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Ameliorate the Quality of Chocolate Spread by Using Orange Pectin as a Fat Substitute

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Abstract

The objective was to improve the quality of low-fat chocolate spread using orange pectin as a fat substitute. Pectin was extracted from the dried orange peels as a byproduct (oven, microwave, and solar drying methods). The characteristics of a low-fat chocolate spread formulated by replacing 50% of the fat with orange pectin were determined. The rheological properties and quality characteristics of the chocolate spread were measured. Oven-dried pectin exhibited an increase in the anhydronic acid content (24.05%) and a decrease in the degree of esterification, while, the microwave-dried pectin had the highest charge particles which was -14. The exothermic temperature of chocolate spread increased from 237.65°C for the pectin standard to 253.92°C for pectin from the solar-dried orange peel. Substitution with pectin induced a higher viscosity than that of the control sample and improved the sensory properties of the chocolate spreads. In conclusion, high-molecular-weight pectin may be an appropriate way to produce high-quality functional food products.

Key words: Chocolate spread; fat substitute; pectin; orange waste; low-fat chocolate.

1. Introduction

Pectin is the methyl ester of polygalacturonic acid, which has 300–1000 galacturonic acid units in its chain. The cell walls and middle lamellae of plants are present. Pectin can also originate in the endo white layer of citrus peels, pectin from citrus is a naturally occurring food ingredient that is commonly used in the food sector and processed as a thickening agent, texturizing agent, emulsifying agent, and stabilizer in jams and jellies; as a filling agent in confections products, dairy products, fruit products, bakery fillings, and frostings; and as a fat replacer in spreads, salad dressing, and emulsifying agent in meat products [1]. As a dietary fibre, it reduces blood cholesterol levels and low density lipoprotein cholesterol fractions while has no effect on high density lipoprotein cholesterol or triglycerides, which are both essential for humans. Pectin demand in the global market exceeds 30,000 tons per year and is increasing at a rate of 4–5% per year [2].

The major by-product of the citrus industry is orange peel waste, which is susceptible to fermentation due to the high moisture content of orange peels, which causes a number of environmental and economic problems. Therefore, the drying process of fresh orange peel was used to avoid its fermentation [3].

The most common methods of drying materials, such as vacuum drying, hot-air drying, and freeze drying, are related to high energy consumption, low efficiency, and long drying times. Microwave and superheated steam drying are environmentally friendly, as are drying using vacuum microwaves, which have gradually replaced conventional drying methods. Microwave treatment of orange peel led to a high yield of extracted pectin, an increase in water absorption, holding capacity, and characteristics of pectin extracted from the peel. [4].

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Hence, there is great concern about the development and application of drying techniques that can minimize both the decrease in quality and the power cost. Some drying methods include the use of microwaves, osmotic dehydration, ultrasound, or electric fields [5].

Oven drying has traditionally been used to dry fruits and vegetables. However, drying the polysaccharides may lead to irreversible changes in the structure and composition of the polysaccharides, decreasing the quality of the dried vegetable by-products [6]. Another significant thing to consider when choosing a process is energy consumption, which is becoming increasingly important as fuel prices rise. Applying microwave energy in the drying process of fruits and vegetables provides an efficient of transferring energy for moisture removal.

Fat substitutes are the ingredients that feel, and/or taste like fats particles. Some of the fat substitute had low calorie, while others substitute are calorie-free. The three important categories of fat substitutes are proteins, carbohydrate and substitute fat-based.

Carbohydrate-based fat substitutes such as starch, pectin (polysaccharides), and natural gums have many unique properties and characteristics. They have a water adsorption capacity, which increases the texture profile and structure that are analogous to those of fat materials. Carbohydrate-based fat substitutes are used to substitute fat in food products such as cakes, cookies, frosting, and dressings. In general, carrageenan, cellulose, or starch-based gels; corn starch; guar gum; polydextrose; and xanthan gum are common carbohydrate fat substitutes in the food industry [7].

Chocolate refers to the homogenous products obtained from a combination of cocoa powder, milk, sugar and/or sweeteners, and some food additives. Chocolate ingredients such as sugar, cocoa butter, and fats play an important role in the quality of chocolate. Other components, excluding corn starch, and other fats or fat substitutes, can be additional to the chocolate formulation [8].

The technological difficulty in chocolate processing is creating chocolate spreads with the same low level of fat and spreadability characteristics as the original product. Therefore, this research aimed to convert orange by-products into a valuable product, evaluate drying methods' effects on extracted pectin characteristics, and determine the physical, rheological, and sensory attributes of chocolate spreads as a fat substitute. This study may provide important information on the possibility of using orange peel by-products as a fat substitute in low-fat functional foods.

