content than in ACO Vaselin, is a solid wax at room temperature. Microcrystalline waxes usually have an oil content of 2–12% [3]. The oil content in petrolatums are greater than this, since petrolatums are considered to be mixtures of microcrystalline waxes and oil.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to distinguish the chemical similarities and differences between the two waxes and whether impurities were present in the waxes. A Perkin Elmer 1720X FT-IR Spectrometer (Perkin Elmer Ltd., England) was used. A small amount of each wax was melted on a KBr pellet and left to cool in room temperature. The wax surplus was removed from the KBr pellet before analysis. Spectra were collected between 4000 and 400 cm^{-1} in transmission mode for three replicates of each wax.

Confocal laser scanning microscopy

The microstructure was analysed using confocal laser scanning microscopy (CLSM). Wax samples were prepared and stained before structural analysis with CLSM. The two waxes were stained with Nile Red, which stains the non-crystalline wax phase, by dissolving the dye in molten wax. The two waxes were melted (ACO Vaselin at 70 °C and Microwax 1847 at 90 °C) together with approximately 0.001% (w/w) Nile Red during stirring for 60 min. The stained waxes were then left to cool in room temperature. Thereafter, 0.3 g of each of the stained waxes were melted in metal cups (15 mm in diameter and 2 mm deep) for 30 min in an oven at 70 °C and 90 °C for ACO Vaselin and Microwax 1847, respectively, and then left to cool in a tempered room set to 23 °C prior to CLSM analysis. One Microwax 1847 sample was also stored after cooling to 23 °C at 50 °C for 24 h prior to CLSM analysis. At 50 °C the crystalline material in Microwax 1847 is partly molten. This state, therefore, shows a greater similarity to the state of the partly molten ACO Vaselin at 23 °C than the state of Microwax 1847 at 23 °C. The microstructure of Microwax 1847 at both 23 and 50 °C was therefore studied. The wax samples were studied with an upright Leica RXA2 connected to a Leica TCS SP2 Confocal Laser Scanning Microscope (Leica Microsystems Heidelberg GmbH, Germany). The light source used was an Ar/ArKr laser using $\lambda_{\mathrm{ex}} = 488$ nm. A water objective with a magnification of 63× (N.A. = 0.9) and a digital zoom of 2× was used. Water was used as the immersion medium, and the wax samples were studied without a cover glass. The microstructure analyses were made at approximately 10 µm below the wax surface. The scanning speed was 400 Hz, and eight scans were averaged during the creation of each micrograph (1024 × 1024 pixels). The samples stored at 23 °C were studied at room temperature, while the sample stored at 50 °C was studied at 50 °C using a temperature-controlled heating table.

Modulated differential scanning calorimetry

ACO Vaselin and Microwax 1847 were analysed with modulated differential scanning calorimetry (MDSC) using a TA Instruments Q100 DSC (TA Instruments, USA) during cooling. Approximately 5 mg of the unstained wax samples and the stained wax samples prepared for structural analysis were analysed. The wax samples were analysed in aluminium pans and were kept isothermal for 5 min at the starting temperatures in all cases. The samples were then cooled between 70 and −20 °C for ACO Vaselin and between 90 and −20 °C for Microwax 1847 in order to study crystallization. The cooling rate was 5°C/min and the temperature was modulated with ±0.531 °C/40 s. Three replicates of each wax sample were analysed.

Rheological measurements

The rheological properties of the two waxes without Nile Red were characterized during cooling with a Stresstech HR Rheometer (Reologica Instruments, Lund, Sweden) in a strain-controlled mode. The temperature scans were made during oscillation in a parallel plate geometry. ACO Vaselin was cooled from 70 to −15 °C with a temperature-controlled Peltier plate and Microwax 1847 was cooled from 90 to 0 °C using an extended temperature cell (ETC), with 2 °C/min for both waxes. The temperature ranges available during the rheological measurements were a little different than for the MDSC experiments, but it was concluded that the main area of interest was covered and that the solidification was almost complete at the lower temperature limits. The diameters of the plates were 30 mm for ACO Vaselin and 20 mm for Microwax 1847, and the gap between the plates was 1 mm for both waxes at the beginning of the measurements. Three different strains, low, intermediate and high (5×10^{-4}, 1×10^{-3} and 1×10^{-2}), were used to evaluate the shear sensitivity of the two waxes. Due to some shrinkage of the wax during the cooling of Microwax 1847, an axial load of 0.01 N was applied at 75 °C to compensate for the decrease in volume. 0.3 g of Microwax 1847 and 0.7 g of ACO Vaselin were applied at 90 °C and 70 °C respectively and then let to melt for 15 min at these temperatures before the cooling ramp was started, in order to properly temper the samples. The experiments were repeated three times for each wax.

X-ray diffractometry

X-ray diffractometry (XRD) was performed on the two waxes. The analyses were run at 23 °C for both waxes, but also at 50 and 70 °C for Microwax 1847 to compare the crystallographic arrangement of ACO Vaselin and Microwax 1847 and to study changes in crystallographic arrangement caused by temperature changes. A small amount of each wax was placed in a sample holder, which was 15 × 15 × 1 mm. A Siemens D5000 X-ray Diffractometer was used, equipped with a Cu source with a wavelength of 0.154 nm. The incident angle of the parallel beams was 8° (2θ) and the sample was scanned from 10 to 90° (2θ) with a step size of 0.05° (2θ) every 2 s. The samples were tempered for 60 s at each temperature prior to analysis.

