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EXPERIMENTAL STUDY OF NATURAL AND SYNTHETIC WAXY MATERIALS USING SEM-BASED STRUCTURAL AND CHEMICAL ANALYSIS

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ABSTRACT

The physical and chemical properties of natural and synthetic materials are very important in any comparative study. This study uses the Scanning Electron Microscopy (SEM), which is the best known and most widely-used surface analytical techniques. In this study, paraffin wax and beeswax are used in the laboratory to simulate steel and reservoir rock, respectively. The physical and chemical analyses of beeswax and paraffin wax have been conducted using Energy-Dispersive X-ray analysis (EDX) coupled with SEM. Experimental results show that in paraffin wax, the composition of carbon varies from 10.33 to 12.99 (as weight basis 34.42-45.14%) and oxygen varies from 0 to 0.13 (as weight basis 0-1.95 %). For beeswax samples, the concentration of carbon varies from 11.14 to 17.62 (as weight basis 42.82-68.17%) and oxygen ranges from 0.40 to 0.67 (as weight basis 5.45-9.10 %). SEM analysis identified that carbon and oxygen are the main components in paraffin wax and beeswax samples. The resulting micrographs indicate the morphology of the beeswax and paraffin wax. The micrographs of paraffin wax show that this type of wax consists of two distinctive shades, one darker with long chains and smaller oblongate shape, and lighter pattern which is background. The micrographs of beeswax samples reveal topographic variations on the wax surface including ridges and valleys. This analysis demonstrates that material properties cannot be only based on the composition of principal components.

Keywords: SEM; EDX; paraffin wax; beeswax; physical and chemical properties; material structure.

INTRODUCTION

SEM, accompanied by X-ray analysis, is considered a relatively rapid, inexpensive, and basically non - destructive approach to surface analysis [1, 2]. For the physical and chemical characterization of solid materials, SEM is one of the best and most widely used techniques. SEM with or without energy or wavelength dispersive X-ray detectors for chemical analysis (also known as microprobe or electron probe micro analysis) has been and still is routinely used in the study of rocks and minerals. In order to use the SEM and the microprobe facilities the samples have to be coated with a thin conducting layer of gold in order to prevent charging of the sample [1, 2]. SEM, using a focused electron beam to scan the surface of a sample, generates a variety of signals. The three most common modes of operation in SEM analysis are Back Scattered Electron imaging (BSE), Secondary Electron Imaging (SEI), and EDS. In this study, EDS coupled with SEM are used to characterize paraffin wax and beeswax samples. The elemental analysis is performed in a spot mode in which the beam is localized on a single area manually chosen within the field of view. The EDS detector was capable of detecting elements with atomic number equal to or greater than six. The intensity of the peaks in the EDS is not a quantitative measure of elemental concentration, although relative amounts can be inferred from relative peak heights.

Paraffin wax is produced by refining and de-waxing light lubricating oil stocks. It consists of a mixture of solid aliphatic hydrocarbons of high molecular weight such as $C_{36}H_{74}$. Its molecular formula is C_nH_{2n+2} [3]. Paraffin wax can be defined as a fraction of petroleum dominated by n-alkanes that are solid at ambient temperature. It contains above C_{8+}, smaller amounts of isoalkanes, cycloalkanes and aromatics [4]. Paraffin waxes are chemically stable and have a negligible degree of sub cooling during nucleation. There is no phase separation, and the phase change process only results in a small volume change. Beeswax is a type of wax from the honeycomb of the honeybees. It is yellow,

brown, or white bleached solid. The color of beeswax changes with age, for example virgin wax is white but darkens rapidly as it ages, often becoming almost black. It has a faint honey odor. It consists largely of myricyl palmitate, cerotic acid and esters, and some high-carbon paraffins. Beeswax is lipid by nature [5]. It has saturated hydrocarbons, acids or hydroxy-acids, alcohols, pigments, mostly from pollen and propolis, as well as minute traces of brood etc. Beeswax has a very stable chemical make-up, alcohols, pigments, mostly from pollen and propolis, as well as minute traces of brood etc. Beeswax was the earliest waxy material exploited by men. However, many other natural substances have been used thereafter. Beeswax is the natural wax made by honey bees in the hive and is also known as Cera alba and Cera flava. A detail SEM-based study of both paraffin was and beeswax are presented by Hossain and co-authors [1, 2]. This paper shows a summary of SEM study on the paraffin wax and beeswax. It establishes their main components and morphology. Finally, this paper shows the different physical and chemical properties of natural and synthetic waxy materials that would be used to simulate rock drilling in the field.