2. Material and methods

2.1. Material and Chemicals

Ripe and fresh orange *(C. Valencia)*. Orange peels were washed by distilled water and cut as cubes of 1 cm^3 before drying processing.

Pectin standard (Galacturonic acid ≥ 73 %) and all chemicals were purchased from Sigma-Aldrich.

2.2. Drying pre-treatment of orange peel

All tested orange peels were dried using different drying methods as follows:

a) Microwave-drying: using Microwave (Samsung, Model MF245), with dimensions of 419 x 245 x 428 mm and frequency of 2.450 MHz, with a power source: 230 V-50 Hz was used. The maximum power of microwave was 900 watts for 6 minutes.

b) Solar-drying: one layer of orange peels was placed on stainless steel plates for 2 days at 50° in solar oven, the plates were removed when the weight of orange peels was becoming constant. According to Mahmoud et al. [9].

c) Air oven drying: The orange peels was placed in the oven for 8 hours at 40°C, the trays were removed when the weight of orange peels was constant. All the dried orange peel was powdered in a mechanical mill.

2.3. Pectin extraction

Step 1. Extraction of pectin

Orange peel powder (100 gm) was mixed with distilled water (2 L) with continuous stirring according to **Mahmoud et al.** [10].

Step 2. Precipitation

All solutions were centrifuged at 4000 rpm (30 min, 4 ºC). The precipitation was using 1:2 V/V ratios of ethanol and stand at chamber temperature, after that, centrifuged at 4000 rpm/20 min/ 4 ºC, all precipitated was collected and dried at 40ºC.

2.3.1. Pectin yield

Pectin yield was calculated based on **Equation (Eq.) (1)**

Pectin yield (%)

$$= \frac{\text{weight of pectin (M0)}}{\text{weight of orange peel powder (M)}} \text{X100} \qquad (1)$$

2.4. Characteristics of pectin

2.4.1. Scanning Electron Microscopy (SEM) of pectin powder

The pectin powder was sprinkled onto an adhesive tape and covered with a layer of gold. Morphological structure of pectin particles were observed by scanning electron microscope (S- 4160 Cold Field-Emission SEM, QUANTA, FEG 250, Thermo Fisher Scientific, USA).

2.4.2. Fourier Transform Infrared Spectroscopy (FTIR)

The structure of pectin samples was conducted by FT-IR. The spectra of pectin samples were recorded by FT-IR 6000 spectrometer (JASCO, Japan) [11].

2.4.3. Zeta potential

The charge of pectin particles was examined using a Zeta-sizer Nano Zs, Malvern Instrument, Malvern, UK [14].

2.4.4. Degree of esterification (DE) using FTIR spectrum

It is definite as the number of esterified carboxylic groups over the number of total carboxylic groups multiplied by 100. It was calculated by the following equation:

$$\textbf{DE}\ (\%) = \frac{\text{A1740}}{\text{A1740} + \text{A1630}} \times 100 \qquad (2)$$

Where A1740 (the peak area at 1740 $cm^{-1)}$ refer to esterified carboxyl groups, and A1630 (the peak area at 1630 cm^{-1}) refer to free carboxyl groups.

2.4.5. Degree of Methylation (DM)

Degree of methylation was determined according to **Wai et al. [13].** The DM was calculated according to the following formula:

$$\textbf{DM}\ (\%) = \frac{\text{V2}}{\text{V2} + \text{V1}} \times 100 \qquad (3)$$

2.4.6. Methoxyl content (MC)

Methoxyl content was determined according to **Castillo-Israel et al.** [12]. It was calculated using the following equation:

Methoxyl content (%)

$$= \frac{\text{volume of alkali (ml)} \times \text{Normality of alkali} \times 3.1}{\text{Weight of pectin sample (G)}} \qquad (4)$$

2.4.7. Anhydrouronic Acid (AUA)

Anhydrouronic Acid (AUA) content was performed using titration method according to **Mahmoud et al**. [10]. Hence, the AUA content was calculated using the following formula

$$\textbf{AUA}\ (\%) = \frac{176 * 0.1\ z * 100}{w * 1000} + \frac{176 * 0.1y * 100}{w * 1000} \qquad (5)$$

Where the molecular weight unit of AUA = 176 g; z = ml of NaOH from the equivalent weight determination; y= ml of NaOH from methoxyl content determination and w = weight of the sample.

