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Blending Petroleum Waxes with Suitable Polymeric Additives as a Simple and Promising Way to Improve the Quality of Petroleum Waxes for Numerous Industrial Applications

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Abstract

Basic waxes resulting from all oil refineries such as Paraffin wax and Microcrystalline wax are to be blended using additives to tailor the wax compound's specifications. Such compounded waxes are suitable to be used in packing, food, labeling, adhesives, and other industrial applications depending on the ratios of paraffin wax (PW) to microcrystalline wax (MCW), in addition to some specific additives affecting the physical, mechanical and thermal properties of the melt. Ethylene Vinyl Acetate (EVA) copolymer is used as a viscosity modifier and tackifing agent, poly hydrogenated dicyclo-pentadiene (HD), and poly alpha-methyl styrene (MS) are wax performing agents based on the desired molecular weight and crystallinity of the wax blends. Different ratios of the polymeric additives were blended with both the basic paraffin and microcrystalline wax. The resulting compounded wax samples were evaluated for their melting behavior: congealing point (CP) and softening point (SP). The drop melting point (DMP) and dynamic viscosities, as well as the hardness, represented as low penetration value) are also investigated. The mechanical properties of the resulting compounded waxes (tensile elongation at break) and the adhesion characteristics are related to the additives composition and percent. All the obtained results showed a complete investigation of all physical, mechanical, and thermal characteristics of the resulted wax blends as a function of their ingredients that were combined with high compatibility within the wax blends. Both the resins, i.e. poly hydrogenated dicyclopentadiene (HD) and poly alpha-methyl styrene (MS) are wax performing agents based on the desired molecular weight and crystallinity of the wax created promising physical, mechanical, and technological properties in all the compounded wax samples.

Keywords: Compounded Wax (CW), Paraffin Wax (PW), Microcrystalline Waxes (MCW), Paraffin (PN), Dynamic Viscosity (DV), Tensile Strength at Break (TS)

Introduction

Petroleum wax is extracted from raw petroleum oil in the local oil refineries, exported for the wax blending process. Then it is imported back after their blending with different additives to gain new tailored properties to suit specific industrial applications such as electric cables, coating materials, and hot melt adhesives, etc. Poly ethylene-wax is extensively added to polyvinyl chloride (PVC) formulations and lubricants as dry mixed. The petroleum waxes are linear or branched hydrocarbon chains up to about forty carbon atoms, $C_{40}H_{82}$ mixed with specific organic and inorganic materials, ductile, and easy to polish lyophilic solids at room temperature. Petroleum waxes are classified depending on sources, crystallinity, and the degree of refining [1-2] and are applied as efficient insulation materials in feul cells [3] The PW includes crude or slack waxes (oil content up to 25%), raffinates, and di-oiled slack waxes. Soft waxes are crude waxes (deoiled slack waxes, filtered (decolorized), and fully refined). The samples of MCW have small particle sizes, and are thin and more flexible than the paraffin wax. Very long hydrocarbon chains cause the plasticity of MCW. The hard MCW consists of the normal hydrocarbon (HC) chain, the hydrocarbon chains of n-paraffin, iso-paraffin, and a small percentage of cycloparaffin [4-6]. The PW and MCW produced using atmospheric distillation, vacuum distillation, and solvent refining have distinct properties [7]. Both PW and MCW types are considered limited application capabilities, and they need to be blended with additives

affecting their uses. The wax additives are mainly polymeric resins and compatibilizers that can affect the wax compounding properties and applications. Many research articles were reported about the problem of wax deposition problems in the oil and gas industries. These problems were solved and mitigated by polymeric chemical additives to improve the crude oil flow along the pipeline via depression of pour point. The improvement of crude oil flow can be achieved to the same extent as obtained from mechanical, chemical, and thermal treatments [8-10]. However, the literature survey about the formulation of new cost-effective compounded waxes combined petroleum waxes and polymeric additives for industrial applications is inadequate. Up to date literature survey about the process of petroleum, waxes showed the following points of interest: lubricating oils from dewaxing of corresponding petroleum fractions and solvent free slack wax deoiling by melt crystallization [1]. A hot melt waxes-polystyrene, isobutylene, and beta-pinene have softening points up to 160°C [2]. Wax content is determined in some selected characterizing petroleum waxes with known solid-solid phase transitions, and the effect of wax content and crosslinkers on the thermal and mechanical properties of was are also explained [3]. Multicomponent paraffin wax with different chain lengths possesses good crystallinity and mechanical strength [4]. The effect of low-density polyethylene on the thermal stability and crystallinity of micro-crystalline waxes has been considered [5]. Moreover, wax candles made from paraffin wax contain mineral oils [6]. Hot melt adhesives, coating waxes containing EVAcopolymers and petroleum waxes, were investigated [4-7]; wax additives such as high molecular weight base polymers, low molecular weight ester copolymer comprising an olefin and ester copolymers resin for hot melt adhesive enhance fast curing low melting viscosity wax [8-11]. Isolate asphaltene fractions by adding pentane, hexane, or heptane, give asphaltene fractions contaminated with microcrystalline waxes ($>C_{40}$) which have ambiguous modeling and treatment programs were reported [12].

Hot melt adhesives contain low-cost inert inorganic fillers and modifying hydrocarbon resin is used for coating and laminating paper against moisture. Wax blended with EVA is used for coating and protecting cheese against environmental conditions; wax coats for papers paraffin wax coating: EVA, microcrystalline wax and a terpene resin. Moreover, wax blends styrene/ethylene-butylene/styrene copolymer is used for coating fibrous materials; candles (wax blended with synthetic thermoplastic rubber copolymer).

All these reported wax formulations lacked the combination of PW, MCW, HD resin, MS resin, and EVA copolymer to formulate new compounded wax with suitable characteristics for various industrial applications, as suggested in our study. Hence the novel experimental work in our study aims at preparing novel wax blends from the synergistic properties of PW and MCW.

The physical, mechanical, and adhesion properties of the wax blends will be measured and correlated to the wt.% of the ingredients of the additives compounds. Scanning the investigated testing results based on the PW and MCW waxes and additive percentages allow tailoring the wax blends needed for specific industrial applications. The novelty of the work in this study is that the formulation of compounded wax (CW) blends from low-cost petroleum products are of high economic importance due to the possible different industrial applications. This study will also increase the value and price of compounded wax-based via the transfer of simple basic petroleum wax such as slack and paraffin wax to sophisticated high economic compounded wax (CW) for many industrial applications due to new gained unique properties from some specified additives.

Materials and Methods
Materials

The main components paraffin (CW) wax was obtained from a local western desert mixture; microcrystalline wax was obtained from the local Marine Baleyim Egyptian crude oil. The HD and MS resins, as traditional additives, were imported as available chemicals of general industrial use. The main components PW and MCW waxes are based on Egyptian crude oil. PW was supplied from Amria Petroleum Co., MCW: Alexandria Petroleum Co., EVA from ARKEMA Chemical Co., whereas HD and MS from EASTMAN Chemicals Co. The general characteristics of heavy paraffin wax are specified according to the American system of testing methods (ASTM) [11, 12]. PW, MCW, and EVA are major blend components, while wt.% of MS and HD additives are low.

The petroleum wax is a branched chain of hydrocarbon (up to about $C_{40}H_{82}$) mixed with organic and inorganic material. These waxes are mixtures of lipophilic compounds that are solid at room temperature, ranging from transparent to opaque, and they are ductile and easily polished.

The wax content in petroleum materials was characterized using the certified Fourier transformer infra-red (FTIR) spectroscopy to determine the functional groups of all compatible certified chemical constituents of the formulated samples of compounded wax according to the method reported [13].