1. EXPERIMENTAL SETUP AND CONDITIONS

In order to use the SEM and the microprobe facilities the samples have to be coated with a thin conducting layer of gold in order to prevent charging of the sample [1, 2, 6]. Figure 1 shows the SEM used in our wax material studies. It is important here to note that this SEM cannot detect the sample elements that are less than 2% by weight.

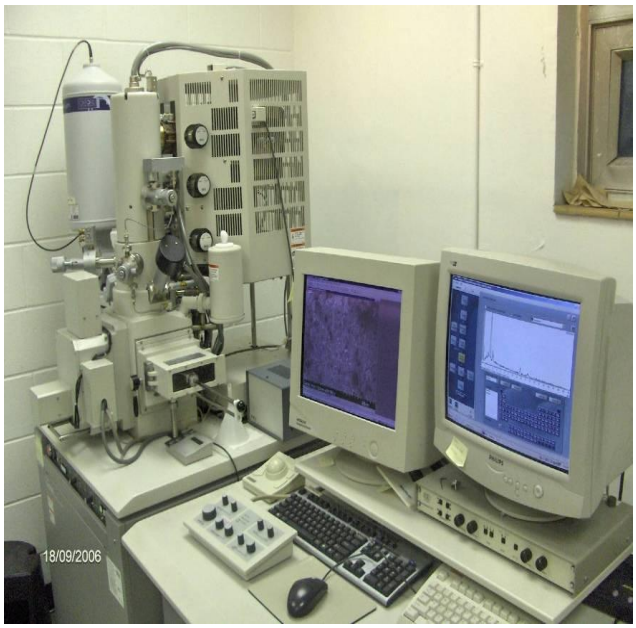

Figure 1. *Scanning Electron Microscope (side view)*

2.1 Preparation of Samples

In order to view non-conductive samples, SEM's require that the samples be electrically conductive [7]. To perform our analysis, bees wax and paraffin wax samples were coated with a thin layer of conductive material gold (Au). To do this a small device called a sputter coater was used. The sputter coater uses argon gas and a small electric field. The bees wax and paraffin wax samples were first fixed on double sided adhesive carbon tapes attached to one end of SEM stubs and then the samples were attached with that carbon tapes. Then the sample is placed in a small chamber which is at vacuum. Argon (Ar) is then introduced and an electric field is used to cause an electron to be removed from the argon atoms to make the atoms ions with a positive charge. The Argon ions are then attracted to a negatively charged piece of gold foil. The Argon ions act like sand in a sandblaster, knocking gold atoms from the surface of the foil. These gold atoms now settle onto the surface of the sample, producing a gold coating. The thickness of coating was 30.00 nm, density 19.32 g/cm^3. The coated samples were investigated using a SEM (Hitachi S-4700, Japan) equipped with an EDS system (INCA, UK) and an accelerating voltage of 20 keV for spectrum analysis. The experimental condition of SEM-EDX is given in Table 1 and the sample coating is shown in Figures 2 and 3.

Table 1. *Experimental condition of SEM-EDS for paraffin wax and beeswax*

Particulars	Paraffin wax	Beeswax
Type	Default	Default
Live time	100 sec	100 sec
Real time	104.4 -104.59 sec	104.68 - 105 sec
Acquisition geometry (°)	Tilt = 0.0	Tilt = 0.0
	Azimuth = 0.0	Azimuth = 0.0
Spectrum processing	No peak omitted	No peak omitted
Number of iteration	3	2-3
Processing option	All elements analyzed	All elements analyzed
Detector	Silicon	Silicon

Figure 2. *A sputter coater coats the sample with gold-palladium atoms.*

Figure 3. *Coated paraffin wax and beeswax samples for SEM tests.*

2. RESULTS AND DISCUSSION

The elemental analysis was performed in a spot mode in which the beam is localized on a single area manually chosen within the field of view. The EDS detector was capable of detecting elements with atomic number equal to or greater than six. The intensity of the peaks in the EDS is not a quantitative measure of elemental concentration, although relative amounts can be inferred from relative peak heights [8]. In order to examine the internal structure and composition of paraffin wax and beeswax, each sample was characterized by randomly selecting 3 fields of view and examining the samples. The SEM data [1, 2] clearly indicate that the main composition of paraffin wax and beeswax are carbon and oxygen that are shown in the Figures 4 to 8. The composition of carbon varies from 10.33 - 12.99 (as weight basis 34.42 % to 45.14%) and oxygen varies from 0 - 0.13 (as weight basis 0 % to 1.95 %). For beeswax samples, the concentration of carbon varies from 11.14 - 17.62 (as weight basis 42.82 % to 68.17%) and oxygen varies from 0.40 - 0.67 (as weight basis 5.45 % to 9.10 %).

