J Mater Sci (2008) 43:1859–1868
DOI 10.1007/s10853-007-2416-x

Ageing of two petroleum waxes

Maria Petersson · Ingrid Gustafson ·
Mats Stading

Received: 13 March 2007 / Accepted: 20 December 2007 / Published online: 18 January 2008

Abstract The effect of ageing at different storage conditions on the microstructure and melting properties of two petroleum waxes, petrolatum and microcrystalline wax, were investigated. The two waxes were stored for a maximum of 50 weeks at different temperatures. Samples were analysed before storage and removed from storage and analysed after different storage times. The effect of storage time and temperature was analysed with confocal laser scanning microscopy and modulated differential scanning calorimetry. Some alteration in the microstructure occurred with longer storage time. The amount of fine and irregular structures seen in the initial petrolatum samples decreased with storage time, and some shadowy, grey areas appeared. The microstructure of the microcrystalline wax stored at 23 °C became more diffuse and more, shadowy, grey areas appeared with time compared to samples stored at 50 °C. These showed coarser crystalline structures and fewer shadowy, grey areas. The results of confocal laser scanning microscopy and modulated differential scanning calorimetry analyses indicated that recrystallization occurred in both waxes during storage. The proposed recrystallization processes taking place during storage were most likely the same in all samples, but the recrystallization occurred to a greater extent in the microcrystalline wax samples stored at 50 °C.

Introduction

Petroleum waxes are complex mixtures of different alkanes and are efficient moisture barriers [1]. Hence, they have been shown to be useful in applications, where a good water vapour barrier is needed, for example in packaging or food coating applications. Wax coatings can also be used to carry moisture sensitive active substances intended to be released from the wax to another medium and to protect these substances until released. The microstructure of a wax is important in respect to the barrier properties. Crystals are impermeable to oxygen and water vapour [2, 3], and the non-crystalline phase, which can work as pathways for diffusing molecules, is therefore of importance for the barrier properties.

When waxes are used in packaging, coating or release applications, for example, it is important to know whether the microstructure and hence the wax properties are stable or alter over time. Storage may have an effect on the crystalline structure in waxes, and recrystallization might occur. When crystals are allowed to grow slowly, they can attain shapes that minimize the interfacial energy between crystals and the material surrounding the crystal [4]. Crystallization processes of fats or waxes are believed to undergo several steps involving formation of nuclei, growth of nuclei into crystals, formation of crystal aggregates, network formation from crystal aggregates and finally crystal network changes [5, 6]. These events often occur as parallel processes and subsequently recrystallization might occur during storage. Recrystallization can

M. Petersson · I. Gustafson
SCA Hygiene Products AB, 405 03 Gothenburg, Sweden

M. Petersson · M. Stading (✉)
SIK – The Swedish Institute for Food and Biotechnology, P.O. Box 5401, 402 29 Gothenburg, Sweden
e-mail: mats.stading@sik.se

M. Petersson · M. Stading
Department of Materials and Manufacturing Technology, Chalmers University of Technology, 412 96 Gothenburg, Sweden

involve a change of crystals, polymorphic transitions and Ostwald ripening [5]. Ostwald ripening of fat crystals embedded in oil is a mechanism that can occur during storage of fats; hence crystal surfaces with lower interfacial energy will grow at the expense of crystal surfaces with higher interfacial energy [4]. Large crystals can thus grow at the expense of smaller ones. Ostwald ripening occurs spontaneously and reduces the total surface energy of the dispersed phase in a system. Recrystallization can result in different crystal size and crystal morphology [7]. The change in crystal size distribution is affected primarily by recrystallization and aggregation. The average size of crystals increases and the number of small crystals decreases during recrystallization [7]. Recrystallization might have an effect on the barrier properties of a wax layer [2]. During storage, recrystallization of the wax can take place and crystals can grow, which can result in more complicated or longer pathways for diffusing molecules.

The aim of this work was to study the effect of storage time and storage conditions on the microstructure and melting properties of two petroleum waxes.

Materials and methods

Materials

Two petroleum waxes were used in this work: a white Vaseline (ACO Vaselin, ACO Hud AB, Sweden), which consists of petrolatum with a high oil content and which had a creamy consistency, and a microcrystalline wax (Microwax 1847, Kahl & Co, Germany), which had a low oil content and was solid 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. These two waxes have comparable chemical composition consisting only of different alkanes [8], but different water vapour permeability properties [9].

Sample preparation

The wax samples were stained with the fluorescent dye Nile Red prior to storage to be able to characterize the microstructure of the waxes with confocal laser scanning microscopy. ACO Vaselin was melted at 70 °C and Microwax 1847 at 90 °C together with approximately 0.001% (w/w) Nile Red for 60 min during stirring. The waxes were then left to cool in room temperature. After cooling, 0.3 g of each wax was weighed into small metal test cups, 15 mm in diameter and 2 mm in depth and melted in the metal cups in an oven at 70 °C (ACO Vaselin) and 90 °C (Microwax 1847) for 30 min. The wax samples were then allowed to cool overnight in a tempered room set to 23 °C.

Table 1 Storage conditions for the wax samples

Storage conditions	ACO Vaselin	Microwax 1847
23 °C, 50% RH	X	X
50 °C, 50% RH	–	X

Ageing

After preparation, the test cups with waxes were placed in different storage conditions according to Table 1.