Results and discussion

Fourier transform infrared spectroscopy

The IR spectra of ACO Vaselin and Microwax 1847 were very similar, Fig. 1. The bands just below 3000 cm^{-1} represent C–H stretches in the alkanes. CH_2 groups have characteristic bands at approximately 1465 cm^{-1} and 720 cm^{-1}. The band at 720 cm^{-1} is called the long-chain band and corresponds to four or more CH_2 groups in a straight chain [11]. A band at approximately 1375 cm^{-1} is associated with methyl groups. All these bands were seen in the spectra of both ACO Vaselin and Microwax 1847 and no other bands appeared in the spectra of either ACO Vaselin or Microwax 1847. It could thus be concluded that the two waxes consisted only of saturated alkanes. The bands just below 3000 cm^{-1} and at ∼720 cm^{-1} are different for ACO Vaselin and Microwax 1847, hence indicating differences in the hydrocarbon composition in the two waxes. The band just below 3000 cm^{-1} is stronger for ACO Vaselin and the band at ∼720 cm^{-1} is stronger for Microwax 1847, which indicates that Microwax 1847 has a greater amount of four or more CH_2 in a straight

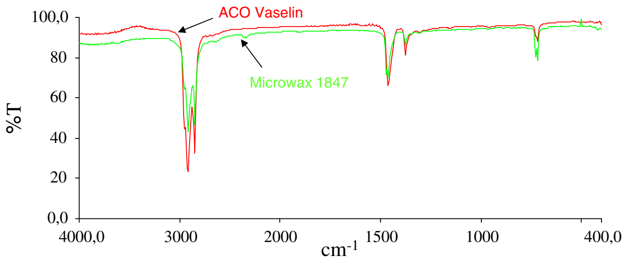


Fig. 1 IR Spectra of ACO Vaselin and Microwax 1847 on KBr pellets

chain than ACO Vaselin. The IR spectra for the two waxes clearly show that none of the waxes contain any functional or polar groups other than the alkanes that can have a great impact on their physical properties, such as their hydrophobicity. In conclusion, ACO Vaselin and Microwax 1847 seemed to have comparable chemical compositions, regarding their content of chemical substances that can have effect on their hydrophobic or polar properties. FTIR analysis does not give any information on the molecular weight distribution of the hydrocarbons present in the waxes, however.

Confocal laser scanning microscopy

Nile Red is used to stain lipids. The staining resulted in red areas representing non-crystalline parts of the wax and black areas representing crystalline parts of the wax, as shown in the micrographs, Fig. 2.

The microstructures of ACO Vaselin and Microwax 1847 at 23 °C were quite different, Fig. 2. There were fewer crystals in ACO Vaselin than in Microwax 1847. The crystals in ACO Vaselin also appeared coarser and more thread-like or bristled at the ends than the crystals in Microwax 1847. An approximation of the size of the crystals in the two waxes was made by measuring the thickness and length of some of the crystals seen in the micrographs. Many of the crystals seen in the micrograph of ACO Vaselin are approximately 0.5–2 μm thick and 5–20 μm long, whereas many of the crystals seen in the micrograph of Microwax 1847 at 23 °C are less than 1 μm thick and less than 15 μm long. The crystals in Microwax 1847 formed a more cross-linked and network-like crystalline structure than the crystals in ACO Vaselin, which were separated from each other to a greater extent. There was also a difference between the microstructure of Microwax 1847 at 23 and 50 °C. Some more shadowy, grey areas could be noted at 23 than at 50 °C and the crystalline structures seen at 50 °C formed a denser crystalline network, and the crystals appeared somewhat coarser than the ones seen at 23 °C.