The physicochemical properties of both the two basic waxes (PW and MCW) in wt.% (100%) of both Paraffin Wax (PW) and Microcrystalline Wax (MCW) are measured according to ASTM standards as shown in Table 1. The paraffin waxes contain n-paraffins and branched isoparaffins, and higher molar mass weakly branched isoparaffins, naphthenes, and alkyl aromatics. Microcrystalline wax contains a higher percentage of branched isoparaffinic hydrocarbons, naphthenic hydrocarbons, and high molecular weight saturated aliphatic hydrocarbons. It is generally darker, more viscous, denser, tackier, and more elastic than paraffin waxes, and it has a higher molecular weight and melting point. The elastic and adhesive characteristics of microcrystalline waxes are related to their non-straight chain components. The typical microcrystalline wax crystal structure is small and thin, making them more flexible than paraffin wax. Oil content ranges from 15 % to 30%. Plastic micro waxes the higher molar mass n- and isoparaffins, and weakly branched isoparaffins and naphthenes are enriched in comparison with petrolatum from which they are easily obtained by deoiling of n-paraffin, iso-paraffin, and cycloparaffin.

Table 1 Comparison between general characteristics of both paraffin wax (PW) and microcrystalline wax (MCW)

Test		ASTMPW[a]	Property in	
			MCW[b]	
Density at 15 °C	g/mL	ASTM D - 4052	0.8169	0.8427
Congealing point	°C	ASTM D-938	61.1	76.1
Softening point	°C	ASTM D-36	62.6	80.0
Drop melting point	°C	ASTM D-127	63.6	81.6
Kinematics viscosity at 100 °C	Cst	ASTM D - 445	3.98	11.63
Color		ASTM D-1500	L 0.5	L 3.0
Flashpoint	°C	ASTM D-92	258	250
Oil content	% wt.	ASTM D-721	1.9	1.6
Needle penetration at 25 °C	mm/10	ASTM D-1321	17	14
Refractive Index at 70 °C		ASTM D-1747	1.4350	1.4430
Molar absorptivity 280-289 290-299 300-360		ASTM D-2008	0.045 0.035 0.024	0.57 0.44 0.32
Molecular weight, Mw. (k Da.)		UOP 375	402	598
Tensile strength at the break at 25°C	psi	ASTM -638	104	188
Structure group analysis % C_{Ar} % C_{N} % C_{P}		ASTM D- 3238	0.04 1.99 97.97	3.08 10.63 86. 29

(a: PW:5 wt.% oil, 20%wt. isoparaffins, and the remainded 80%n-parrafines), and b: MCW: 20 wt.% oil, 10% n-paraffins, 20% isoparaffins, 30% and the remainder wt.% cycloparaffin).

The polymeric additives to the basic paraffin wax (PW) wax and microcrystalline wax (MCW) to formulate new compounded waxes (CW) where the base polymer becomes the backbone of the new formulated systems [14], varying in characteristics depending on the ingredients weight percentages (wt.%) that affected the blended characteristics required for specific applications. The EVA copolymer is used as an additive to the base, [15], as it has special characteristics such as versatile adhesives and cohesive strength; compatibility to many tackifiers, and broad formulating latitude that is necessary for many applications, quick setting, and retention of properties at low temperatures [13-18].The other additives (HD and MS) were also chosen according to their excellent thermal stability and weathering-resistance ability, high transparency and distinguished initial adhesion, best initial adhesion and cohesive intensity and intensity of stripping, low volatility, high viscosity, and good compatibility with polymers. The properties of the EVA copolymer as a polymeric additive to the compounded wax and the selected additives were also investigated and measured according to the standard methods as shown in Tables 2-4 [16].

Methods
Preparation of Paraffin Wax (PW) and Microcrystalline Wax (MCW)
The appropriate wt.% of PW was added to a clean glass beaker and heated gently to melt, and microcrystalline waxes (MCW) wt.% were mixed with the melted PW and continuously heated up to 90 °C using a slow, continuous electric mixer until a homogenous PW-MCW melt was obtained.

Table 2 Characteristics of EVATANE 24-03 (EVA copolymer)

Test		Method	Value
Melt index(190°C/2.16 kg), g/10 min.		ASTM D 1238	2.5-3.5
Vinyl acetate	Wt. %	FTIR(INTERAL METHOD)	23-25
Density	g/cm³	ISO 1183	0.94
Vicat softening point	°C	ASTM D1525	46
Melting point	°C	ASTM D 3418	80
Elongation at break	%	ASTM D638	600-900
Tensile strength at break	MPa.	ASTM D638	27
Hardness shore A		ASTM D2240	83

Table 3 Characteristics of Kristalex F100 alpha-methyl styrene (MS) resin [17]

Test		Method	value
Ring and ball softening point	°C	ASTM E-28	99
Color, Gardner Initial 24 hours at 177°C		50% resin solids in toluene	<1 4
Density at 25°C	kg/dm³	ISO 1183	1.06
Bromine number	g/100 g		7
Average molecular weight (k Da.)		Gel Permeation Chromatography (GPC) using polystyrene standards	
$\overline{M_w}$			1400
$\overline{M_n}$			800
$\dfrac{\overline{M_w}}{\overline{M_n}}$ (polydispersity index)			1.8
Mz			2200
Melt viscosity (MPa) or (centipoise, cP) at: 120 °C 60 °C The melt viscosity was decreased from 760 cP to 37000 cP on rising the temperature from 60 °C to 120 °C.			 37000 760

Table 4 Characteristics of Escorez 5400 (HD) resin [18]

Test	Test method	value
Ring and ball softening point,°C	ASTM E-28	104
Color, Gardner Initial 5 hrs. at 175°C	50% resin solids in toluene	0.5 2
Glass transition temp.Tg,°C		54
Flashpoint COC, °C		>180
Molecular weight, M_w (kDa)	Gel Permeation Chromatography (GPC) using polystyrene standards	630
Melt viscosity at 160°C, (cP) MPa		800

The specified wt.% of EVA was then added, and the temperature was raised gradually to 140 °C during mixing until reaching a fully molten composition. The HD and MS resins (wt.%) were added during continuous mixing until complete melting was obtained. The blending process conditions are agitation speed of the magnetic stirrer (200-300 rpm), melting temperature (90-140°C), and melting time (60-90 min). Table 5 collected the ingredients of basic formulas

of compounded waxes (CW) and the new formulas prepared according to formulas with varying the wt.% PW and wt.% of MCW at constant polymeric additives (HD resin, MS resin, EVA Copolymer) wt.%. The FTIR vibrational spectra of the first microcrystalline (MCW) sample of each group of the MCW samples were collected in Figure 1.

Table 5 Ingredients composition of the formulated compounded waxes: Basic components (PW) and MCW; viscosity modifier EVA copolymer; and the additives HD and MS resins.