ACO Vaselin samples were stored at 23 °C whereas Microwax 1847 samples were stored at both 23 and 50 °C, since it is partly molten at 50 °C and hence more comparable to the partly molten ACO Vaselin at 23 °C. 23 °C was achieved in a tempered room and, to achieve an approximate RH of 50%, the samples of ACO Vaselin and Microwax 1847 were placed in a desiccator containing a saturated aqueous salt solution of $Mg(NO_3)_2 \cdot 6H_2O$ prepared according to ASTM E104-85 [10]. Samples of Microwax 1847 were also stored in a climate cabinet set to 50 °C and 50% RH. The wax samples were stored in the conditions given in Table 1, and samples for confocal laser scanning microscopy analyses were taken after 4, 7 or 8, 12, 28 and 50 weeks. Samples for modulated scanning calorimetry analyses were taken after 30 and 50 weeks. Samples were also studied with confocal laser scanning microscopy and modulated differential scanning calorimetry before storage, and Microwax 1847 samples were also studied with confocal laser scanning microscopy after 24 h at 50 °C.

Confocal laser scanning microscopy

The wax samples were analysed with an upright Leica RXA2 connected to a Leica TCS SP2 Confocal laser scanning microscope (CLSM) (Leica Microsystems Heidelberg GmbH, Germany). The light source used was an Ar/ArKr laser using $\lambda_{ex} = 488$ 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 analysed without a cover glass. The scanning speed was 400 Hz and eight scans were averaged during the creation of each image (1024 × 1024 pixels). The samples stored at 23 °C were studied at room temperature, while the samples stored at 50 °C were studied at 50 °C using a temperature-controlled heating table. The samples analysed at 50 °C were subsequently left to cool to room temperature and then analysed again with CLSM at room temperature to make comparisons with the samples stored at 23 °C. The microstructure analyses were made at approximately 10 µm below the wax surface.

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). The melting properties of the waxes were analysed to investigate the effect of ageing on the crystalline structure, and the crystallization properties of the waxes were analysed to distinguish whether any molecular degradation had occurred during storage. Crystallization does not give information on the effects of storage on the crystalline structure, since crystallization analyses begin from totally molten wax samples.

The wax samples for MDSC analyses were prepared in the same way as the samples for CLSM analysis. Approximately 5 mg of the stained wax samples was analysed. The wax samples were analysed in aluminium pans and were kept isothermal for 5 min at the starting temperatures in all cases. ACO Vaselin samples were heated between −20 and 80 °C and Microwax 1847 between −20 and 100 °C to study melting. In order to study crystallization the ACO Vaselin samples were cooled between 70 and −20 °C and the Microwax 1847 samples between 90 and −20 °C. The heating and cooling rates were 5 °C/min and the temperature was modulated with ±0.531 °C/40 s. Three replicates of each sample were analysed during heating and another three during cooling.

Results and discussion

Confocal laser scanning microscopy

Nile Red stains fats, and the crystalline parts of the microstructure are seen as black areas in the micrographs shown below since the dye does not penetrate and stain crystals. The non-crystalline parts are seen as red areas.

ACO Vaselin

Before storage, the microstructure of ACO Vaselin can be described as rather coarse crystals embedded in a matrix consisting of oil or non-crystalline material. The crystals were thread-like or bristled at the ends, with some fine and irregular crystalline structures stretching out from the crystals. Many of the crystals seen in the micrographs before storage were approximately 0.5–2 µm thick and 5–20 µm long. The crystals were quite separated from each other and did not form a continuously networked crystalline structure. Some changes in the microstructure were detected with increased storage time, Fig. 1. The finer, thread-like and more irregular crystalline structures, seen before storage, decreased in number with prolonged storage time. Some of these crystalline structures had disappeared after only 4 weeks of storage and even more after 12 weeks. After 28 weeks of storage, the appearance of the crystals was less distinct than was seen before storage and some of the finer, thread-like crystalline structures had disappeared. Some shadowy, grey areas also appeared during ageing. No great differences were observed between the samples aged for 28 and 50 weeks.

From the changes of the microstructure of ACO Vaselin observed in the CLSM micrographs during storage the conclusion was made that a recrystallization process of wax crystals occurred. The finer, thread-like crystalline structures, which decreased in number during storage, recrystallized and aggregated with the coarser crystals. During the sample preparation, when the wax was cooled, crystal nuclei were most likely formed. These could have grown into small crystals and somewhat larger crystals or fine, network-like crystalline structures were also formed through an ongoing recrystallization process during storage. This proposed recrystallization mechanism can be an explanation to the appearance of some shadowy, grey areas in the micrographs during storage. Crystal nuclei can probably not be detected by CLSM, due to limitations in resolution, but small crystals or fine, network-like crystalline structures, however, can appear as shadowy, grey areas. ACO Vaselin has a great content of liquid oil and is partly molten at room temperature. The oil can work as a dilution medium of crystalline structures, which result in long distances between different types of crystalline structures. This can be an explanation to why crystal nuclei and appearing small crystals did not aggregate to a greater extent with the coarser crystals during storage and hence why only a limited ripening process of the coarser crystals at the expense of new small crystals occurred during the recrystallization.