EDS microanalysis of all spectrums in the paraffin wax and beeswax samples confirm the presence of carbon and oxygen as illustrated in Figures 4 to 8. The other peaks appearing in those figures might be due to the sample coating process, which indicates the presence of gold, palladium, or both.

2.1. Structural Analysis of Paraffin Wax and Beeswax

Sample handling, coating and preparation for SEM cause sample alteration, which modifies its composition and morphology structure. Therefore the quality of the micrographs obtained is affected as well. Figures 9 to 11 show the SEM micrographs for paraffin wax following three magnifications of 250, 1050, and 2000 respectively. Some micrographs are affected by charging that alters the brightness and contrast levels. For example, the bright spots in Figure 9 exhibit the charging effect due to the presence of electrons that did not penetrate the wax. Figures 12 to 14 illustrate the SEM micrographs for beeswax at three magnifications of 250, 1100, and 2000 respectively. In these figures, the bright spots are more dominant than in the case of paraffin wax, which implies that beeswax is more resistant to electron storming by SEM than paraffin wax. This indicates that beeswax has a lower electric conductivity than paraffin wax.

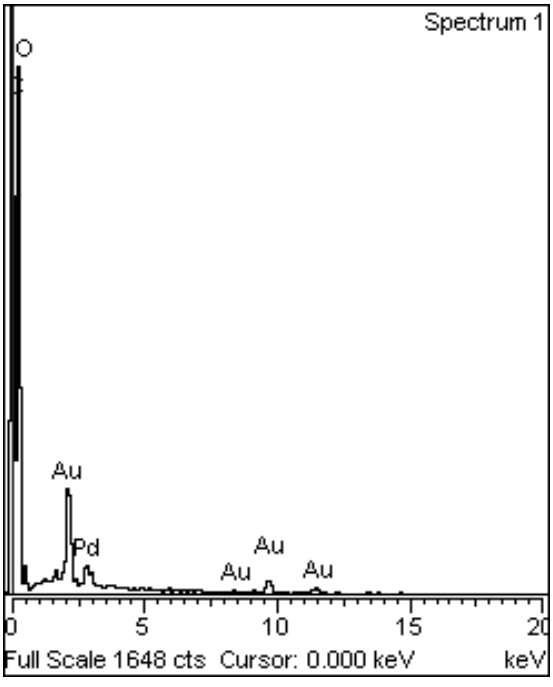

Figure 4. *Spectrum analysis for paraffin wax for Run 1.*

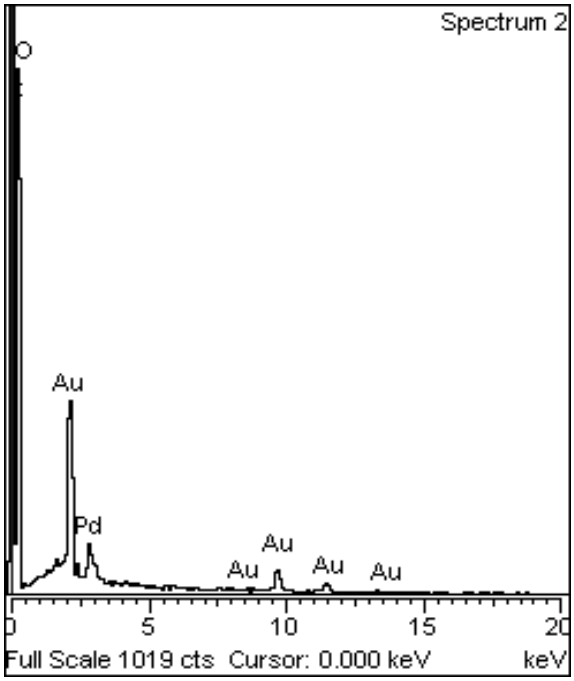

Figure 5. *Spectrum analysis for paraffin wax for Run 2*.