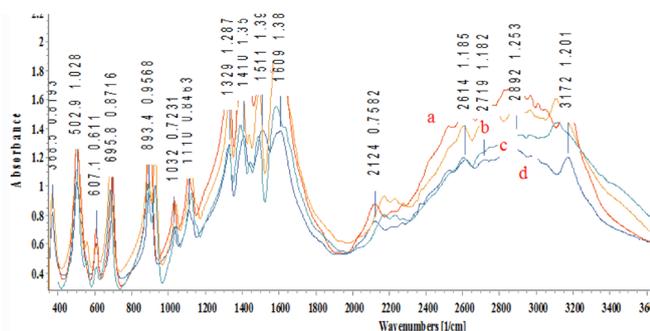| Formula code	NO.of group	PW	MCW	HD resin	MS resin	EVA copolymer
1		40	32			
2		45	27			
3*	Ia	50	22	7.5	2.5	18
4		55	17			
5		60	12			
6		50	24			
7		55	14			
*8	Ib	60	14	1.25	3.75	21
9		65	9			
10		70	4			
11		57	10			
12	Ic	52	15	10	0	23
13*		47	20			
14		4	70			
15		14	60			
16*		24	50			
17		34	40			
18	Id	44	30	0	0	26
19		54	20			
20		64	10			
21		74	0			

*Ingredients of basic formulas

Fig. 1 FTIR spectra of the first sample of each group of the formulated MCW (sample group: 1a, 1b, 1c, and 1d)

From Figure 1, it is clear that vibrational IR spectra of some selected MCW samples show the absence of the absorption band above 3200 cm⁻¹, indicating no polar functional groups (NH_2 or OH^-) are found in the chemical compositions of the formulated compounded wax samples. The extensive absorption bands from the wavenumber, $\bar{v}$ range: (3000-2400 cm⁻¹), and $\bar{v}$ from (1800-400 cm⁻¹) reflect the compatibility

between all wt.% of MCW ingredients. Where the vibrational bands of PW appeared at the vibrational frequency (2840, 2920 and 2960 cm⁻¹); MCW at (3000, 1500, 600 cm⁻¹); HD (30000, 2000-1000 cm⁻¹), EVA copolymer (3000, 1800-500 cm⁻¹), and ploy methyl styrene (30000, 1900-700 cm⁻¹) . The different vibrational modes of IR spectra of MCW ingredients overlapped, giving rise to the sharp, intense IR bands extended from the wavenumber (3000-500 cm⁻¹) [19]. The twenty-one formulated samples of compounded wax (CW) were classified (Ia-Id) according to variation in the wt.% PW and MCW at fixed EVA, HD, and MS wt.%. The analytical tests for the prepared compounded wax samples were done according to ASTM standard methods. In Table 6, the waxy quality is characterized and evaluated. Physical, mechanical, and adhesion properties were measured according to ASTM [14, 16, 17]. All tests were carried out at the Alexandria petroleum Co. (APC), Alexandria specialty petroleum products Co. (ASPPC), Alexandria Faculty of Engineering, and Institute of Graduate Studies and Research (IGSR) - Alexandria University.

Table 6 Testing procedures for the prepared compounded wax samples.

TEST	ASTM	American Society for Testing and Materials (ASTM International)
Dynamic Viscosity (DV)	*ASTM D- 3236*	05.01
Congealing Point (CP)	ASTM D-938	02.01
Softening Point (SP)	ASTM D-36	04.04
Drop Melting Point (DMP)	ASTM D-127	05.01
Penetration	ASTM D-5	04.03
Tensile Strength	ASTM D-638	08.01
Elongation	ASTM D-638	08.01
Cross-Hatch	ASTM D-3359	06.01

Results and Discussion

The physicochemical, mechanical, and adhesion properties of the compounded wax samples were shown in Table 7 to clarify the effect of PW replacement by MCW on the physicochemical properties of compounded wax samples. Figure 2 showed the effect of wt.% PW on CP of CW by changing PW% and MCW% at constant wt.% of other ingredients: HD, MS, and EVA.

In Figure 2, curve I shows that CP has decreased from 75.0 to 61.4 °C when PW-wt. % increases from 4 to 74%, MCW wt.% decreases from 70 to 0 % at constant other ingredients; Curve II shows that CP decreased from 64.0 °C to 61.0°C on increasing the wt.% of PW from 50 to 70 % and decreasing wt.% MCW from 24 to 4 % at constant other ingredients:1.25% HD resin, 3.75% MS resin and 21% EVA copolymer; Curve III shows that CP decreased from 65.6 to 60.6 °C when wt.% PW increased from 40 to 60 % and wt.% MCW decreases from 32 to 12% at constant other ingredients: 7.5% HD resin, 2.5% MS resin and 18% EVA copolymer; Curve IV shows that CP decreased from 62.8 °C to 61.0 °C when wt.% PW increased from 47 to 57%, and wt.% MCW decreases from 20 to 10% at constant other ingredients:10 % HD resin, 0 % MS resin and 23% EVA.

Table 7 The effect of PW replacement by MCW on the compounded waxes properties.

| Formula code	Congealing Point,ºC	Softening Point, ºC	Drop Melting Point, ºC	Penetration at 25 °C, dmm	Dynamic Viscosity at 140 °C, cP	Tensile Strength at the break at 25 °C psi	Elongation at the break at 25 °C %	Cross cutter tester
1	60.6	72.4	74.4	11	450	789	8.42	5B
2	61.6	75.2	76.0	10	482	809	8.67	5B
3	63.4	76	76.6	10	521	813	8.77	5B
4	65	77	77.2	9	526	839	9.09	5B
5	65.6	77.8	78.0	8	560	846	9.25	5B
6	61.0	72.4	75.0	9	723	846	9.56	5B
7	61.6	73.6	75.4	8	738	884	9.91	5B
8	62.0	75.6	76.0	7	753	930	10.12	5B
9	62.4	75.8	77.2	6	768	965	10.52	5B
10	64.0	76.6	78.2	6	774	974	11.91	5B
11	62.8	76	76.2	7	1515	998	12.46	5B
12	61.2	75.0	76.0	7	1350	929	12.15	5B
13	61.0	73.8	74.0	8	1296	901	11.96	5B
14	61.4	72.4	73.4	10	1563	1042	12.90	4B
15	62.2	74.8	75.4	10	1600	1064	13.04	4B
16	63.2	76	76.8	9	1752	1085	13.12	4B
17	65.4	77.4	78.5	9	2000	1105	13.51	4B
18	67.6	78.4	79.5	8	2190	1120	13.92	4B
19	70	80.1	80.2	7	2494	1138	14.82	4B
20	71.8	81.2	82.0	6	2564	1155	15.42	4B
21	75.0	82.2	82.8	5	2769	1160	15.76	4B
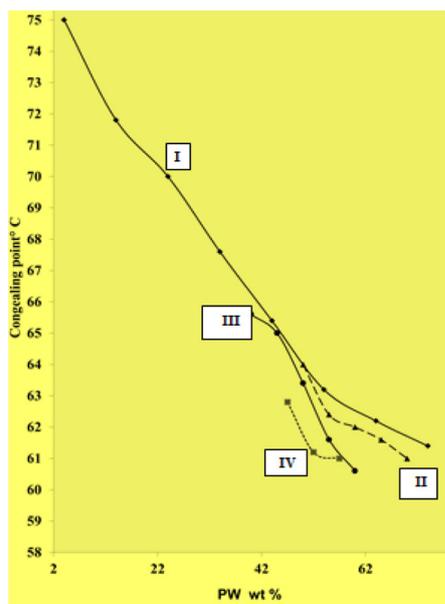
Fig. 2 Effect of varying wt. % of PW and MCW on CP of CW.
(I) PW (4-70) wt.%, MCW (70-4) wt.%
(II) PW (4-70) wt.%, MCW (70-4) wt.%
(III) PW (4-70) wt.%, MCW (70-4) wt.%
(IV) PW (47-57) wt. %, MCW (20-10 wt. %)