Microwax 1847

More crystalline areas were found in Microwax 1847 before storage than in ACO Vaselin, and many of the crystals seen in the micrographs of Microwax 1847 were less than 1 µm thick and less than 15 µm long, thinner than those seen in ACO Vaselin. The crystals formed a more networked and cross-linked crystalline structure in Microwax 1847 than in ACO Vaselin. Some shadowy, grey areas

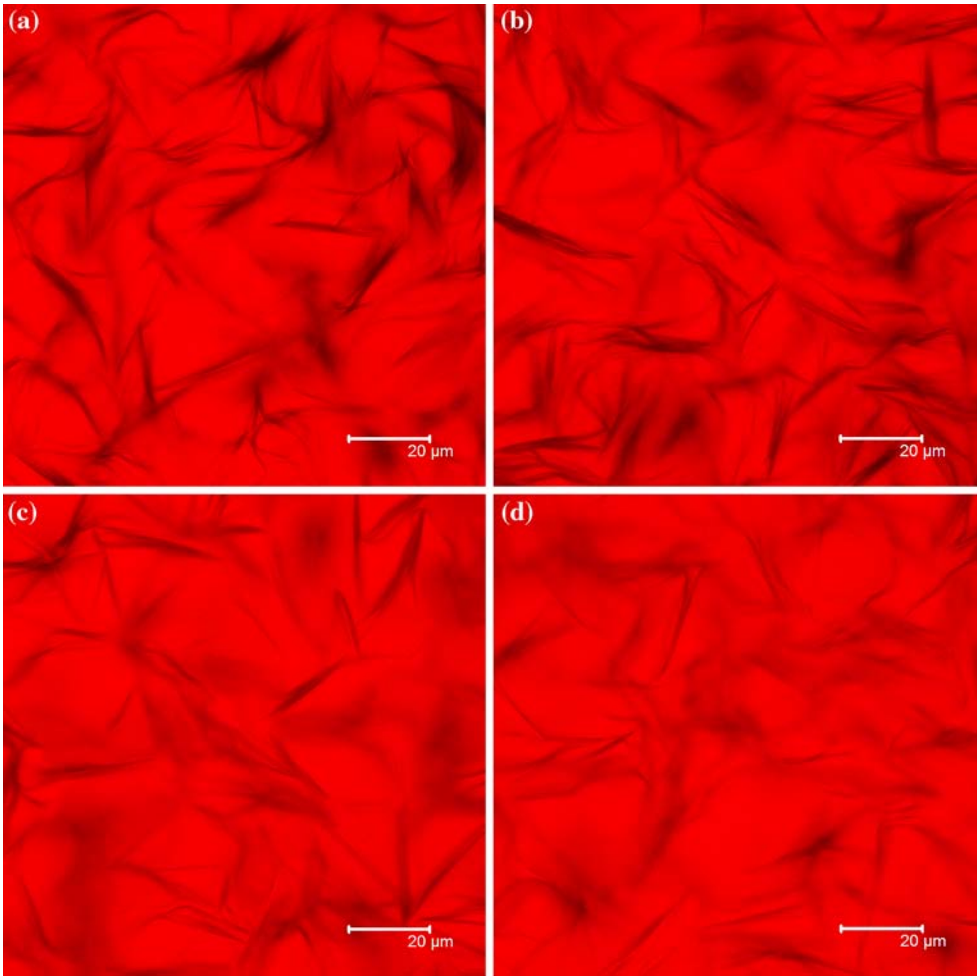

Fig. 1 CLSM micrographs of ACO Vaselin before and after storage at 23 °C. The samples were studied (**a**) before storage and after (**b**) 4, (**c**) 12 and (**d**) 28 weeks (Scale bar represents 20 µm, 2× digital zoom)

were also noted in the CLSM micrographs before storage, Fig. 2a. These shadowy, grey areas are most likely small crystals or a fine crystalline network, which were formed when the wax samples were cooled during the sample preparation.

Storage at 23 °C and analyses at room temperature During storage of Microwax 1847 at 23 °C a few more shadowy, grey areas appeared and the crystals became somewhat less distinct, Fig. 2. These changes can be related to an ongoing recrystallization process of the wax. Between 28 and 50 weeks, no further alterations were observed in the microstructure, which indicates that the recrystallization process had stopped.

The appearance of more shadowy, grey areas during storage can be explained by growth of small crystals from crystal nuclei and the formation of more fine crystalline networks through recrystallization, as in the case of ACO Vaselin. The crystal nuclei were formed during cooling of the wax during the sample preparation. Microwax 1847 is in an almost totally solid state at 23 °C. Hence, the mobility in the wax is low and the recrystallization process was in this case, therefore, most likely somewhat hindered at 23 °C. Due to the reduced mobility, the fine crystalline structures, which are seen as shadowy, grey areas, could not reorganize and aggregate with the larger crystalline structures and hence no clear ripening of the larger crystalline structures was observed during storage.

Storage and analyses at 50 °C Storage of Microwax 1847 samples at 50 °C had a greater effect on the microstructure than storage at 23 °C. Differences in the microstructure were detected after only 24 h at 50 °C, Fig. 3. The crystalline areas had become coarser and more distinct. Some of the shadowy, grey areas was still seen in the samples stored for 24 h at 50 °C, but became fewer with increased storage time. After 12 weeks of storage the crystals had become more distinct and coarser, forming a denser crystalline network with many cross-links. The crystalline network had become even denser after