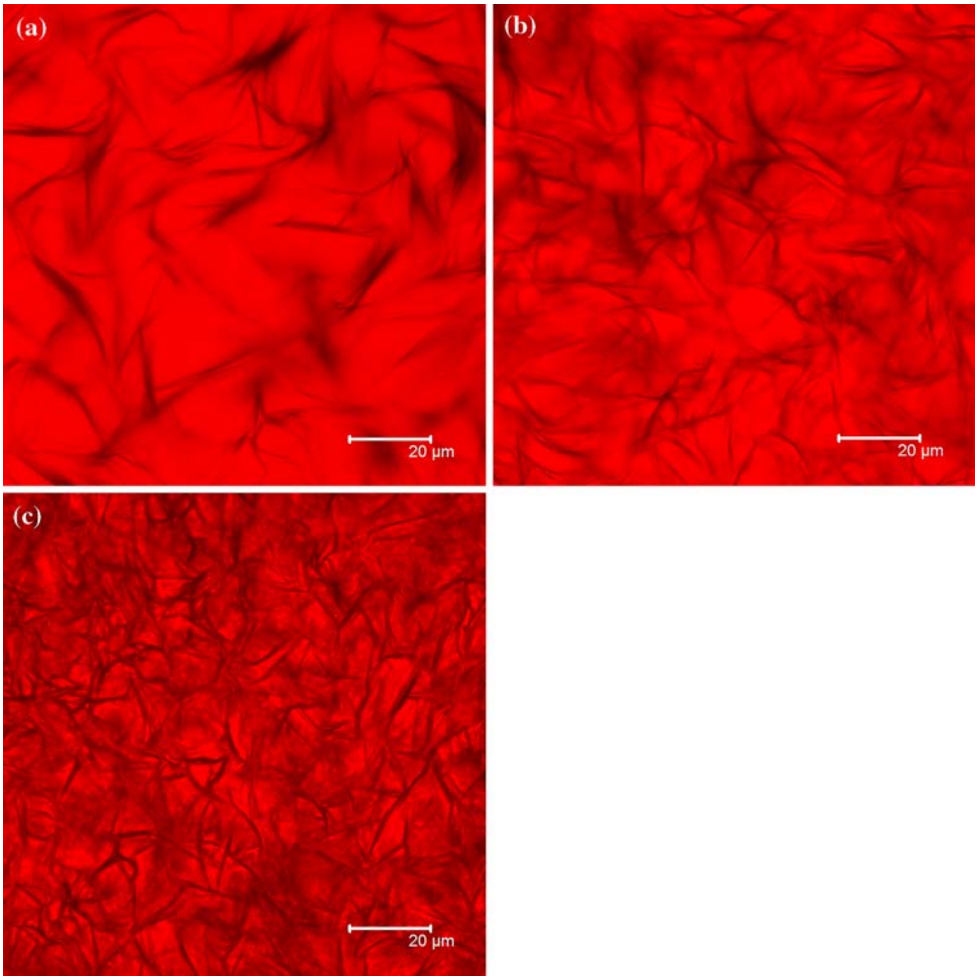


Fig. 2 CLSM micrographs of (**a**) ACO Vaselin at 23 °C, (**b**) Microwax 1847 at 23 °C and (**c**) Microwax 1847 at 50 °C. The scale bars represent 20 μm. At 50 °C the crystalline material in Microwax 1847 is partly molten. This corresponds better to the state of ACO Vaselin at 23 °C

Modulated differential scanning calorimetry

The crystallization characteristics of both waxes were analysed with MDSC. In order to evaluate the effect of the preparation of the samples for the CLSM analyses, the crystallization process of the two waxes both with and without Nile Red were examined with MDSC. Crystallization proceeded from a totally molten sample; hence the thermal history would have no effect on the MDSC results.

The sample preparation with Nile Red did not seem to have any effect on the waxes, e.g. degradation of molecules due to heating, indicated by an almost identical appearance of the MDSC crystallization heat flow curves of the samples with and without Nile Red, Fig. 3. Since no effect of sample preparation could be detected, the crystallization results of only the waxes prepared with Nile Red are henceforth discussed.

Great differences in the heat flow signals were found in the MDSC analyses of ACO Vaselin in comparison with Microwax 1847 during crystallization, Fig 4. The results of ACO Vaselin showed a broad peak between approximately −10 and 60 °C, with an indication of a small peak between approximately 45 and 60 °C. The results of Microwax 1847 on the other hand showed one broad transition, between approximately 10 and 80 °C, which consist of two