A gradual decrease in CP of CW blend is directly proportional to an increase in wt.% PW and decrease of wt.% MCW while keeping the other additives constant. The structures of compounded wax (CW) are related to the properties of PW that have: Mw. 402 g.mol^{-1}, very low aromatic component 0.04 %, naphthenes component of about 1.99 % and ≈97.97% paraffin component. The MCW has Mw. 598 g.mol^{-1}, 3.08 % aromatics, 10.63 % naphthenes, and 86.29 % paraffin. The Mw of both PW and MCW were determined according to UOP 375 (the standard method for determination of the Mw. of PW). However, Mw. determination by Z or Z+2 for all compounded formulations is not possible due to the dependence of Mw on the composition of the ingredients of PW and MCW. From the chemical composition viewpoint of individual alkanes, it is known that the normal n-paraffins have a higher melting point than the corresponding branched-chain paraffin and alkyl naphthenes; consequently, the wax samples containing higher proportions of n-paraffins must show higher MP than those waxes which have lower ones. A relationship between MP and n-paraffin content of blends cannot be expected because the nature of HC molecules and the average Mw, the average number of carbon atoms, and the percentage of oil content are all affecting the melting behavior [3]. The general formula for paraffin wax (PW) involves C_nH_{2n+2} as represented. In the production of PW in the petroleum refineries, different amounts of refining can change the mix of hydrocarbons and affect some of the wax properties, such as its melting point. Further modifications of the wax are achieved by removing the oil from waxy byproducts of the petroleum distillation.
The raw wax material has 0.04 wt% aromatic and 1.99 wt% naphthenes. The MCW has 3.08 wt.% aromatic and 10.63 wt.% naphthenes; the wax should not have any double bond to be approved by FDA. Finally, CP increased when wt.% MCW increased, and PW decreased at fixed wt.% of other

all additives. The degree of crystallinity of macro-crystal-line wax is higher than that obtained for microcrystalline wax (MCW). This is because MCW contains the highest aromatic content (3.08 wt.%). This finding indicates that the main factor affecting the crystalline and amorphous structure of the wax is its molecular weight [1]. The cyclic paraffin component has a higher molecular weight (Mw) than the aromatic components. Those affect the amorphous shape of MCW whose crystals appear in large and loose needle form according to the chemical composition of wax, and MCW crystallizes in as microscopic crystals. The Mw. of the prepared CW decreased, and the crystallinity increased due to the increase in wt.% of PW of low Mw, high crystallinity, and consequently, CP decreased [20].
According to the ASTM D-938 method, congealing point (CP) is the temperature at which solid compounded waxes (CW) melt when allowed to be cooled under prescribed conditions specified according to ASTM D-938.
The softening point (SP) of the compounded waxes is the temperature at which the solid compounded waxes begin to soften according to ASTM D-36 specified conditions [21]. Figure 3 showed the change in SP when the percentages of PW and MCW have changed at constant other ingredients; HD resin, MS resin, and EVA. The SP of the various grades of prepared CW having SP ranges from 72.4 to 82.2 °C. Curve I showed the variation of SP of CW with the chemical composition of wax ingredients.
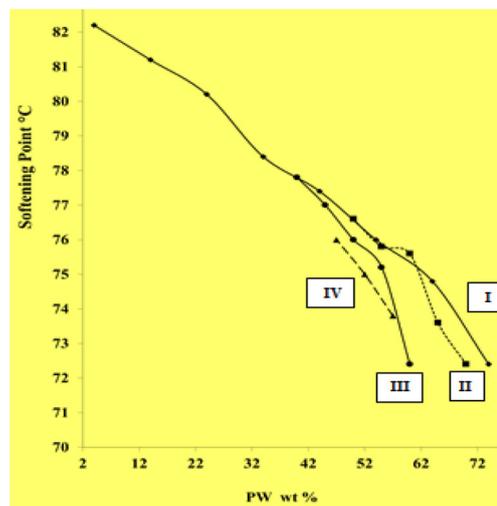

Fig. 3 Effect of replacing PW wt.% by MCW wt.% on SP of CW.
(I) PW (4-70) wt.%, MCW (70-4) wt.%
(II) PW (4-70) wt.%, MCW (70-4) wt.%
(III) PW (4-70) wt.%, MCW (70-4) wt.%
(IV) PW (47-57) wt. %, MCW (20-10 wt. %)

In addition that the SP decreased from 82.2 to 72.4 °C when wt.% PW increased from 4 to 74%, and MCW wt.% decreased from 70 to 0% at constant other ingredients (0 % HD, 0 % MS, and 26% EVA). Also, curve II shows that SP decreases from 76.6 °C to 72.4 °C when PW wt. % increases from 50 to 70%, wt.% MCW decreased from 24 to 4% at constant other ingredients (1.25 % HD, 3.75% MS, and 21% EVA). Furthermore, curve III shows that SP decreases from 77.8 to 72.4 °C when PW wt. % increases from 40 to 60%, and MCW wt.% decreased from 32 to 12% at constant other

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ingredients (7.5% HD, 2.5% MS and 18 % EVA). Moreover, curve IV shows that SP decreases from 76.0 °C to 73.8 °C when wt.% PW increases from 47 to 57%, and MCW wt.% decreases from 20 to 10 % at 10% HD resin, 0% MS resin and 23% EVA ingredients. The gradual decrease in SP of compounded wax (CW) blends is directly proportional to the wt.% of PW, and it is inversely proportional to the wt.% MCW while keeping the wt.% of other additives constant. Since Mw. of PW is smaller than MCW, and crystallinity of PW is higher than MCW so there is a direct proportionality between increased Mw. of CW with increased PW wt.% rather than MCW wt.%, where inverse proportionally between the crystallinity and the increased PW- wt.% consequently, SP decreased as due to of increased PW wt.% [33]. Figure 4 showed the change in DMP of the compounded wax blends when the percentages of %PW and MCW changed without changing other ingredients (HD resin, MS resin, and EVA copolymer).
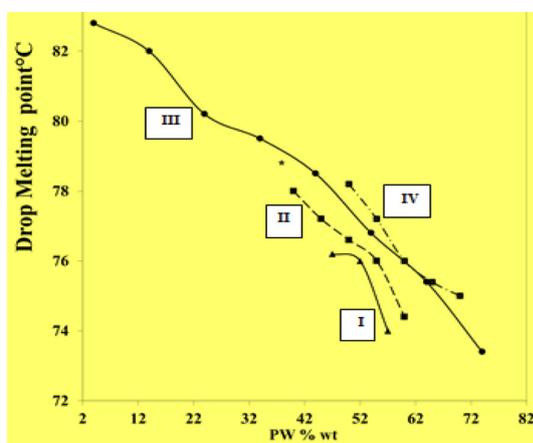

Fig. 4 Effect of replacing PW wt. % by MCW wt. % on DMP of CW.
(I) PW (4-70) wt.%, MCW (70-4) wt.%
(II) PW (4-70) wt.%, MCW (70-4) wt.%
(III) PW (4-70) wt.%, MCW (70-4) wt.%
(IV) PW (47-57) wt. %, MCW (20-10 wt. %)

Figure 4 showed that the various prepared grades of the compounded wax samples (CW) have DMP range from 73.4 to 82.8 °C, as shown in the four different blends (I-IV). Curve I has shown that DMP decreases from 76.2 to 74.0°C on increasing wt.% PW from 47 to 57 % and decreases MCW wt.% from 20 to 10 wt. % at (10% HD, 0 % MS and 23 EVA); Curve II has shown that DMP decreases from 78.0 °C to 74.4 °C when PW wt.% increases from 40 to 60% and MCW wt.% decreases from 32 to 12% at constant other ingredients (7.5 % HD resin, 2.5 % MS and 18 % EVA); Curve III has shown that DMP decreased from 82.8 to 73.4 °C when the wt.% of PW increases from 4 to 74 % and MCW wt.% decreases from 70 to 0% at constant other ingredients (0% HD, 0 % MS and 26 % EVA); Curve IV has shown that DMP decreases from 78.2 °C to 75.0 °C on increasing the wt.% of PW from 50 to 70 wt.% and decreasing MCW wt.% from 24 to 4 % at constant 1.25 % HD resin, 3.75 % MS resin and 21% EVA.
The gradual decrease in DMP of the wax blend is directly proportional to an increase in wt.% of PW and a decrease wt.% MCW while keeping other additives constant.