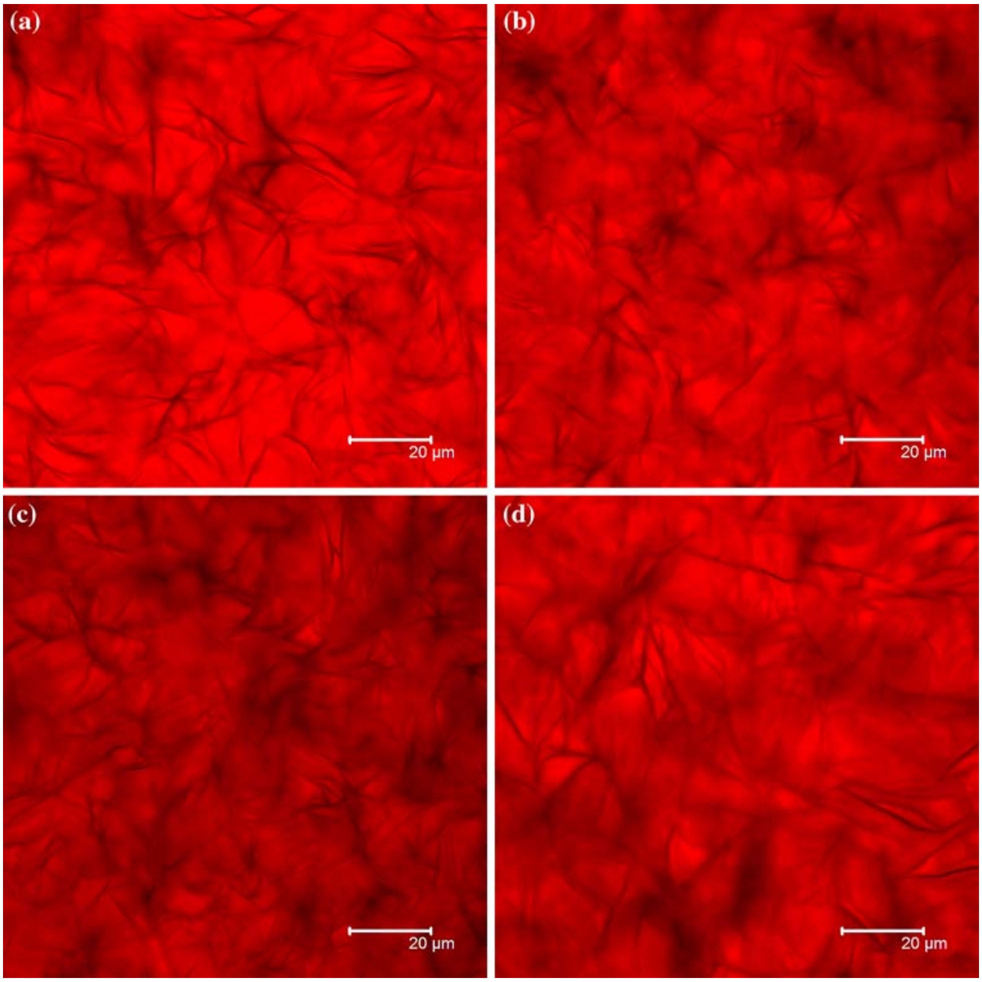

Fig. 2 CLSM micrographs of Microwax 1847 before and after storage at 23 °C. The samples were studied (**a**) before storage and after (**b**) 4, (**c**) 12 and (**d**) 28 weeks (Scale bar represents 20 µm, 2× digital zoom)

28 weeks of storage. The red areas in the micrographs representing zones of non-crystalline material also seemed to become more distinct during storage, probably related to the disappearance of shadowy, grey areas. Microwax 1847 was partly molten during storage at 50 °C and the mobility was thus higher than during storage at 23 °C. Recrystallization would explain the alterations of the microstructure seen during storage at 50 °C. An explanation to the alterations of the microstructure observed with CLSM can be that recrystallization of the wax that involved aggregation of small crystals with and hence ripening of the larger crystalline structures, occurred during storage at 50 °C. The reduction of the shadowy, grey areas, was related to the crystalline network becoming denser and more distinct and to the red areas becoming more distinct. The fine crystalline structures, i.e. the shadowy, grey areas, in this case recrystallized and aggregated with the larger crystalline structures. The larger crystalline structures thus ripened owing to the aggregation of more crystalline material and became coarser, denser and more distinct. The red areas, which represent zones of non-crystalline material, became more distinct with increased storage time since the shadowy, grey areas were reduced in number owing to the proposed recrystallization process.

Storage at 50 °C and analyses at 23 °C After analysis of Microwax 1847 samples at 50 °C the wax samples were left to cool till room temperature and then analysed with CLSM, in order to more clearly observe the effects of storage at 50 °C compared to storage at 23 °C. The cooling procedure from 50 °C to room temperature could lead to the formation of some fine crystalline structures. These structures would, if detected by the CLSM, only be noted as a few shadowy grey areas, however. After storage for 24 h the microstructure appeared quite similar to the structure seen in the wax samples before storage, Figs. 2a, 4a. During further storage, however, the microstructure of the samples stored at 50 °C and cooled to room temperature appeared to be somewhat different than the microstructure of the samples stored at 23 °C, Figs. 2, 4. The crystals or the crystalline network appeared more clear and distinct after only 4 weeks at 50 °C. The red areas, which represent zones of non-crystalline material, also