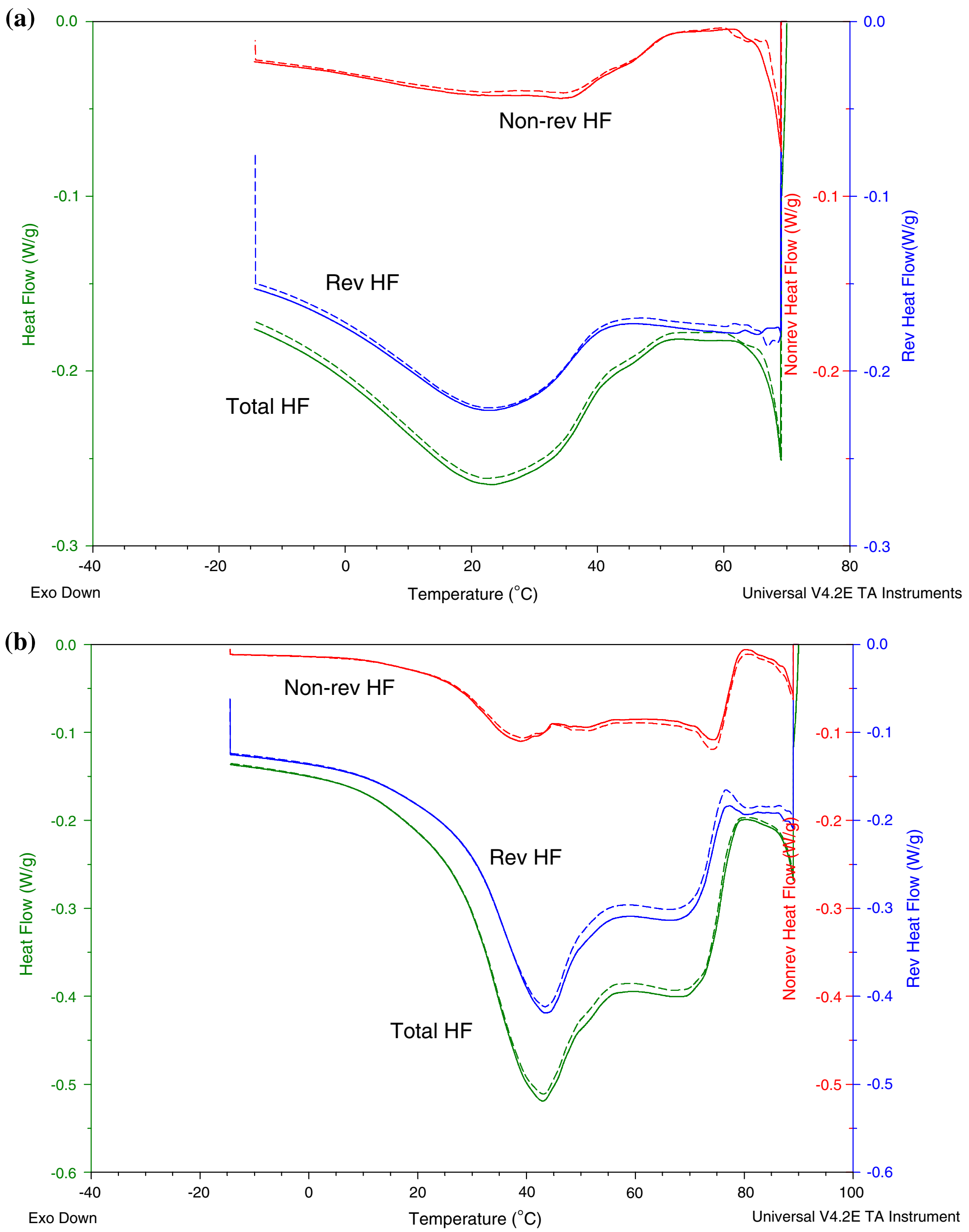
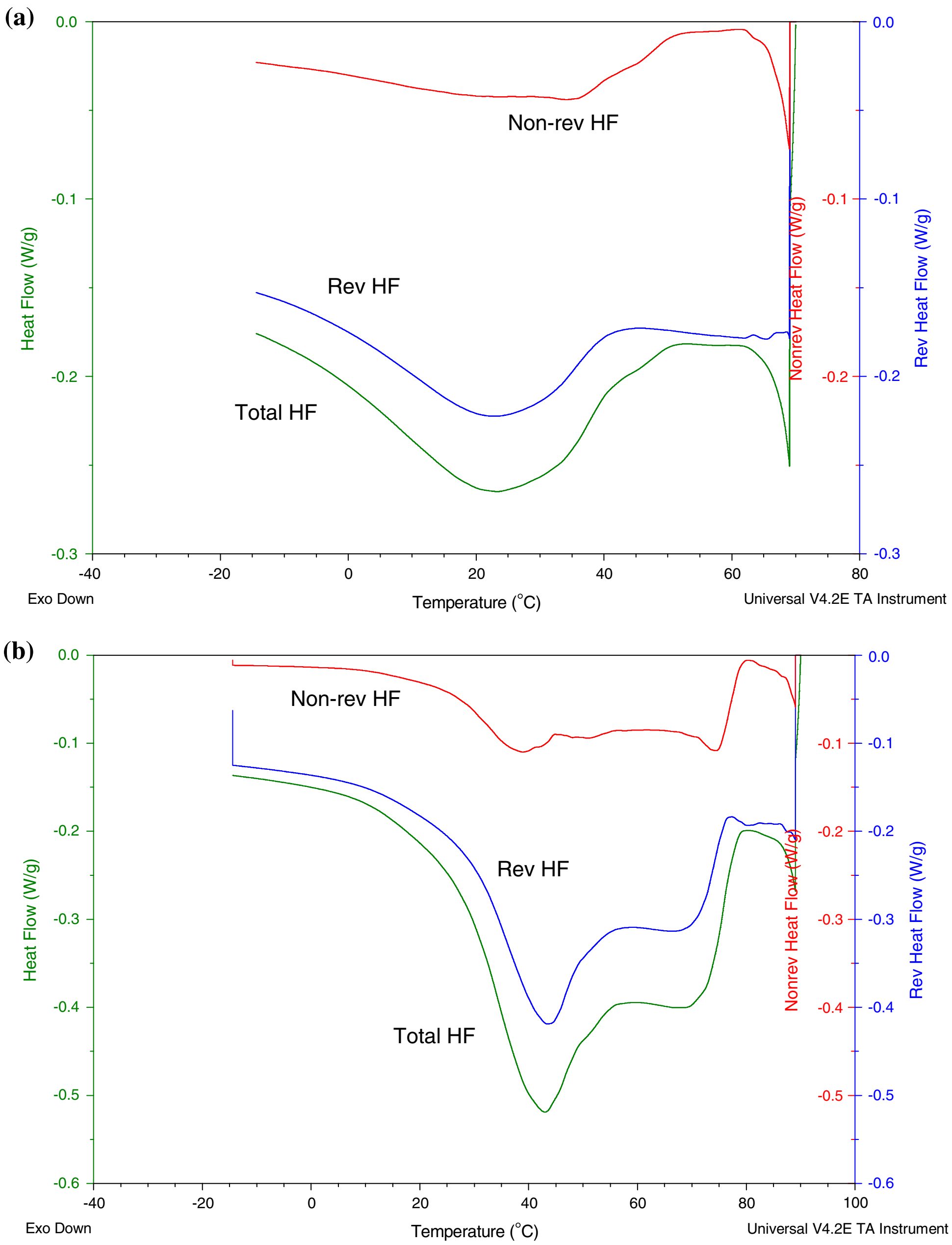


