

Thermo- physical characterization of paraffin and beeswax on cotton fabric

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Abstract

Cotton fabric (CF) has been widely used as a batik clothing material due to its suitable physical characteristics. Cotton woven fabrics were treated with droplets of different types of waxes including paraffin and beeswax. The physical and thermal properties of the waxes were characterized. This article presents an experimental study of the deposition of small droplets of molten waxes on CF surfaces. The method is based on an evaluation of the chemical functional groups of the waxes that were characterized by using fourier transform infrared spectroscopy (FTIR). The thermal properties of the waxes were analyzed by using a differential scanning calorimeter (DSC). The viscosity of the molten waxes was measured with a viscometer. The spread of the molten waxes was determined in terms of the contact angles of the droplets on the CF surface. It was indicated that the contact angle of beeswax droplets on the CF surface is higher than that of paraffin. It should be noted that the contact angle correlates to the viscosity of the molten wax samples.

Keywords: Cotton fabric (CF);Paraffin; Beeswax; waxes.

1. Introduction

Batik is a type of cloth that is traditionally made by hand with a wax resistant and dyeing technique. In southern Thailand, batik is easily found in the form of resort uniforms and decorations in many places. It is also used for local casual wear in the forms of sarongs, shirts and blouses. Batik is usually made from cotton fabric.

Wax, such as paraffin, beeswax, and turpentine, is introduced to the cotton fabric surface, followed by heating in the range of 80-100 °C prior to the color painting process.

In the wax drop process, the molten wax droplets are introduced to the cotton fabric surface at a certain drop rate. After wax removal, the cotton fabrics are immersed in boiling water. In this paper, paraffin and beeswax droplets have been applied to cotton fabrics for batik utilization. The prepared molten wax drop can improve the contact angle and viscosity properties.

Chemically, waxes are mixtures of organic substances, which are usually long chain molecules. They are composed of hydrocarbons [1], tri- di-or mono-esters of

medium length fatty acids, long chain alcohols, free long chain alcohols, aldehydes, ketones, β -diketones, sterols, triterpenols and triterpenic acids [1-2]. Their chemical compositions depend on their animal, vegetal or mineral origin [1,3].

In this work, cotton fabrics were treated with droplets of paraffin and beeswax in an attempt to develop molten wax droplets that exhibit a low contact angle spread on cotton fabric and a low thickness. Good wettability of a surface is a prerequisite for ensuring good adhesive bonding. The characterization of the molten waxes was studied through a variety of techniques.

2. Materials and methods

2.1. Materials

Cotton fabric (CF) was purchased from Krisna Store Thai Silk Co., Ltd., Thailand. Paraffin and beeswax were purchased from Saiburi herbal Co., Ltd., Thailand. The FTIR transmittance spectra of the waxes were also analyzed in order to confirm chemical functional groups of the wax mixture.

2.2. Differential scanning calorimetric (DSC) analysis

The thermal characteristics of paraffin and beeswax were analyzed with a differential scanning calorimeter (DSC), specifically a PerkinElmer DSC7. The sample weight was about 5 mg. All analyses were performed in the scanning mode from 20 to 200 °C at the heating rate of 10°C/min. Dry nitrogen gas was introduced into the DSC cell as the purging gas.

2.3. Viscosity measurement

A Rheometer (RVDV-II, Brookfield, USA) was used to measure the viscosity in our experiment. The device is an advanced controlled stress, direct strain and controlled

rate rheometer with a magnetic-levitation thrust bearing and a drag cup motor to allow torque control. A wide range of cones and plates, often called geometry, is available for use with a Peltier setup or an oven.

Temperature control can be achieved using a heated plate setup, a fluid bath or an oven, allowing temperatures from 25°C to 150°C with the temperature resolution of 0.02°C. The device is controlled by a rheology advantage software. Before the measurements, the rheometer was carefully calibrated with pure base fluid.

2.4. Fabrication of wax-droplet cotton fabrics

Before the introduction of the wax droplets, the fabrics were immersed in 1 M. NaOH solution 24 h. and leached with water. Then, wax was melted in the oven at 100°C. Cotton fabric (3×8 cm.) was stretched on a glass slide. The melted wax was immediately dropped onto the CF and left it dry at room temperature. The formation of the wax droplet in terms of contact angles was investigated at room temperature using a contact angle meter (OCA15EC). The gap distance between eject head and cotton fabric surface was 1 mm., and the wax volume was at 14 μ L. The wax droplet thickness was measured using a micrometer specifically the Mitoyo series 103.