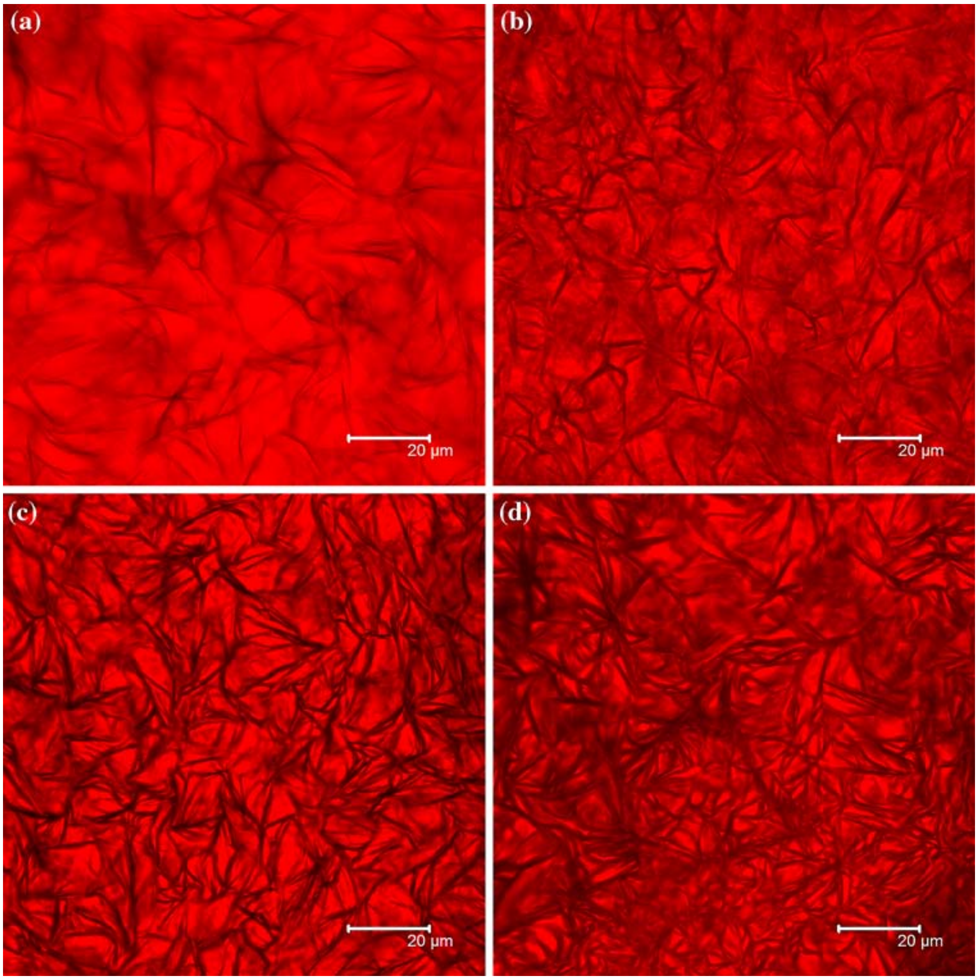

Fig. 3 CLSM micrographs of Microwax 1847 (**a**) before storage and after (**b**) 24 h, (**c**) 12 and (**d**) 28 weeks of storage at 50 °C (Scale bar represents 20 µm, 2× digital zoom)

appeared more distinct in these samples, since the amount of shadowy, grey areas which represent fine, crystalline structures, were reduced to some extent. The shadowy, grey areas that were observed before storage and in the samples stored at 23 °C were not as obvious in these samples and were reduced in number during storage at 50 °C. The crystalline structures were more distinct and somewhat coarser and fewer shadowy, grey areas were noted compared to after storage at 23 °C. These results confirm the observed alterations in the microstructure seen when these samples were analysed at 50 °C and also the proposed recrystallization process, which took place during storage at 50 °C, where the finer crystalline structures recrystallized and aggregated with the coarser crystalline network, which then ripened. This indicates that recrystallization of the wax during storage at 50 °C occurred more rapidly and to a greater extent than in the samples stored at 23 °C. The crystalline structures were less coarse at room temperature than when the samples were analyzed at 50 °C. Hence, the coarsening of the crystalline structures during storage at 50 °C can partly be explained by ripening due to recrystallization, but to some extent also by volume expansion of the wax at higher temperatures.

Modulated differential scanning calorimetry

Previous work showed that the sample preparation had no significant effect, i.e. there was no molecular degradation, on ACO Vaselin and Microwax 1847 [8]. The crystallization behaviour of the two waxes before and after storage was studied to distinguish whether any molecular changes had occurred during storage. It was concluded that storage did not have any effect on the crystallization characteristics of either ACO Vaselin or Microwax 1847, indicating that no molecular degradation had occurred during storage. Thus, only the melting characteristics of the two waxes are discussed below. In order to investigate the effect of different storage conditions, the melting characteristics of the two waxes were studied with MDSC before storage and after 30 and 50 weeks in samples stored at 23 and 50 °C.