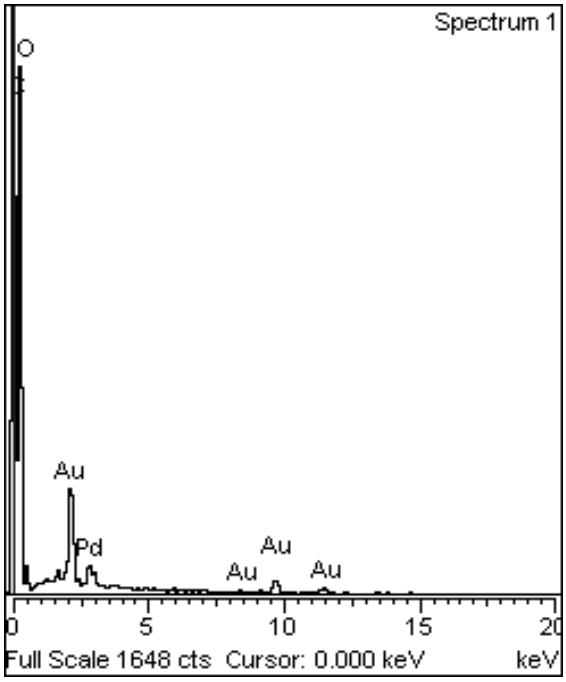

Figure 6. *Spectrum for beeswax for Run 1*.

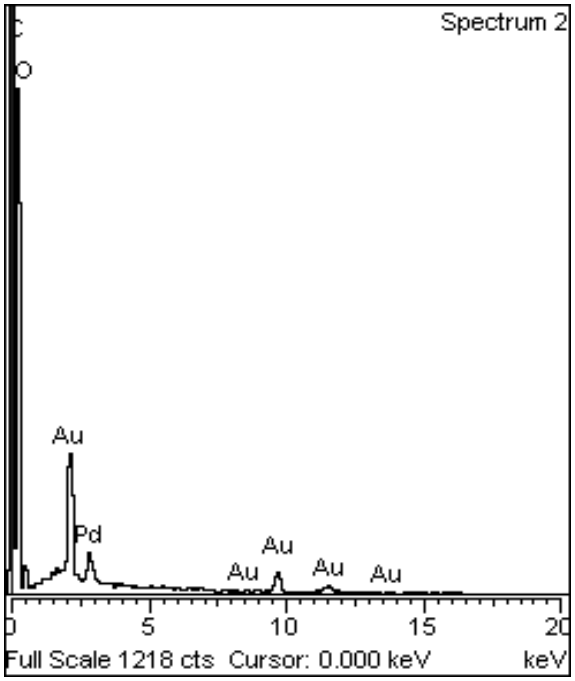

Figure 7. *Spectrum for beeswax for Run 2*.

Regarding the wax morphology, Figures 9 to 11 expose the lamellar structure of paraffin wax, this means that the corresponding sample consists of a blend of polymers. Paraffin-wax crystals are long and narrow and form in plates. In the fully refined grades they are dry, hard, and glossy. The paraffin wax is characterized by its homogeneous constitution and distribution due to its refining process. Then the separation between the polymers is complete in the paraffin wax samples as indicated in Figures 9 to 11. The beeswax is secreted by the honeybees in a liquid state at the ambient temperature. Then, it crystallizes at the same ambient temperature. It consists of various components and is characterized by long hydrocarbon chains. It is made largely of a blend of myricyl palmitate, cerotic acid and esters, and some high-carbon paraffins. This reveals the heterogeneous constitution and distribution of beeswax, due to its polymers diversity. According to Figure 12, the beeswax consists of superposed plates. At higher magnifications, the beeswax SEM micrographs (see Figures 13 and 14) display pasty, colloidal, and cloudy structure due to the amorphous and heterogeneous nature of polymers composing the beeswax.

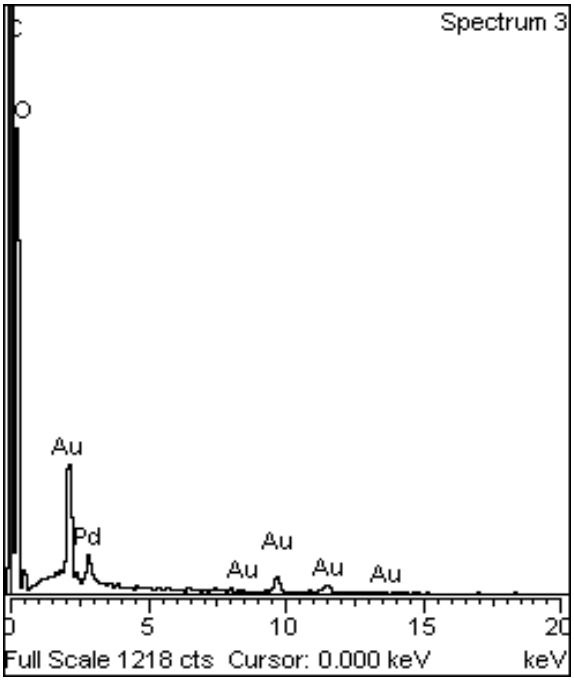

Figure 8. *Spectrum for beeswax for Run 3*.