3. Results and discussion

3.1. FTIR analysis

The band frequencies of the spectra obtained with their assignment [4-6] are given in Table 1. The FTIR spectra of the waxes covering paraffin and beeswax consisted of five main groups of absorption bands in the wavelength range of 400–3900 cm^{-1} (Fig. 1). The bands in the region of 719-730 were

assigned to the deformation vibrations of a long-chain hydrocarbon.

Table 1. FTIR analysis of paraffin and beeswax with major peak frequency (cm^{-1}) and assignment.

Range/cm ⁻¹		Assignment	Vibrating group	Intensity
Samples				
Paraffin	Beeswax			
720	719	ρ(CH ₂)	(CH ₂) _n , n>3	w-m
	1162	ν(ring)	Heterocyclics and their aromatically	w-m
	1260	ν(ring)	Ethers, aliphatic (Epoxides)	m-s
	1268	ν _{as} (O-CO-O)	Carbonates aliphatic	vs
	1367	ν(ring)	Heterocyclics and their aromatically	m-s
1371		δ _s (CH ₃)	Aliphatic hydrocarbons	m-s
1463	1463	δ(CH ₂)	Aliphatic hydrocarbons	m
	1691	ν(C=O)	Aromatic-COOH	vs
	1733	ν(C=O)	Esters of aromatic carboxylic acids with alcohols	vs
2846	2846	ν _s (CH ₂) ₃	Aliphatic hydrocarbons	m
2910	2910	ν _{as} (CH ₂)	Aliphatic hydrocarbons	m-s

Note: s:strong, m:medium, w:weak, v:very, ν :stretching vibration, γ : out of plane deformation vibration, ρ : rocking vibration, δ : in plane deformation vibration, $s^{(\text{as subscript})}$: symmetric, $as^{(\text{as subscript})}$: antisymmetric.

The bands in the region of $1366\text{--}1382\text{ cm}^{-1}$ $\delta_{\text{s}}(\text{CH}_3)$ and $1458\text{--}1475\text{ cm}^{-1}$ $\delta(\text{CH}_2)$ can be assigned to the wax aliphatic hydrocarbons. Bands appearing in the region of $1689\text{--}1691\text{ cm}^{-1}$ $\nu(\text{C}=\text{O})$ and $2848\text{--}3000\text{ cm}^{-1}$ $\nu(\text{CH}_2)$ were assigned to the wax aromatic and aliphatic hydrocarbons respectively. The predominant components of the wax samples were aliphatic hydrocarbons. Long-chain esters and acids have also been found.

This phenomenon maybe caused by the fact that beeswax has wetting hydrophobic more effective than paraffin due to a higher wax aromatic hydrocarbon structure. Beeswax was adsorbed by the cotton fabric with the hydrophobic spreading. This behavior also confirms that the beeswax has a higher wax aromatic hydrocarbon structure than paraffin does.

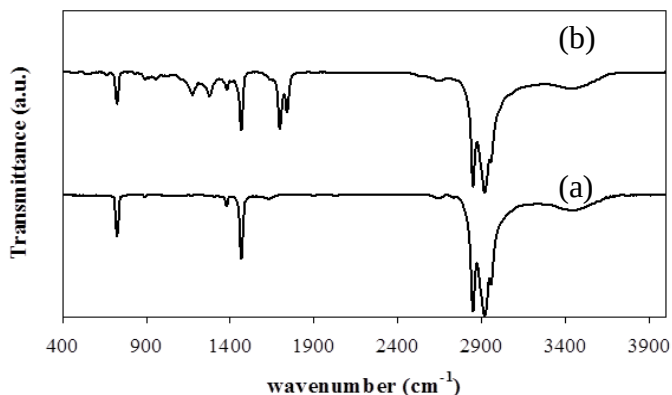


Fig.1. FTIR spectra of: (a) paraffin and (b) beeswax.

3.2. DSC curves of waxes samples

There were 1 to 2 heat absorbing peaks or heat releasing peaks clearly seen in the melting or crystallizing curves of DSC diagrams according to different samples. DSC analysis is designed such that different peaks occur with different chemical compositions, so it was inferred from the curves that waxes were not single chemicals. For its high sensitivity, a slight change of heat could be measured by DSC. Thus, the small amounts of the chemical constituents of the waxes were also shown in the diagram, and the DSC was able to identify the wax purity.