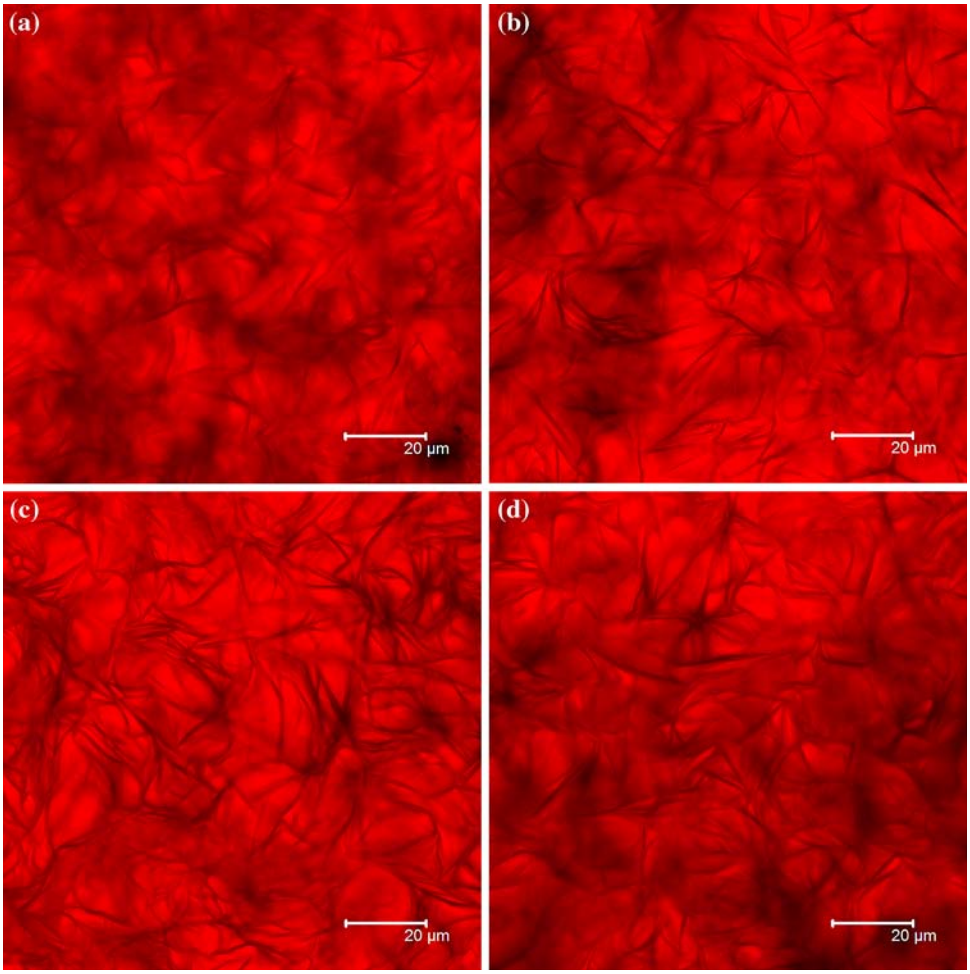

Fig. 4 CLSM micrographs of Microwax 1847 after (**a**) 24 h, (**b**) 4, (**c**) 12 and (**d**) 28 weeks of storage at 50 °C and cooled to room temperature (Scale bar represents 20 µm, 2× digital zoom)

MDSC analysis results in a total heat flow signal, which is the sum of the reversing and non-reversing heat flow signals. The reversing heat flow represents heating rate dependent transitions, whereas the non-reversing heat flow represents transitions dependent on absolute temperature [11]. In the results below, the changes only in the total heat flow curves are discussed, although these changes originated from changes in both the reversing and non-reversing heat flow signals. The reversing and non-reversing heat flow did not give any further information on the ageing mechanisms in this case.

ACO Vaselin

Ageing affected the melting properties, and hence the crystalline structure of ACO Vaselin. The melting of the samples analysed before storage proceeded over a broad temperature range between approximately −10 and 60 °C, with one broad peak between approximately −10 and 45 °C and an indication of a small peak between approximately 45 and 60 °C in the total heat flow curve, Fig. 5. Ageing resulted in two changes in the MDSC thermogram. Firstly, the broad peak became slightly narrower in the high temperature region, mainly observed as a slightly steeper slope of the curve, Fig. 5 arrow A. Secondly, the small peak between approximately 45 and 60 °C, which

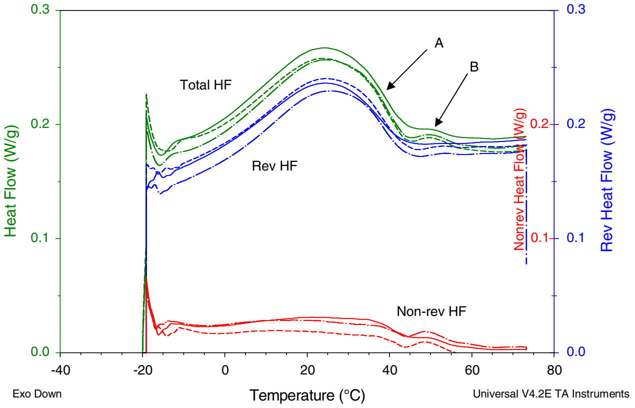

Fig. 5 Melting of ACO Vaselin before storage (solid line) and after storage for 30 weeks (short dashed line) and 50 weeks (dot-dashed line) at 23 °C

was seen in the curve before storage, became slightly larger during storage Fig. 5 arrow B. These two changes of the melting properties after ageing are most likely related and indicate that recrystallization of the wax took place during storage. From these results the conclusion was made that more stable crystalline structures, which melt at higher temperatures, were formed through recrystallization of crystalline material melting at lower temperatures. This would explain why the large peak became slightly narrowed at higher temperatures and why the small peak instead became larger during storage. The CLSM micrographs also showed that the crystalline structures in ACO Vaselin changed somewhat during storage.

Microwax 1847

Before storage, the melting of Microwax 1847 proceeded over a broad temperature range between approximately 10 and 80 °C, with two peaks between approximately 10 and 55 °C and between approximately 55 and 80 °C as observed in the MDSC thermogram, Fig. 6. An indication of a third, very small peak between the two large ones at approximately 50 °C, can also be noted, but this was almost totally merged together with the peak between 10 and 55 °C. The melting characteristics changed during storage and it was concluded that the storage temperature had an effect on the melting characteristics of the wax. After ageing at 23 °C, it was seen that the peak between 10 and 55 °C was somewhat broader towards higher temperatures, Fig. 6 arrow A. It was concluded that this change of the melting properties during storage was, as discussed for ACO Vaselin, caused by recrystallization of the wax, which involved the formation of more stable crystalline structures, which melt at slightly higher temperatures.