Fig. 3 MDSC thermograms of the crystallization process for (**a**) ACO Vaselin and (**b**) Microwax 1847 with and without Nile Red. (Solid lines represent wax with Nile Red and dashed lines represent wax without Nile Red)

Fig. 4 Crystallization of (**a**) ACO Vaselin and (**b**) Microwax 1847



large peaks between approximately 10 and 55 °C and between approximately 55 and 80 °C. There was also an indication of a third small peak between the two others, at approximately 50 °C. Both ACO Vaselin and Microwax 1847 crystallized over a broad temperature range, indicating that the waxes were mixtures of molecules with different melting points, which has also been observed for waxes in bitumen [12]. Microcrystalline waxes often show only one broad peak due to melting in DSC, whereas paraffin waxes often show two distinct peaks: one sharp peak due to melting and another peak due to a solid–solid transformation at temperatures just below the melting peak [4]. Paraffin waxes mainly consist of *n*-alkanes of different molecular weight, whereas microcrystalline waxes contain mainly iso- and cycloalkanes of different molecular weights. In this case the broad temperature range of the crystallization peaks for ACO Vaselin and Microwax 1847 indicates that the waxes were mixtures of molecules melting at different temperatures and that they contained iso- and cycloalkanes. The smaller peaks seen in the MDSC curves for both ACO Vaselin and Microwax 1847 did not appear at temperatures below the larger peaks and were thus not related to a solid–solid phase transition, which is common for n-alkanes and paraffin waxes. The shape of the MDSC curves, especially for Microwax 1847 with one broad peak consisting of two peaks, can more likely be explained by the crystallization behaviour, caused by the alkane composition together with the ability of the different alkanes to crystallize and form different crystalline structures or networks. The difference between the MDSC curves of ACO Vaselin and Microwax 1847 could be explained by the greater amount of oil in ACO Vaselin than in Microwax 1847, and the oil would have an effect on the crystallization behaviour of the wax. It has been observed that, when a microcrystalline wax is mixed with paraffinic oil, the melting behaviour of the wax becomes more like the melting behaviour of a vaseline [13]. The mean molecular weight and the molecular weight distribution could also affect the crystallization characteristics.

Exothermic processes in polymers, i.e. crystallization, are typically observed as an exotherm only in the non-reversing heat flow signal [14]. For ACO Vaselin and Microwax 1847, however, the crystallization was also seen as an exotherm in the reversing heat flow signal, Fig. 4. This was probably because the waxes had a distribution of molecules that crystallized at specific temperatures, which means that the crystallization process can be stopped at a specific temperature during cooling without further crystallization occurring, in contrast to polymer crystallization. When polymer crystallization is initiated it can continue isothermally. Waxes, on the other hand, show a temperature-dependent solid/liquid ratio. In conclusion, both ACO Vaselin and Microwax 1847 showed a crystallization behaviour during cooling that indicated that they consist of fractions crystallizing at different temperatures.

Rheological measurements

The results of the rheological measurements indicated different solidification behaviour in the two waxes. Cooling of ACO Vaselin showed an ordinary congealing behaviour when a low or intermediate strain was applied, Fig. 5. This indicates that the solidification of ACO Vaselin and the formation of crystalline structures took place through a one-step process. When a high strain was applied, however, the loss modulus, G″, increased more than the storage modulus, G’, even at low temperatures. This indicates that ACO Vaselin remained in its viscous state even at low temperatures. In this case the solidification process was hindered by the strain applied being too high for the wax to solidify. The crystalline structures formed when lower strains were applied were too weak to form when a high strain was applied.

Microwax 1847 showed a more complicated solidification behaviour than ACO Vaselin, Fig. 6. For low and intermediate strain experiments, a clear break could be seen in the storage modulus at approximately 50 °C, noted as an abrupt change of the G′ curve taking place over only a small temperature range. This indicates that the solidification of and formation of crystalline structures in Microwax 1847 took place through a two-step process and that two crystalline structures were formed. When a high strain was applied, however, no break in G′ was seen, thus indicating that the crystalline structures were formed in a two-step process only at lower strains. The first structure formed during cooling, i.e. the structure formed at higher temperatures, was weak and could therefore not form when a high strain was applied. The first structure formed was strengthened by the formation of a crystalline structure during the second step of solidification when more material solidified. When a high strain was applied the two structures were probably formed simultaneously when a sufficiently low temperature was reached. The crystalline structures formed are not necessarily two separate crystalline structures, but could be a combination of e.g. small crystals and a