For instance, the waxes shown in Fig. 2 consisted of have at least two composed chemicals, were one in a small amount with a low melting peak at 40 to 60 °C, and another in a larger amount with an orderly significant peak at 60 to 70°C. It was known with wax composition that the change in the slope in the chart between 40 and 60°C was due to the heat absorbed from the free acids and the hydrocarbons [7]. From the DSC curves shown in Fig.2, the values of the melting point, the softening point, the melting peak, melting and crystallization enthalpies were obtained as shown in Table 2.

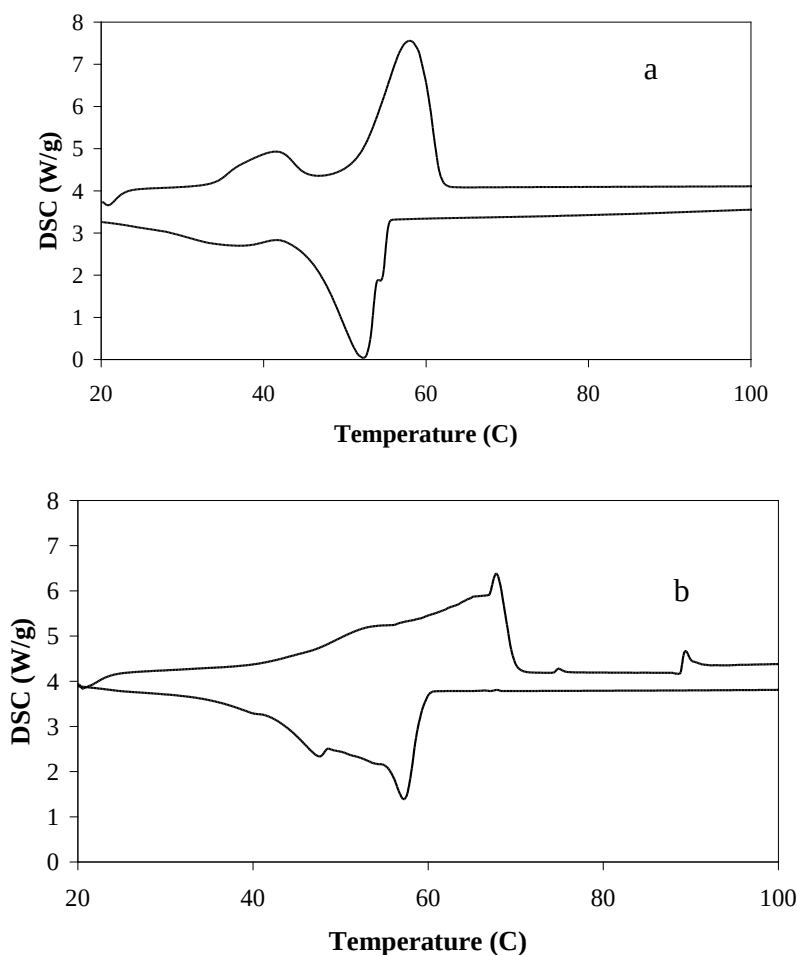


Fig.2. DSC curves of (a) paraffin and (b) beeswax.

According to the DSC curves in Fig. 2 and the data in Table 2, from the starting to the ending temperatures, the summit temperature of the melting or crystallization peak of the waxes varied due to their different compositions. The melting point of the beeswax was higher than that of the paraffin. In Table 2, the melting points of the paraffin were lower than those of the beeswax because the structure of paraffin was simple with some chain alkanes and because

its molecular weight was smaller than that of beeswax, which is composed of mix esters in high molecular weights and complicated structures. From Table 2, it was inferred that there were great variances among melting enthalpy of the waxes. The enthalpy of the beeswax was higher than that of the paraffin. It was known from the above that there were some relations between the enthalpies and the melting points of the waxes.

Table 2. The starting, ending and summit temperatures of the melting peak of the waxes.

sample	sample weight (mg)	T ₀₁ (C°)	T _{m1} (C°)	T _{f1} (C°)	T ₀₂ (C°)	T _{m2} (C°)	T _{f2} (C°)	Melting enthalpy (J/g)	Crystallization enthalpy (J/g)
Paraffin	5.37	51.49	58.00	61.80	54.76	52.30	45.30	132.58	114.63
Beeswax	5.78	42.26	67.83	69.89	59.42	57.30	47.63	176.00	162.42

Note: 1) T₀₁: softening point 2) T_{m1}: melting peak temperature 3) T_{f1}: melting point (ending temperature of melting) 4) T₀₂: starting temperature of crystallizing 5) T_{m2}: peak temperature of crystallizing 6) T_{f2}: ending temperature of crystallizing.