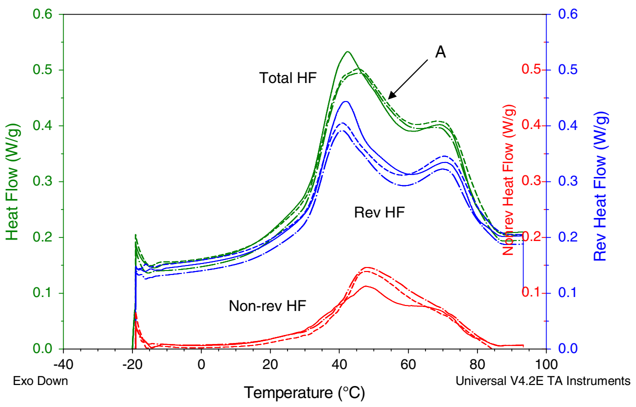

Fig. 6 Melting of Microwax 1847 before storage (solid line) and after storage for 30 weeks (short dashed line) and 50 weeks (dot-dashed line) at 23 °C

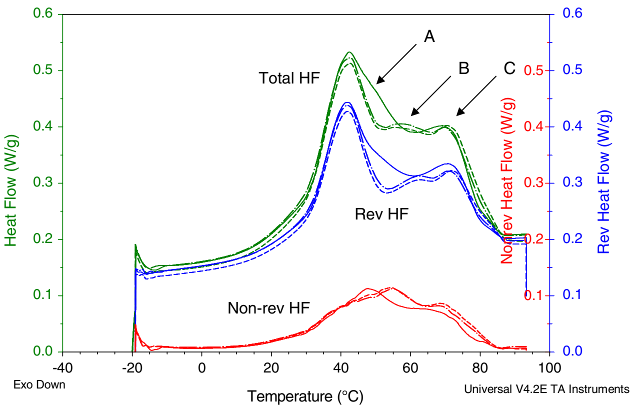

Fig. 7 Melting of Microwax 1847 before storage (solid line) and after storage for 30 weeks (short dashed line) and 50 weeks (dot-dashed line) at 50 °C

Ageing at 50 °C had a greater effect on the melting characteristics than ageing at 23 °C. The peak between 10 and 55 °C became narrower in the high temperature region, i.e. shifted to approximately 50 °C and a new small peak between approximately 50 and 65 °C appeared, Fig. 7 arrow A and B. The peak between 55 and 80 °C, Fig. 7 arrow C, also became somewhat narrower than before ageing as an effect of the appearance of the third peak. These changes of the melting properties indicate that recrystallization of the wax occurred and that a more stable crystalline structure, which melt at higher temperatures, was formed during storage at 50 °C, since a new small peak appeared in the MDSC thermogram. Crystalline material, which melts at lower temperatures, recrystallized and a new, more stable crystalline structure was then formed. This proposed recrystallization process explains why the peak at lower temperatures became narrower and why a new peak appeared at somewhat higher temperatures.

The MDSC results for Microwax 1847 indicate that the recrystallization processes occurring in the wax during storage at 23 and at 50 °C were similar. The peak between 10 and 55 °C was broadened towards higher temperatures during ageing at 23 °C and ageing at 50 °C resulted in a more narrow peak at lower temperatures together with the formation of a new peak between 50 and 65 °C. It therefore seems as though the MDSC result for the wax stored at 23 °C very slowly was approaching the shape of the MDSC result for the wax stored at 50 °C. The mobility in the wax was lower during ageing at 23 than at 50 °C and the recrystallization could therefore have been somewhat hindered by the lower mobility during storage at 23 °C and therefore stopped before the same state was reached. Storage at 50 °C affected the melting characteristics of Microwax 1847 more than storage at 23 °C. This indicates that the recrystallization process therefore occurred more rapidly and to a greater extent when the wax was stored at a higher temperature. The CLSM micrographs also showed greater differences of the microstructure after storage at 50 than at 23 °C.

In conclusion, storage had an effect on the crystalline structure in both waxes stored at 23 °C, and an even greater effect in Microwax 1847 stored at 50 °C as indicated by the results from CLSM and MDSC analyses. Preparation of the wax samples involved cooling from 70 °C (ACO Vaselin) and 90 °C (Microwax 1847) to 23 °C. This subtraction of heat could lead to molecular conformations that are not energetically favourable. The molecules can have an opportunity to rearrange into more stable and energetically more favourable conformations during storage. The interfacial energy in the system can be reduced by the growth of large crystals at the expense of smaller ones through recrystallization. Observations made in CLSM and MDSC analyses indicate a similar mechanism during storage in both ACO Vaselin and Microwax 1847. This mechanism can be explained by recrystallization, which involved a ripening process of crystalline structures. Storage of ACO Vaselin and Microwax 1847 at 23 °C had effect on the microstructure and the melting properties. More pronounced effects were observed in Microwax 1847 aged at 50 °C, however. It was concluded that during storage of Microwax 1847 at 50 °C recrystallization took place, which involved aggregation of finer crystalline structures with the larger crystalline network and hence ripening of this network. The large crystalline structures thus grew and ripened at the expense of the finer crystalline structures and the interfacial energy was most likely reduced. This explains the coarsening of the crystalline structures and reduction of the amount of shadowy, grey areas, which are believed to be fine crystalline structures, observed during storage at 50 °C. The CLSM and MDSC results indicated that this recrystallization process was somewhat hindered in Microwax 1847 and ACO Vaselin during storage at 23 °C. Microwax 1847 was almost totally solid at 23 °C, which can have resulted in a reduced mobility and thus a hindered ripening of the large crystalline network by aggregation of finer crystalline structures. ACO Vaselin had a great oil content, which can have worked as a dilution medium of the crystalline structures. The ripening of the coarse crystals by aggregation of small crystals was thus hindered due to the long distances between the different types of crystalline structures in ACO Vaselin. Instead, the amount of shadowy, grey areas therefore increased in both Microwax 1847 and ACO Vaselin during storage at 23 °C, indicating an ongoing recrystallization process in which crystal nuclei aggregated and formed small crystals and a fine crystalline network. These fine crystalline structures continued to grew and ripen during storage through recrystallization. The proposed recrystallization processes taking place during storage were, however, most likely the same in both waxes, but affected by the mobility in Microwax 1847 due to the different storage temperatures and by the oil content in ACO Vaselin.