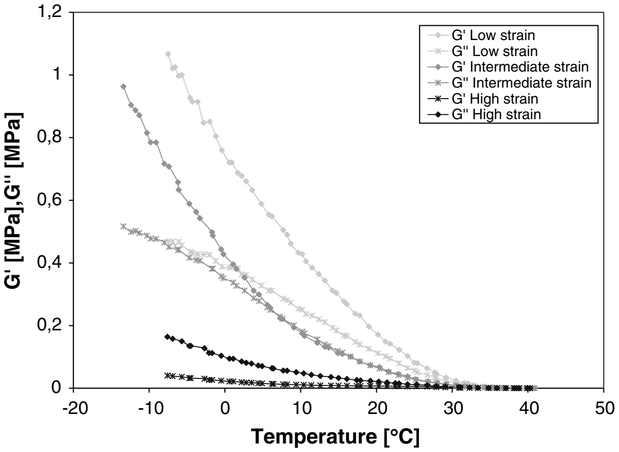


Fig. 5 Rheological behaviour of ACO Vaselin. (Low strain = 5 × 10^{-4}, intermediate strain = 1 × 10^{-3} and high strain = 1 × 10^{-2})

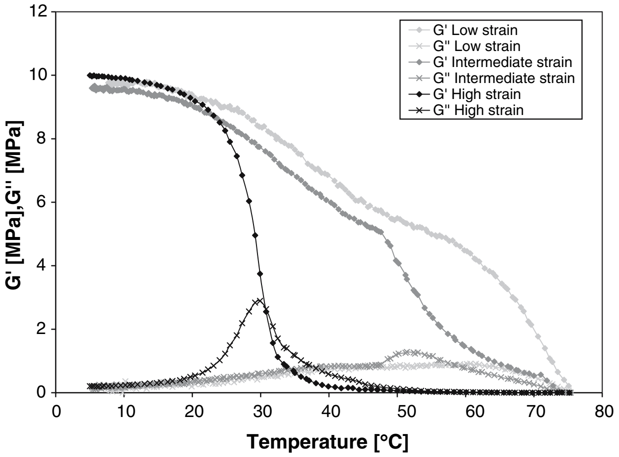


Fig. 6 Rheological behaviour of Microwax 1847. (Low strain = 5 × 10^{-4}, intermediate strain = 1 × 10^{-3} and high strain = 1 × 10^{-2})

crystalline network. They are, however, formed through a two-step process and the structure formed during the second step strengthened the first structure formed.

For Microwax 1847 a peak could be noted in the G″ curves, most clearly noted for high and intermediate strains, Fig. 6. Such a peak is typical for a change of state occurring e.g. at the gel point during gelation. For ACO Vaselin, however, no peak was noted in the G″ curves, Fig. 5, due to the lack of formation of a mechanically strong crystalline network, in contrast to the solidification of Microwax 1847 where a networked crystalline structure was formed.

X-ray diffraction

The results of the XRD analyses showed that the peaks representing crystalline material ($2\theta \sim 22$, 24 and 39–42) in Microwax 1847 appeared at the same angles at all three temperatures, meaning that the crystal packing and the symmetry in the crystal lattice were the same. Thus it could be concluded that the crystallographic arrangement in Microwax 1847 was the same at all three temperatures, Fig. 7. One small difference was noticed in the sample analysed at 23 °C as compared to the samples analysed at 50 and 70 °C. At 23 °C one of the peaks ($2\theta \sim 24$) was somewhat shifted to a greater angle, meaning closer crystallographic packing. This could be related to a displacement in the crystal lattice or to the fact that most materials expand when heated. It was also clear that when the temperature was increased the amount of non-crystalline material in the wax increased and the amount of crystalline material decreased, since the peaks became less distinct at higher temperatures. It can be concluded that ACO Vaselin had the same crystallographic arrangement, i.e. the same crystal packing and the same symmetry in the crystal lattice, as Microwax 1847, since the peaks representing crystalline material appeared at the same angles (at $2\theta \sim 22$, 24 and 39–42) as for Microwax 1847, Fig. 8. The results also showed that ACO Vaselin consisted of a high amount of amorphous material at 23 °C and that Microwax 1847 had a higher degree of crystallinity than ACO Vaselin since the peaks mentioned above are more distinct for Microwax 1847.

General discussion

The MDSC results, Fig. 4a, and the results of the rheological measurements, Fig. 5, showed that ACO Vaselin existed in a state in which the crystalline wax phase is partly molten at 23 °C. Microwax 1847 was in an almost totally solid state at 23 °C, Figs. 4b and 6, whereas Microwax 1847 was in a partly molten state at 50 °C. ACO Vaselin is in a 50% molten state at 23 °C, whereas Microwax is in a 50% molten state at 50 °C. Hence, the state of Microwax 1847 at 50 °C was more comparable to the state of ACO Vaselin at 23 °C. However, the total degree of crystallinity was lower in ACO Vaselin than in Microwax 1847 and a greater amount of crystalline structures was noted in CLSM micrographs of Microwax 1847 at both 23 and 50 °C than in ACO Vaselin. The crystalline parts appeared coarser at 50 °C than at 23 °C in Microwax 1847. Most materials expand when heated, and this was probably also the case for the crystalline parts in Microwax 1847, thus explaining the coarser crystalline structures at 50 °C. During the rheology experiments, some shrinkage of the Microwax 1847 samples during cooling could also be determined and the XRD results indicated a closer crystallographic packing at 23 °C than at higher temperatures. The volume decrease during solidification and crystallization in some microcrystalline waxes has been