3.2. Viscosity tests

The experiments to analyze the changes of the viscosity curve were performed on the fluid samples with different waxes (Paraffin and Beeswax). The viscosity measurements indicated that the melted waxes change the fluid's viscosity significantly at different

temperatures as shown in Fig. 3. It was found that the viscosity of the molten beeswax is higher than that of paraffin. Since the melted waxes were expected to change the precipitated wax crystal's size distribution [8-9], it is understandable that this also affects the fluid viscosity [10].

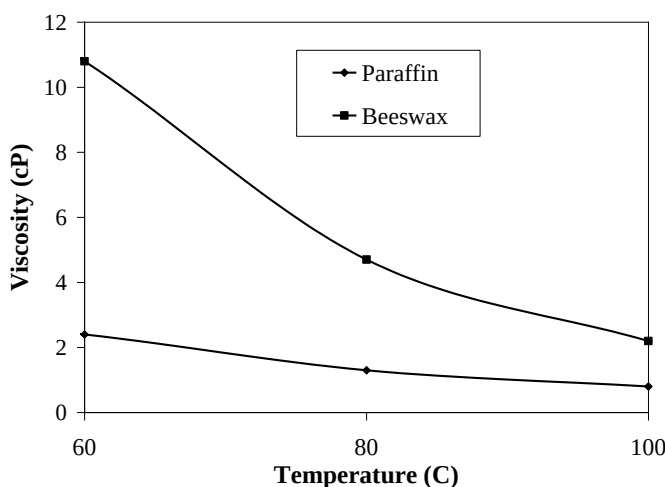


Fig.3. Viscosity for different waxes

3.3. Wax droplet contact angle

When a droplet of molten sample impacts the cotton fabric surface, which is at a lower temperature than the molten sample, it spreads out and may retract, producing a sample bump (or sample dot) sticking to the cotton fabric surface.

The process of impact can be divided into two stages: the spreading, driven by inertial forces, and the subsequent oscillation, driven by surface tension forces [11]. Both stages involve viscous dissipation and solidification. For a liquid droplet impacting a solid surface without a phase change, the final shape of the droplet is determined by its equilibrium state depending on the properties of the liquid, the substrate materials and the temperature [12-13]. The deposition, including the solidification, of small molten droplets on cotton fabric surfaces is a complex fluid/thermal problem. The final shape of the droplets is not determined by the fluid flow alone, but depends on the thermal histories of the droplets during the impact since they may freeze before reaching their equilibrium shape.

The coupling between solidification and fluid dynamics can lead to a variety of solidified shapes and textures of deposited droplets. There are no simple models to predict what these will be. The final shape can be characterized the contact angles of the bases of the droplet and their thickness. Contact angle measurements of molten the samples carried out in ambient air environments are shown in Fig. 4.

It was found that paraffin has a significant effect on lowering the contact angle of sample droplets due to their enhancement of the molten samples, in turn lowering the viscosity of the compared to beeswax samples. The contact angle of the sample droplets on the cotton fabric surface not only depends on the type of sample but also on the temperature and the viscosity. It should be noted that

contact angle correlates with the viscosity of the molten samples. The smaller contact angle corresponded to the low viscosity. The paraffin samples displayed smaller contact angles than the beeswax sample did. The paraffin sample droplets with a contact angle of 39° were observed at 100°C (Figs. 4 and 5). The contact angle images of the molten sample droplets on sample that have been treated at different temperatures and their contact angles, are shown in Figs 5 and 4, respectively. It was observed that the contact angles of paraffin were smaller than those of the beeswax samples due to the fluid viscosity effect of the sample mixture. It was found that beeswax has the structure of aromatic hydrocarbon which is not found in paraffin wax, so the paraffin wax has a better spread than beeswax does.

The final thicknesses of droplets ejected at different temperatures and landing on the cotton fabric surface were measured. The average thickness values on the cotton fabric surface region of these molten samples are shown in Table 3. The effect of the contact angles can be seen through a comparison of the thicknesses in Table 3. Smaller spread diameters and larger contact angles are formed on the cotton surface. Earlier studies showed that the dynamic contact angle increases with the equilibrium contact angle [14] and that the maximum spread of a droplet decreases as the dynamic contact angle increases [15-17]. Very low thickness molten droplets are formed from high molten temperatures (100°C) and a increased thickness molten droplet at low molten temperatures ($70, 80$ and 90°C) as shown in Table 3. The use of paraffin rendered the thicknesses to be much lower, with thickness values reduced to only approx. 0.99 mm .