Conclusions

It was concluded from CLSM and MDSC analyses that storage had an effect on the crystalline structures in both ACO Vaselin and Microwax 1847 and the results indicated that recrystallization occurred during storage. Some of the fine and irregular crystalline structures stretching out from the coarser crystals seen in ACO Vaselin before storage disappeared during storage and some shadowy, grey areas appeared. The shadowy, grey areas seen in Microwax 1847 before storage increased in number during storage at 23 °C. Storage of Microwax 1847 at 50 °C had a greater effect on the crystalline structure. Some of the shadowy, grey areas seen before storage disappeared, and the larger crystalline structures became somewhat coarser during storage. MDSC analyses indicated that more stable crystalline material, which melted at higher temperatures, formed during storage of ACO Vaselin at 23 °C and of Microwax 1847 at both 23 and 50 °C, being most evident for Microwax 1847 stored at 50 °C, however. The proposed recrystallization processes hence seemed to occur more rapidly and to a greater extent in Microwax 1847 stored at 50 °C.

CLSM and MDSC analyses indicated that recrystallization occurred in both waxes, and in Microwax 1847 at both temperatures, during storage and that the proposed mechanism taking place during storage most likely was the same. When the wax samples were cooled from the melt to 23 °C during the sample preparation, crystal nuclei were formed. During storage of ACO Vaselin and Microwax 1847 at 23 °C it was concluded that fine crystalline structures grew and ripened through recrystallization and aggregation of crystal nuclei or small crystals. This explains the increased amount of shadowy, grey areas in the non-crystalline areas in both ACO Vaselin and Microwax 1847 samples during storage at 23 °C. Some shadowy, grey areas were noted in Microwax 1847 also before storage, but these increased in number during storage. Ripening of the larger crystalline structures in ACO Vaselin and Microwax 1847 by recrystallization and aggregation of finer crystalline structures was limited during storage at 23 °C, however, most likely owing to the great oil content in ACO Vaselin, which diluted the crystalline structures, and the reduced mobility in Microwax 1847. During storage of Microwax 1847 at 50 °C, however, the mobility in the wax was less limited and a recrystallization process occurred, in which the larger crystalline structures grew and ripened at the expense of finer crystalline structures. This explains the coarsening of the larger crystalline structures and the reduced amount of shadowy, grey areas during storage of Microwax 1847 at 50 °C.

The proposed recrystallization process taking place during storage of ACO Vaselin at 23 °C and of Microwax at both 23 and 50 °C therefore seemed similar. At 23 °C fine crystalline structures grew and ripened through aggregation of crystal nuclei and small crystals. At 50 °C the larger crystalline structures ripened through aggregation of finer crystalline structures. In both waxes, and for Microwax 1847 at both storage temperatures, recrystallization thus seemed to occur, in which larger crystalline structures grew and ripened at the expense of smaller ones.

Acknowledgements The Knowledge Foundation through its graduate school YPK is acknowledged for financial support. Paula Olofsson and Maud Langton are also acknowledged for their valuable comments on the interpretation of the CLSM micrographs, and Niklas Lorén is acknowledged for valuable discussions. MS gratefully acknowledges funding from the EU project NovelQ and Vinnova (The Swedish Governmental Agency for Innovation Systems).

References

1. MacLaren FH (1951) TAPPI 34:462
2. Fox RC (1958) TAPPI 41:283
3. Salame M, Steingiser S (1977) Polym-Plast Technol Eng 8:155
4. Larsson K (1994) Lipids – molecular organization, physical functions and technical applications. The Oily Press Ltd, Scotland
5. Walstra P, Kloek W, van Vliet T (2001) In: Garti N, Sato K (eds) Crystallization processes in fats and lipid systems. Marcel Dekker Inc., New York, p 289
6. Freund M, Csikós R, Keszthelyi S, Mózes GY (1982) In: Mózes GY (ed) Paraffin products. Properties, technologies, applications. Elsevier Scientific Publishing Company, Budapest
7. Aquilano D, Sgualdino G (2001) In: Garti N, Sato K (eds) Crystallization processes in fats and lipid systems. Marcel Dekker Inc., New York, p 1
8. Petersson M, Gustafson I, Stading M (2008) J Mater Sci (in press). doi:10.1007/s10853-007-2417-9
9. Loth C (2004) Diploma thesis. Chalmers University of Technology
10. ASTM E104-85 (1985) Annual book of ASTM standards. ASTM, p 853
11. Gill PS, Sauerbrunn SR, Reading M (1993) J Therm Anal 40:931