Figures 12 to 14 prove that the multiple polymers in the beeswax did not separate. So these polymers are still solidly interconnected, which explains the beeswax toughness and resistance to electric conductivity. The beeswax is natural. It is younger and fresher than the paraffin wax since the former has a shorter pathway period than the latter [1, 2]. The beeswax did not undergo refining stages whereas the paraffin wax was extracted from crude petroleum after refining and purification. This is explained by Figures 9 to 14.

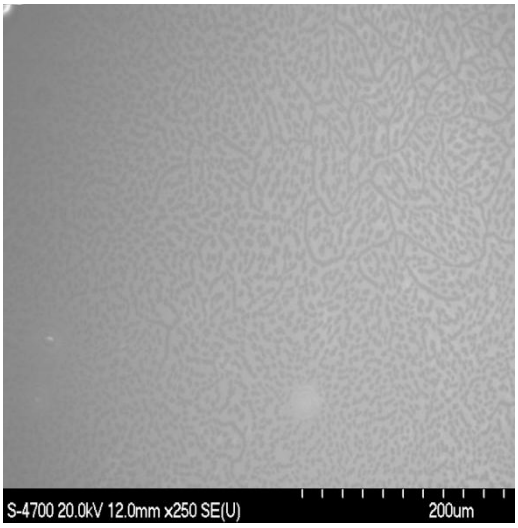

Figure 9. *Micrograph of paraffin wax sample, showing two distinctive shades, one darker with long chains and smaller oblongate shape, and lighter pattern which is background Condition: Vacc=20kV, Mag=x250, WD=12mm.*

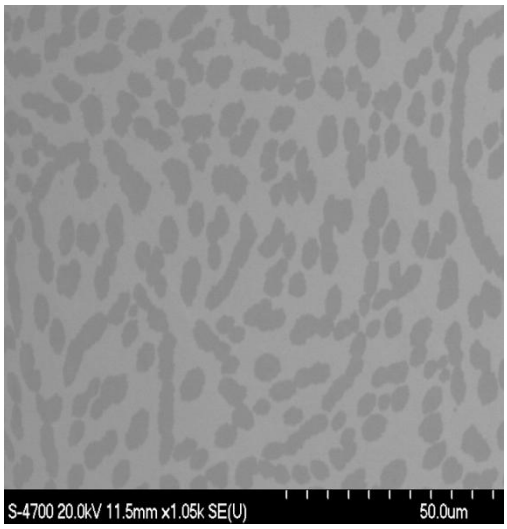

Figure 10. *Micrograph of paraffin wax sample in details illustrating the long and short chains, and as well as individual oblongated patterns that are more visible. The background is shown in lighter color. Condition: Vacc=20kV, Mag=x1.05k, WD=11.5mm.*

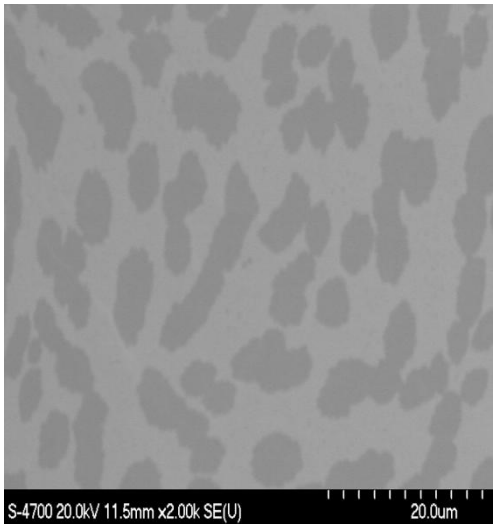

Figure 11. *Paraffin wax sample with 2000 magnification indicating that long chains consist of oblongated patterns joining together. Condition: Vacc=20kV, Mag=x2.00k, WD=11.5mm*