The Mw. of CW depends on Mw of its components, so Mw. of CW decreased when wt.% of PW is greater than wt.% of MCW, where crystallinity increased, so DMP decreased. The melting behaviors represented in the temperature of (CP, SP, and DMP) are inversely proportional by increasing wt.% PW, decreasing wt.% MCW at fixed wt.% of other ingredients because Mw. of PW was lower than Mw of MCW, and crystallinity caused by PW is higher than MCW, so the molecular weight (Mw) of compounded wax decreased and the crystallinity increased by increasing the wt.% of MCW [37].
Figure 5 showed the effect of the wt.% of PW on the penetration of wax blend when PW and MCW changed without changing wt.% of HD resin, MS resin, and EVA.
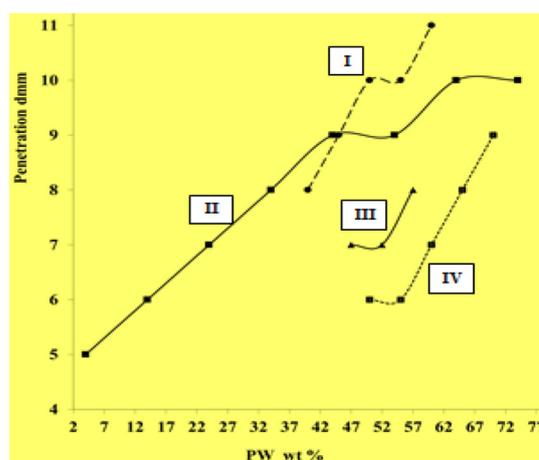

Fig. 5 Effect of replacing PW wt.% by MCW wt.% on the penetration of CW.
(I) PW (4-70) wt.%, MCW (70-4) wt.%
(II) PW (4-70) wt.%, MCW (70-4) wt.%
(III) PW (4-70) wt.%, MCW (70-4) wt.%
(IV) PW (47-57) wt. %, MCW (20-10 wt. %)

The various grades of the formulated CW samples have penetration ranges from 4 to 11 dmm. Curve I shows that penetration increases from 8 to 11 dmm when wt.% of PW increases from 40 to 60% and wt.% of MCW decreases from 32 to 12% at constant other ingredients (7.5 % HD, 2.5 % MS, and 18 % EVA); Curve II shows that penetration increases from 5 to 10 dmm when wt.% PW increases from 4% to 74 %, wt.% MCW decreases from 70 to 0% at constant other ingredients (0 % HD, 0 % MS and 26 EVA); Curve III shows that penetration changes from 7 to 8 dmm when PW wt.% increases from 47 to 57 wt.%, the composition of MCW wt.% decreases from 20 to 10 wt.% at constant other ingredients (10% HD, 0% MS and 23% EVA; Curve IV shows that penetration increases from 6 to 9 dmm when wt.% of PW increases from 50 to 70% and the wt.% of MCW decreases from 24 to 4 wt.% at constant other ingredients (1.25 % HD resin, 3.75% MS and 21% EVA. All these findings indicated that the penetration of wax blend is directly proportional to increase in PW wt.% and decrease of MCW wt.% at constant wt.% of other additives. The resistance to penetration is closely related to all of these factors: the solid-solid interaction in CW, and the melting transitions (phase changes-temperature), and the extent of transformation at this temperature. Also, the penetrations depend on contact time, temperature, load, and

heating rate. Significant factors affected penetration of CW samples including oil %, molecular weight (Mw.) of the hydrocarbon chain, and structures of both PW and MCW. The MCW has oil% lower than PW, Mw. and the number of carbon atoms of MCW is higher than PW. Therefore, the penetration decreased when wt.% MCW in the wax blend, and increased as wt.% of PW decreased. The high wt.% of MCW increased Mw. of the compounded wax (CW) samples, decreased crystallinity, and consequently decreased the penetration [22].
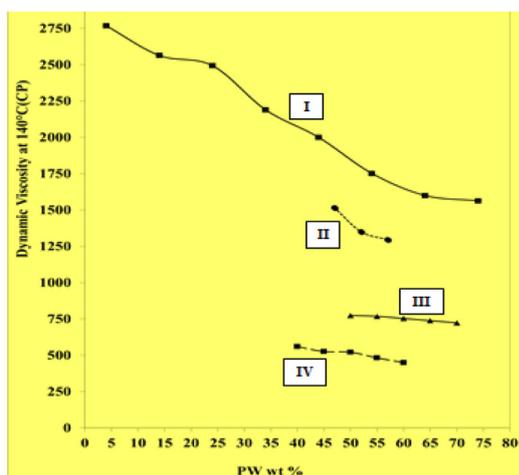

Fig. 6 The effect of replacing PW wt.% by MCW wt.% on DV at 140 oC of CW
(I) PW (4-70) wt.%, MCW (70-4) wt.%
(II) PW (4-70) wt.%, MCW (70-4) wt.%
(III) PW (4-70) wt.%, MCW (70-4) wt.%
(IV) PW (47-57) wt. %, MCW (20-10 wt. %)

Various prepared grades of compounded wax samples have dynamic viscosity (DV) ranging from 39 to 4349 cP. Curve I shows that DV decreases from 2769 to 1563 cP when PW wt.% increases from 4 to 74%, and MCW wt.% decreases from 70 to 0% at constant other ingredients (0 % HD, 0 % MS, and 26% EVA). Also, curve II shows that DV decreases from 1515 to 1296 cP when PW wt.% increases from 47 to 57% and MCW wt.% decreases from 20 to 10 % at constant other ingredients (10 % HD resin, 0% MS resin and 23 % EVA). Moreover, curve III shows that DV decreases from 774 to 723 cP when the composition of PW wt.% increases from 50 to 70 % and MCW wt.% decreased from 24 to 4 % at constant: 1.25 % HD resin, 3.75 % MS and 21 % EVA; Curve IV shows that DV decreases from 560 to 450 cP when PW wt.% increased from 40 to 60 % and MCW wt.% decreased from 32 to 12 wt.% at constant 7.5 wt.% HD, 2.5 wt.% MS, and 18% EVA.

This means that a gradual decrease in DV of the wax blend is inversely proportional to an increase in the wt.% of PW and a decrease wt.% of MCW in blend while keeping the other polymeric additives constant. The DV is affected by: temperature, Mw, and the number of carbons atoms of wax components. Generally, raising the temperature decreases DV. However, in our study, DV was determined at a constant temperature of 140 °C, so no temperature effect was found. The linear fall in DV on increasing wt.% PW is since wax viscosity is directly proportional to Mw of wax blends [34]. By increasing PW wt.% rather than wt.% of MCW, DV de-

creased as Mw. decreased, crystallinity increased by increasing PW wt.%. The replacing PW wt.% by MCW wt.% affect DV as this dynamic viscosity of wax blends is directly proportional to the tensile strength (TS), melting behavior (D.M.P, SP, CP), and inversely proportional to the penetration, which is directly proportional to the hardiness.