Fig. 7 Diffractograms of Microwax 1847 at 23, 50 and 70 °C

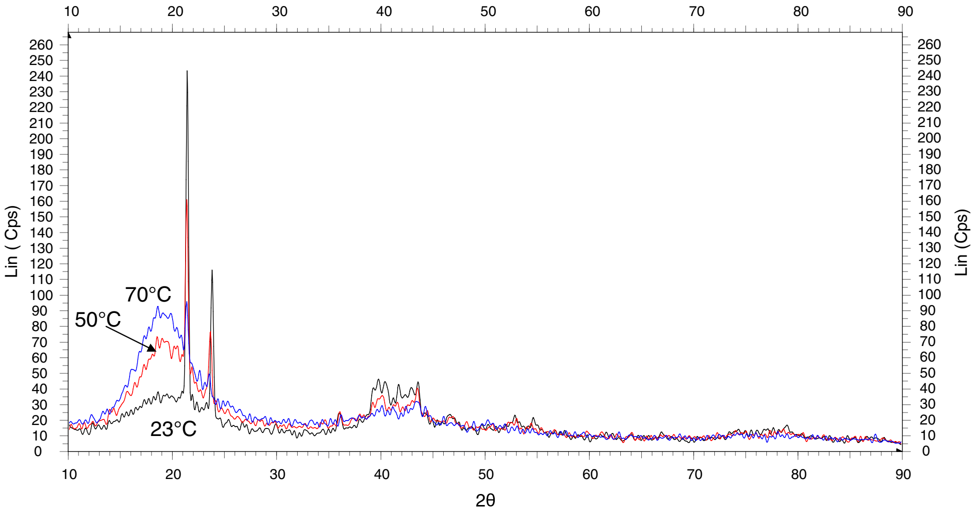
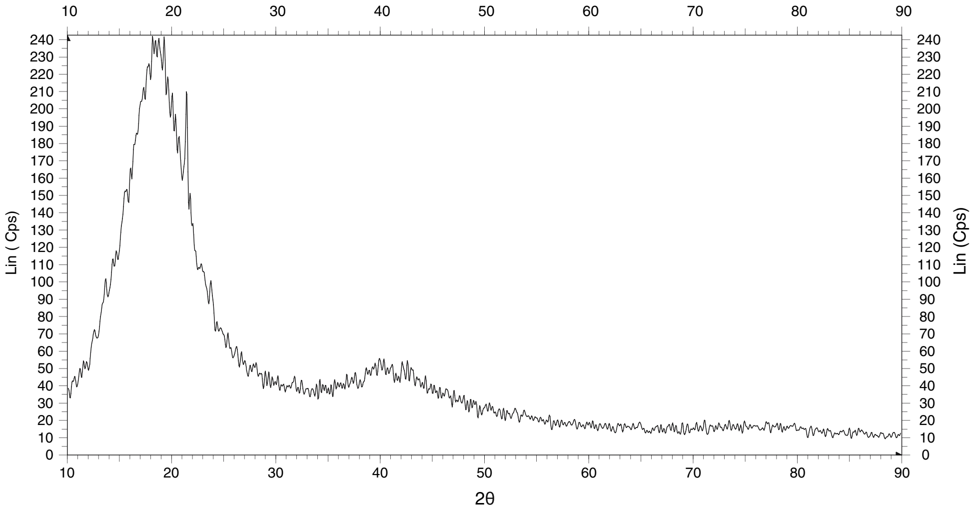


Fig. 8 Diffractogram of ACO Vaselin at 23 °C



reported to be between 12 and 16%, calculated from the densities of the waxes at 10° above the melting point and at 25 °C [2].

According to the results of MDSC and rheological measurements the solidification of ACO Vaselin took place through a one-step process, whereas the solidification of Microwax 1847, took place through a two-step process. According to the literature, many alkanes and paraffin waxes have different crystallographic arrangements at different temperatures. For example, paraffin waxes often have a hexagonal crystallographic arrangement just below the melting temperature and an orthorhombic crystallographic arrangement at lower temperatures [15]. The XRD results in this work showed that the crystallographic arrangement in ACO Vaselin and Microwax 1847 was the same and that the crystallographic arrangement in Microwax 1847 did not alter between 70 and 23 °C. It could therefore be concluded that the two-step process taking place during the solidification of Microwax 1847 observed in the MDSC and rheology experiments could not be related to or explained by transitions between different crystallographic arrangements.