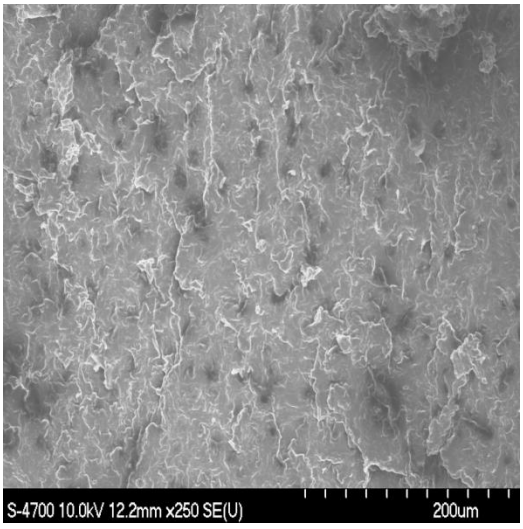

Figure 12. *Micrograph of beeswax sample showing topographic variations on the surface. Condition: Vacc=10kV, Mag=x250, WD=12.2mm.*

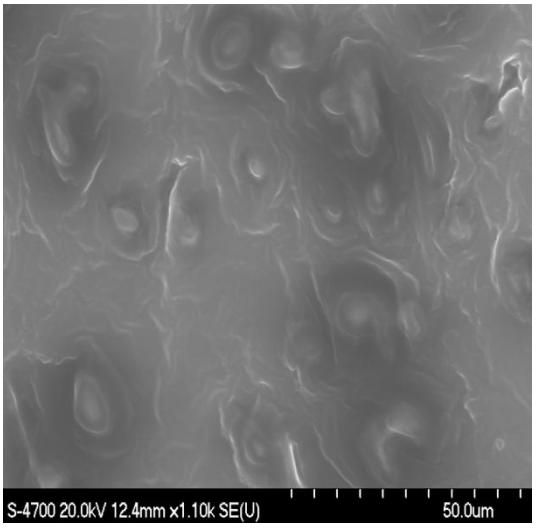

Figure 13. *Beeswax sample with 1100 magnification. Closer observation of the beeswax surface with more details showing irregular ridges and valleys. Condition: Vacc=20kV, Mag=x1.10k, WD=12.4mm.*

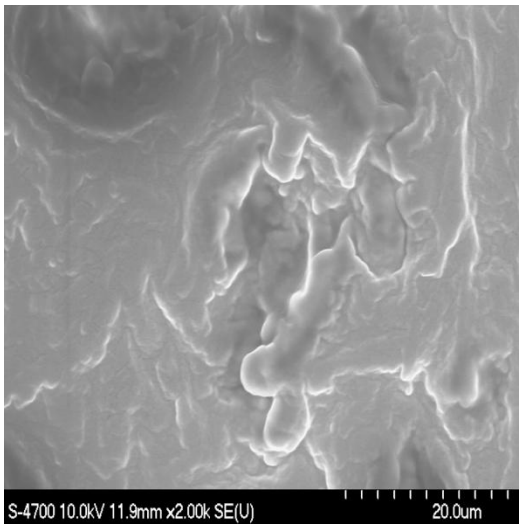

Figure 14. *Beeswax sample with 2000 magnification. Detail of the beeswax surface with well visible ridges and valleys, indicating that the sample is not very hard, based on visual observation. Condition: Vacc=10kV, Mag=x2.00k, WD=11.9mm.*

3. CONCLUSIONS

In order to examine the internal structure and composition of paraffin wax and beeswax, each sample was characterized by randomly selecting 3 fields of view and examining the samples. The SEM data clearly indicate that the main composition of paraffin wax and beeswax are carbon and oxygen. EDS microanalysis of all spectrums in the paraffin wax and beeswax

samples confirm the presence of carbon and oxygen. The other peaks appearing in those figures might be due to the sample coating process, which indicates the presence of gold, palladium, or both. However, this could also be due to minor amounts of 'other elements' that are removed from refined wax. As a result, the micrographs of paraffin wax samples exhibit a perfect distinction between the polymers formed within this wax type since it underwent refining and purification, which eliminated many wax inherent components and structures. The micrographs of beeswax samples display complex structure due to the beeswax natural state. Beeswax is younger and tougher than the paraffin wax. The former did not suffer refining or purification whereas the latter was submitted to those processes, which eroded its intrinsic components, bonds, and qualities. This inherent distinction could not be explained through composition of main components alone as the bulk compositions were the same for both types of waxes.

4. ACKNOWLEDGEMENTS

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