Figure 7 shows the effect of PW wt.% on the tensile strength (T.S.) at the break of the wax blend when the wt.% of PW and MCW changed without changing other ingredients; HD resin, MS resin, and EVA copolymer. The T.S. of CW samples showed four stages of changes with varying PW wt.% and MCW wt.%.
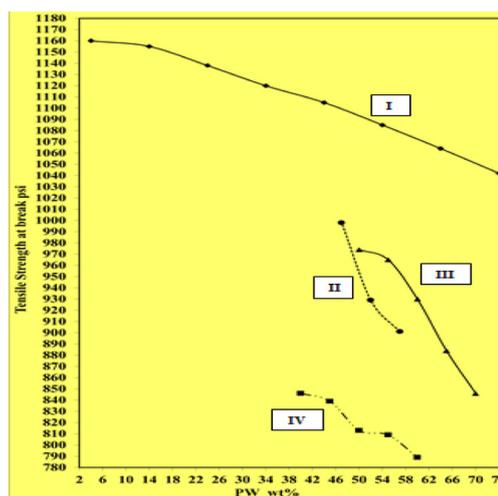

Fig. 7 Effect of replacing PW wt.% by MCW wt.% on T.S. at break of CW.
(I)PW (4-70) wt.%, MCW (70-4) wt.%
(II) PW (4-70) wt.%, MCW (70-4) wt.%
(III) PW (4-70) wt.%, MCW (70-4) wt.%
(IV) PW (47-57) wt. %, MCW (20-10 wt. %)

Figure 7 showed that various grades of CW had a tensile strength at break ranging from 485 to 1447 psi. The obtained results can be interpreted as follows [23]. Curve I shows that T.S. at break decreases from 1160 to 1042 psi when PW wt.% increases from 4 to 74 % and MCW wt.% decrease from 70 to 0 % at constant other ingredients (0 % HD, 0% MS, and 26 % EVA). Moreover, curve II shows that T.S. at break decreases from 998 to 901 psi when wt. % of PW increases from 47 to 57 % and MCW wt.% decreases from 20 to 10% at constant other ingredients (10% HD, 0% MS, and 23 % EVA). Furthermore, curve III shows that T.S. at break decreases from 974 to 846 psi when PW wt.% increases from 50 to 70% and MCW wt.% decreases from 24 to 4% at other constant ingredients (1.25% HD, 3.75 % MS and 21 % EVA). Also, curve IV shows that T.S. at break decreases from 846 to 789 psi when PW wt.% increases from 40 to 60% and MCW wt.% decreases from 32 to 12% at constant other ingredients (7.5 % HD, 2.5 % MS and 18 % EVA). The gradual decrease in T.S. at the break of the blend is directly proportional to the increase in PW wt.% and the decrease of MCW wt. % while keeping the other additives constant. The MCW has T.S. of 188 psi was added to PW having T.S. of 104 psi blends (1-21) was obtained having T.S. higher than that of any starting material of PW and MCW at the constant composition of another ingredient (EVA copolymer, HD resin, MS resin). The physical state of the branched hydrocarbons is important;

where low melting hydrocarbon which is soft and plastic at test temperature, decreased the tensile strength (T.S.), while the branched paraffin which improves the tensile strength is relatively hard at the test temperature and has higher Mw. more than the normal paraffin making up the bulk of the wax. The higher Mw. of the branched-chain of MCW is more effective than those naturally present in PW. In addition, the n-paraffin content is effective, but its Mw and melting point are directly proportional to the T.S. of the formed CW. The decrease in Mw. and the increase in crystallinity of CW are due to the rise of PW wt.% where the decrease in MCW wt.% lowers the T.S. at break of CW.

Figure 8 showed the effect of the wt.% of PW on the elongation at break % of the wax blend when PW and MCW% replaced each other's without changing wt.% of the other ingredients; HD resin, MS resin, and EVA copolymer in each compounded wax sample.
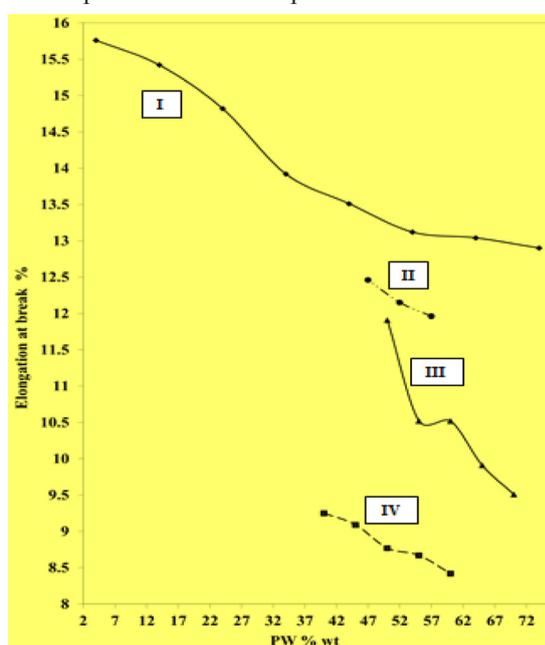

Fig. 8 Effect of replacing wt.% PW by wt.% MCW on the elongation at break % of CW.
(I)PW (4-70) wt.%, MCW (70-4) wt.%
(II) PW (4-70) wt.% , MCW (70-4) wt.%
(III) PW (4-70) wt.% , MCW (70-4) wt.%
(IV) PW (47-57) wt. %, MCW (20-10 wt. %)

Various grades of compounded waxes can be prepared which have an elongation at break ranging from 6.84 % to 22.73%. The explanation of these findings can be summarized as follows [24]:

Curve I shows that elongation at break decreases from 15.76 to 12.90% when PW wt.% increases from 4 to 74%, and MCW wt.% decreases from 70 to 0% at constant other ingredients: 0% HD, 0% MS, and 26% EVA; Curve II shows that elongation at break decreases from 9.25 to 8.42 % when PW wt.% increases from 40 to 60 wt.% and MCW wt.% decreases from 32 to 12 wt.% at constant other ingredients (7.5 wt. % HD, 2.5 wt % MS and 18 wt.% EVA). Also, curve III shows that elongation at break decreases from 12.46 % to 11.96 % when the composition of PW wt.% increases from 47 to 57%, the wt.% of MCW decreases from 20 to 10% at constant wt.% of other ingredients (10% HD resin, 0% MS

resin and 23 % EVA copolymer). Moreover, curve IV shows that elongation at break decreases from 11.91 to 9.56 % when wt. % of PW increases from 50 to 70% and MCW wt.% decreases from 24 to 4% at constant other ingredients (1.25 % HD resin, 3.75 % MS resin, and 21% EVA). The gradual decrease in the elongation at break % of the blend is directly proportional to the increase in wt.% PW and decrease wt.% of MCW while keeping other additives constant. Petroleum waxes generally possess high plasticity and the ability to deform plastically. The PW begins to deform plastically at very low stress and shows little plastic range, i.e. small deformation occurs before fracture. Therefore, paraffin waxes are brittle. While the highly elastic material such as micro wax or their blends with the higher paraffin wax content is rigid. MCW is more plastic and malleable than PW because the MCW wax has a branched chain represented in the iso-paraffin component more than PW, so elongation increased when MCW increased, and PW decreased while other ingredients are constant. The Mw and crystallinity are two important properties of the compounded wax (CW) samples and high wt.% MCW and low wt.% PW lead to an increase in Mw and decreases crystallinity of CW, and consequently, the elongation at break increased [24].

The crosshatch tape test measured the adhesion strength of coatings to ensure bonding to the substrate and satisfactory performance for all formulas. Some of them were found on ISO class [25]: 0/ASTM:5B, which is described by completely smooth edges of cuts; none of the lattice squares is detached. Other formulas are of class 1/ASTM: 4B, which are described by the detachment of small flakes of the coating at the intersections of the cuts.