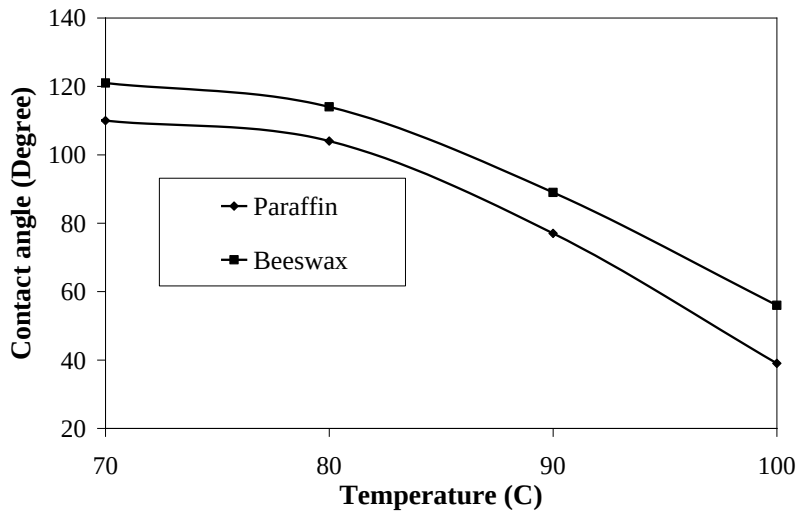


Fig.4. Molten sample contact angles vs. temperature of paraffin and beeswax sample.

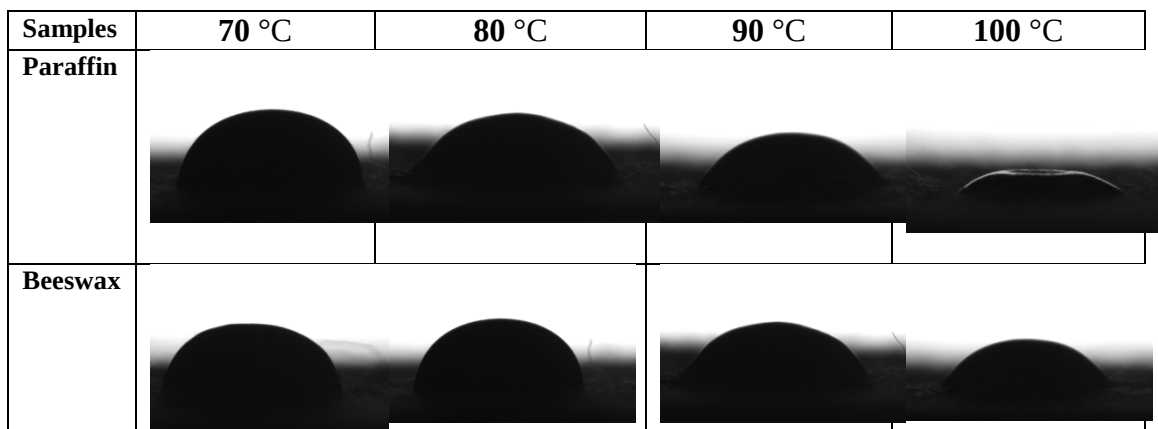


Fig.5. Images of molten waxes droplets on cotton fabric surface compared with those of different temperature during 70–100 °C.

Table 3. Thickness values of wax droplets on cotton fabric surface at different temperature conditions.

Samples	Thickness (mm)			
	70 °C	80 °C	90 °C	100 °C
Paraffin	2.41	1.99	1.53	0.99
Beeswax	2.50	2.25	1.61	1.12

4. Conclusions

Paraffin exhibited lower contact angles than beeswax did. It should be noted that contact angles correlate with the viscosity of the molten samples. It was found that molten samples could decrease the contact angle (hydrophilicity) on the cotton fabric surface. Molten paraffin was excellent and spread on the cotton fabric surface. The utilization of beeswax only increased the droplet contact angles and the thicknesses of the droplets.

In summary, DSC was available for thermal characteristic determination of paraffin and beeswax qualitatively and quantitatively, with better accuracy than traditional mercury surface measurement. FTIR is a convenient way to preliminarily evaluate the wax chemical composition.

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