The processes taking place during solidification of ACO Vaselin and Microwax 1847 can more likely be explained by the formation of different crystalline structures or networks. The solidification of ACO Vaselin took place through a one-step process only, indicated by an ordinary solidification behaviour between approximately 35 and −10 °C in the rheology results, Fig. 5, and as one broad crystallization peak between approximately 60 and −10 °C in the MDSC results, Fig. 4a. The process taking place during solidification of ACO Vaselin can be explained by the formation of crystals during cooling. As the cooling proceeded more crystals were formed, which perhaps also formed a networked crystalline structure. A networked crystalline structure is not seen in the CLSM micrographs, but these were made at 23 °C where the wax was partly molten. The results from the rheological measurements show that G′ increased at temperatures below approximately 35 °C, which indicate the formation of a crystalline structure providing some mechanical strength to the wax. ACO Vaselin has a high content of liquid oil, which can have diluted the crystalline material. The crystalline structure was therefore weak and did not form when a high strain was applied. The presence of only a few, separate crystals at long distances from each other, due to a high oil content, would not provide much mechanical strength to the wax and hence no clear response in the rheological measurements above 35 °C. As the cooling proceeded more crystals were formed, which provided some mechanical strength to the wax and thus a response in the rheological measurements. MDSC measurements, however, show the whole crystallization process and that is a likely reason to why the crystallization is detected at higher temperatures for ACO Vaselin in MDSC analyses than with rheological measurements.

Solidification of Microwax 1847 took place through a two-step process, seen by a clear break at approximately 50 °C in the G′ curve in the rheology results, Fig. 6, and by a broad crystallization transition consisting of two peaks in the MDSC results, Fig. 4b. The first step represents the process taking place between approximately 80 and 55 °C and the second step represents the process taking place between approximately 55 and 10 °C. It was concluded that two crystalline structures were almost fully developed at 23 °C, whereas only one of the structures was fully developed at 50 °C. This was not as evident in the CLSM micrographs.

At both 23 and 50 °C the CLSM micrographs showed a networked crystalline structure and it could not be clearly observed that more or different crystalline structures were present at 23 than at 50 °C, except for some more shadowy, grey areas being noted at 23 °C. The process taking place during the first step of solidification, i.e. between 80 and 55 °C, can therefore be explained by the formation of crystals, which subsequently also aggregated and formed a networked crystalline structure, which is seen in the CLSM micrographs at 50 °C, Fig. 2. The crystalline structures formed during this first step were weak, since they were not formed at these high temperatures when a high strain was applied during the rheological measurements.

Since the CLSM micrographs did not show any great differences in the amount of crystalline structures between 50 and 23 °C, the structures formed during the second step of solidification could probably be explained by the formation of either new small crystals forming a very fine crystalline network in the non-crystalline areas, further growth of the first formed crystalline network or a combination of these. However, the structure formed during this step strengthened the first structure formed and it did not result in any new clearly observable structures in the CLSM micrographs, except for some more shadowy, grey areas. The formation of small crystals or a very fine crystalline network would explain the greater amount of shadowy, grey areas seen in the CLSM micrographs at 23 °C. Due to limitations in the resolution of CLSM (~0.22 µm with the 63× objective) small crystals or a very fine crystalline network would probably only appear as shadowy, grey areas in the micrographs. New, small crystals could also most likely have aggregated with the crystalline structures formed during the first step. Both these proposed mechanisms, i.e. formation of small crystals forming a very fine network and aggregation of new, small crystals to the first formed structures, would strengthen the structure formed during the first step. The formation of two crystalline structures could be the result of alkanes of different molecular weight and complexity and thereby also with different ability to crystallize.

ACO Vaselin and Microwax 1847 can be used as water vapour barriers thanks to their hydrophobic properties. Water vapour measurements have showed that vaselines have better water vapour permeability properties than microcrystalline waxes [13]. ACO Vaselin had a more open crystalline structure with fewer crystals than Microwax 1847 at room temperature as shown by CLSM micrographs. Since crystals are believed to be impermeable to water vapour, Microwax 1847 ought to be a better moisture barrier than ACO Vaselin. The analyses made in this work have shown some differences of the physical properties of ACO Vaselin and Microwax 1847, but none of these can clearly explain their different barrier properties. ACO Vaselin has a greater content of liquid oil than Microwax 1847, however, and liquid oil is most likely a more effective barrier than an amorphous phase due to the existence of free volume in an amorphous phase. The liquid oil in ACO Vaselin can act as a filler in the amorphous areas, thus giving a less permeable phase. In Microwax 1847 there could be areas in the amorphous phase, which are not filled with oil and thereby could act as pathways for permeating molecules.

Conclusions

It was concluded from IR experiments that ACO Vaselin and Microwax 1847 consist only of saturated alkanes and can therefore be considered chemically comparable substances. XRD indicated that ACO Vaselin and Microwax 1847 had the same crystallographic arrangement. The microstructure, i.e. how the crystalline and non-crystalline parts are distributed, differed in the two waxes. Great differences in the microstructure between ACO Vaselin and Microwax 1847 were observed in CLSM micrographs. ACO Vaselin had a more open structure with crystals that were separated from each other to a greater extent. Microwax 1847 had a more network-like crystalline structure and also more crystalline areas than ACO Vaselin.

The crystallization characteristics of the two waxes were different. Both waxes, however, crystallized over a broad temperature range. From the MDSC and rheological measurements it was concluded that Microwax 1847 formed two crystalline structures or networks during solidification. This was not the case in ACO Vaselin, which formed only one crystalline structure during solidification.

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