A cross-cut area not significantly greater than 5% is affected. Therefore, formulas are divided into two classes 4B and 5B. For the 21 CW samples formulated in this study, the formulas (14-21) have classification 4B, and the formulas (1-13) follow 5B classification. Generally, all formulas were found to have a good adhesion characterization, but the formula had 2.5 to 10 wt.% HD and MS resins showed the better tacking power. The results obtained in this study are in good agreement with that previously reported [26-34] concerning waxes: Green plastics, animal and vegetable fats, oils, and waxes, bioenergy; and biorefinery for circular bio-economy; Oil based on wax properties, wax crystallization and effect of crystal modifiers and dispersants on paraffin-wax particles in petroleum.

All the characterization methods, in addition to the viscoelastic and adhesion properties of hot melts and the molecular dynamics simulation of the microscopic mechanisms of the dissolution, diffusion, and aggregation processes for waxy crystals in crude oil mixtures, the formulated waxes are made according to the annual book of American Society for Testing and Materials (ASTM international) [32].

The morphological study for the compounded wax blends was carried out using the analytical scanning electron microscope, SEM: JSM-5300 Jeol, Japan, operated at 15 keV accelerating voltage and magnification, x500. The samples were sputter-coated with gold up to a thickness of 400 Å; this was carried out by JFC-1100 E auto fine coater from Jeol, Japan. The gold layer increases the surface conductivity. The samples were scanned, and the digitized images were recorded and studied.

Figures 9 (a-d) indicated the SEM micrographs of different samples of wax. The microcrystalline wax particles are in random orientation. It also shows resin-rich areas, air bubbles, weak matrix-MCW adhesion, and EVA fillers particle size. The possible crack in the compounded wax formula is the presence of cavities. At the lower filler concentration, filler-matrix interaction improves by the addition of EVA that enhances the crystallization of wax blends. The SEM micrographs also showed the improved mechanical properties of wax blends containing PW, MCW, HD resin, MS resin, and EVA copolymer.
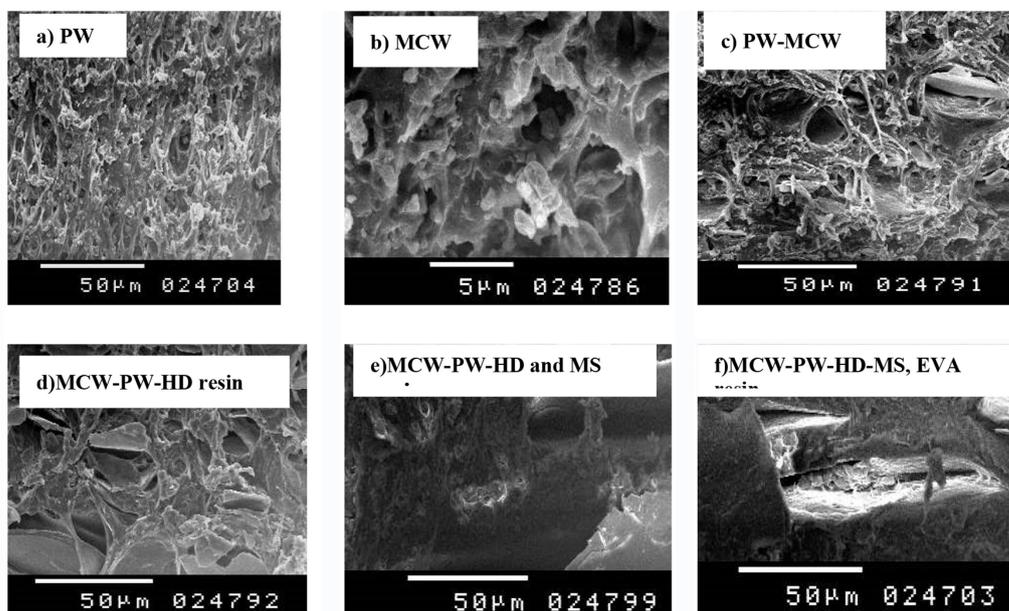

Fig. 9 SEM micrographs for different wax samples: a) PW, b)MCW, c) PW-MCW, d)MCW-PW-HD resin, e)MCW-PW-HD and MS, f) MCW-PW-HD-MS, EVA.

Blending petroleum wax with high melting point microcrystalline wax enhanced crystallinity, and as a result, will elevate the melting point to be used in different industrial applications. Wax blend samples containing additives to MCW and PW showed fine crystals in contrast to amorphous paraffin wax (Figure 9 a). The SEM micrographs also showed that the loaded MCW gets resin loosely packed into PW (Figure 9 b). The hydrocarbon resin cross-linkers HD and MS resins enhanced the crystallinity of compounded wax samples (Figure 9 d, e). Methyl polystyrene increased the hardness of wax blends. Combining ternary additives: HD, MS, and EVA significantly improved the crystallinity and morphology of the wax blend sample (Figures 9 e and f). The improved crystallinity will enhance the thermal stability and mechanical properties of wax blends prepared by mixing PW, MCW, and petroleum additives.

All the wax blends are miscible in the crystalline phase. Crystallization of the wax blends improved the mechanical properties. Ethylene-vinyl acetate (EVA) copolymers improved the crystal size of the wax blends.

EVA acted as a nucleating agent or a growth inhibitor. EVA co-crystallized with paraffin in wax crystals and improved tensile strength, hardness, softening points, and gloss, without markedly increased viscosity or shrinkage of the wax blends.

Conclusions

The work in this study simply and successfully formulated new compounded high compatible blends of Paraffin wax (PW) and microcrystalline waxes (MCW) of specific properties. The viscosity of the formulated samples was modified using EVA copolymer, which acted as tackifing agent. The poly hydrogenated dicyclopentadiene (HD) and poly alpha-methyl styrene (MS) enhanced wax performance based on Mw of hydrocarbon chains and crystallinity. The blend compatibility, melting behavior (congealing point (CP), softening point (SP) and drop melting point (DMP)), dynamic viscosity, hardness (low penetration value), the mechanical properties (tensile strength and elongation at break) as well as adhesion property are all dependent on the composition of the wax blends. Novel highly compatible CW samples were prepared using local petroleum waxes based on Western Desert mixture and Marine Baleyim Egyptian crude oil. The main ingredients are PW, MCW, EVA copolymer, poly hydrogenated dicyclopentadiene resin, and poly alpha-methyl styrene resin. By changing wt.% of PW and MCW, new formulations of CW were prepared. The Mw. and crystallinity of each component control the blend characterization, where all the measured properties were functions of the total Mw of each blend. The compatibility of the blend depends on wt.% of additives to basic wax composition. Increasing MCW wt.% by reducing PW wt.% in CW blend leads to an increase in the melting behavior: (congealing point, softening point, and drop melting point), dynamic viscosity, hardness (low penetration value), and the mechanical properties (tensile strength and elongation) of CW. Adding traces of the a/m polymeric additives in different wt.% to the basic wax blends led to a new explored CW of controllable specific characteristics that can be tailored according to the new wax compound requested.

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References

1. Ivanova I K, Kashirtsev V A, Semenov M E, Glyaznetsova Y S, Chalaya O N, Zueva I N, Portnyagin A S (2020) Effect of the solvent composition on the content of the crystalline phase and melting temperature of paraffin waxes, Russian Journal of Applied Chemistry, 93: 603-610.

2. Ivanova I K, Kashirtsev V A, Semenov M E, Glyaznetsova Y S, Chalaya O N, Zueva I N, Portnyagin A S (2020) Effect of the solvent composition on the content of the crystalline phase and melting temperature of paraffin waxes, Russian Journal of Applied Chemistry, 93: 603-10.

3. Soliman F S (2020) Introductory chapter: petroleum paraffins. Paraffin: an Overview, 3: 9-1.

4. 4. Du W, Liu Q, Lin R, Su X (2021) Preparation and characterization of microcrystalline wax/epoxy resin microcapsules for self-healing of cementitious materials, Materials, 14, 7: 1725.

5. Yousef S, Eimontas J, Zakarauskas K, Striūgas N (2021) Microcrystalline paraffin wax, biogas, carbon particles and aluminum recovery from metalized food packaging plastics using pyrolysis, mechanical and chemical treatments, Journal of Cleaner Production, 25, 290:125878.

6. Ishigaki T, Nakagawa I (2020) Improving Physical Properties of Wax-Based Fuels and Its Effect on Regression Rate, Journal of Propulsion and Power, 36, 1:123-8.

7. Eghbali Babadi F, Yunus R, Masoudi Soltani S, Shotipruk A (2021) Release Mechanisms and Kinetic Models of gypsum–sulfur–zeolite-coated urea sealed with microcrystalline wax for regulated dissolution, ACS Omega, 6, 17: 144-154.

8. Adebiyi F M (2020) Paraffin wax precipitation/deposition and mitigating measures in oil and gas industry: a review, Petroleum Science and Technology, 38, 21: 962-71.

9. van der Geest C, Melchuna A, Bizarre L, Bannwart AC, Guersoni VC (2021) Critical review on wax deposition in single-phase flow, Fuel, 293: 120358.

10. Obaseki M, Elijah P T (2021) Dynamic modeling and prediction of wax deposition thickness in crude oil pipelines, Journal of King Saud University-Engineering Sciences, 33, 6: 437-445.

11. Santos S M, Nascimento D C, Costa M C, Neto A M, Fregolente L V (2020) Flashpoint prediction: Reviewing empirical models for hydrocarbons, petroleum fraction, biodiesel, and blends, Fuel, 263: 116375.

12. Joonaki E, Hassanpouryouzband A, Burgass R, Hase A, Tohidi B (2020) Effects of waxes and the related chemicals on asphaltene aggregation and deposition phenomena: Experimental and modeling studies, ACS omega, 5, 13: 7124-34.

13. Fetouh H A, Hefnawy A, Attia A M, Ali E (2020) Facile and low-cost green synthesis of eco-friendly chitosan-silver nanocomposite as novel and promising corrosion inhibitor for mild steel in chilled water circuits, Journal of Molecular Liquids, 319:114355.

14. Anisuzzaman S M, Fong Y W, Madsah M (2018) A review on various techniques and recent advances in polymeric additives to mitigate wax problems in crude oil, Journal of Advanced Research in Fluid Mechanics and Thermal Sciences, 48, 1:53-64.

15. Jayapal S N, Dubey V K, Dinesh S, Wahab A, Khaleel A A, Kadiresh P N (2021) Thermal stability and kinetic study of blended Beeswax-ethylene vinyl acetate-based hybrid rocket fuels, Thermochimica Acta, 702: 178989.

16. Mahottamananda J S, Kumar D V, Afreen A K, Dinesh S, Ashiq W, Kadiresh P N, Thirumurugan M (2021) Mechanical Characteristics of Ethylene Vinyl Acetate Mixed Beeswax Fuel for Hybrid Rockets, In Advances in Design and Thermal Systems, 389-400.

17. Baena-González J, Santamaria-Echart A, Aguirre J L, González S (2020) Chemical recycling of plastic waste: Bitumen, solvents, and polystyrene from pyrolysis oil. Waste Management, 118: 139-149.

18. Su D, Chen X, Wei X, Liang J, Tang L, Wang L (2021) Comparison of thermal stability between dicyclopentadiene/hydrogenated dicyclopentadiene petroleum resin: Thermal decomposition characteristics, kinetics and evolved gas analysis by TGA/TG-MS, Thermochimica Acta, 699: 178853.

19. Taha A A, Shaban S M, Fetouh H A, Taha S T, Sabet V M, Kim D H (2021) Synthesis and evaluation of nonionic surfactants based on dimethylaminoethylamine: Electrochemical investigation and theoretical modeling as inhibitors during electropolishing in-ortho-phosphoric acid, Journal of Molecular Liquids, 328: 115421.

20. Jeanlin F T, Larissa T D, Patel J, Nagar A (2021) Physico-chemical studies of crude oil of western onshore, International Journal, 6: 6.

21. Yengejeh A R, Shirazi S Y, Naderi K, Nazari H, Nejad F M (2020) Reducing production temperature of asphalt rubber mixtures using recycled polyethylene wax and their performance against rutting, Advances in Civil Engineering Materials, 9, 1:117-127.

22. Robertson D, van Reenen A, Duveskog H (2020) A comprehensive investigation into the structure-property relationship of wax and how it influences the properties of hot melt adhesives, International Journal of Adhesion and Adhesives, 99: 102559.

23. Ishigaki T, Nakagawa I (2020) Improving Physical Properties of Wax-Based Fuels and Its Effect on Regression Rate. Journal of Propulsion and Power, 36, 1: 123-8.

24. Yousef S, Eimontas J, Zakarauskas K, Striūgas N (2021) Microcrystalline paraffin wax, biogas, carbon particles and aluminum recovery from metallised food packaging plastics using pyrolysis, mechanical and chemical treatments, Journal of Cleaner Production, 290:125878.

25. McIntosh K, Sarver J, Mell K, Terrero D J, Ashby Jr C R, Reddy C, Neil G O, Ramapuram J B, Tiwari A K (2020) Oral and dermal toxicity of alkenones extracted from Isochrysis species, Frontiers in bioscience (Landmark edition), 25:817-37.

26. Stevens E S (2020) Green plastics, 1st edition, Princeton University Press, 1-154.

27. Lusas E W, Riaz M N, Alam M S, Clough R (2017) Animal and vegetable fats, oils, and waxes. InHandbook of Industrial Chemistry and Biotechnology, 5: 823-932.

28. Konwar L J, Mikkola J P, Bordoloi N, Saikia R, Chutia R S, Kataki R (2018) Sidestreams from bioenergy and biorefinery complexes as a resource for circular bioeconomy, InWaste Biorefinery, 3: 85-125.

29. Taheri-Shakib J, Rajabi-Kochi M, Kazemzadeh E, Naderi H, Shekarifard A A (2018) Modified investigation of WAT of crude oil based on wax properties: experimental study. InSaint Petersburg, European Association of Geoscientists & Engineers., 1: 1-5.

30. Ruwoldt J, Sørland G H, Simon S, Oschmann H -J, J Sjöblom (2019) Inhibitor-wax interactions and PPD effect on wax crystallization: new approaches for GC/MS and NMR, and comparison with DSC, CPM, and rheometry, Journal of Petroleum Science and Engineering, 177: 53-68.

31. Sun M, Naderi K, Firoozabadi A (2019) Effect of crystal modifiers and dispersants on paraffin-wax particles in petroleum fluids, SPE Journal, 24, 1: 32-43.

32. Annual book of Standards, 2019; 5: 1-11.

33. Moyano, MAa, París, R b, Martín-Martínez, J M (2019) Viscoelastic and adhesion properties of hot-melts made with blends of ethylene-co-n-butyl acrylate (EBA) and ethylene-co-vinyl acetate (EVA) copolymers, International Journal of Adhesion and Adhesives, 88: 34-42

34. Gan Y, Cheng Q, Wang Z, Yang J, Sun W, Liu Y (2019) Molecular dynamics simulation of the microscopic mechanisms of the dissolution, diffusion and aggregation processes for waxy crystals in crude oil mixtures, Journal of Petroleum Science and Engineering, 179: 56-69.