2.4.8. X-ray diffraction analysis (XRD)

Pectin powder (0.5 gram) was scanned from 5° to 60° diffraction angle (2θ) with voltage 40 kV. Using an X-Ray Diffractometer (X'Pert3 Powder, PANalytical, Netherlands) [10].

2.4.9. Differential scanning calorimetry (DSC)

Differential scanning calorimetery DSC131 evo (SETARAM Inc., France) was used to perform the differential scanning calorimeter analysis. The thermogram results were processed using (CALISTO Data processing software v.149).

2.5. Chocolate spread production

Chocolate spread production was carried out according to **Nur *et al*. [15]** with some modifications. cocoa liquor 19.5, oil 27, sugar 36, skim milk 16.41, vanilla 0.02, salt 0.07 % as a control samples, 1 % pectin from different drying methods was add as a fat substitute (50% of fat content) for each formula and mixed with high speed homogenizer (1000 rpm) at room temperature.

2.6. Characteristics of chocolate spread

2.6.1. Color measurement

Chocolate spread color were carried out by a Hunterlab colorimeter, USA. The color was calculated by equations as follows:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad \text{-------- Eq.(6)}$$

$$H^* = \tan\text{-}1[b^*/a] \quad \text{-------- Eq.(7)}$$

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad \text{--------- Eq.(8)}$$

$$BI = \frac{100}{0.17}\left(\frac{a^*+1.75L^*}{5.647\ L^*+a^*-3.012\ b^*} - 0.31\right) \quad \text{---------- Eq.(9)}$$

$$WI = 100 - \sqrt{a^2 + b^2 + (100 - L*)^2}$$ ---------- Eq.(10)

Where: ΔE, L*, a*, and b* are the color parameter values of chocolate spread samples.

Browning index (BI) and Whitening Index (WI) was calculated according to **Heikal et al.** [16].

2.6.2. Rheology of chocolate spread

2.6.2.1 Viscosity

The viscosity of chocolate spread samples were determined at room temperature using a Brookfield viscometer (Middleboro, MA 02346, USA) [17].

The shear rate data were analyzed according to:

$\tau = k.\gamma^n$ ……..Eq. (10)

To test the non-Newtonian behavior of the chocolate spread samples, where:

T = shear stress values (dynes/cm^2), γ = shear rate values (S^{-1}), n = behavior index (–), k = consistency coefficient (dynes. S^n/cm^2).

$\eta a = k.n^{-1}$ ….. Eq. (11)

Where ηa = the viscosity value at defines shear rate values.

2.6.2.2. Texture analysis

All texture parameters of the chocolate spread samples were determined by a conical probe (texture analyzer, TA.HD Plus, Stable Micro System, Godalming, UK) with a compression force of 55 mm and a speed of 3 mm/s, according to **Azab et al.** [18].

2.6.3. Sensory analysis

Sensory analysis of the chocolate spread substituted with pectin was carried out with 20 panelists who were experts on confectionery technology. Chocolate spread samples were mixed homogeneously to analysis. **[19]**. The study was reviewed and approved (Approval Number 20036).

2.7. Statistical analysis

The results were analyzed statistically using SPSS (version 20). ANOVA was used to analyze the data. The results are presented as the means ± SDs. The significance level was set at 0.05.

3. Results and discussion

3.1. Yield of pectin

Table 1. Shows that the yield of pectin extracted from orange peels ranged from 13.1 to 19 for the oven, microwave, and solar drying methods. Pectin DE ranged from 63.77 (pectin standard) to 64.101% (solar drying). Generally, extraction of pectin under very harsh conditions such as high power (such as microwave), long irradiation time, and low pH results in a pectin with low DE because these conditions encourage the polygalacturonic chains deesterification [20].

3.2. AUA content of pectin and DE, DM, and methyl content

Table 1 show that the AUA ranged from 21.41% (PS) to 24.05% (PO). There was a significant difference between the AUA content extracted from orange peels dried by different methods, as shown by the ANOVA results. The degree of esterification calculated from the FTIR chromatogram was equivalent to the degree of esterification calculated with the titration method. The highest degree of esterification among all methods was observed for pectin extracted via the solar drying method. The degree of esterification (DE) value, which closely affected the solubility properties of pectin particles, gelation agent, and emulsifying properties of the orange pectin samples. The DE values of pectin extracted from the microwave dried method and pectin standard samples were (4.16 and 64.96, respectively) which indicates that they were high methoxyl pectin (Table 1)

Table 1. Characterization of pectin extracted from orange peel dried using different methods

sample	Yield extraction* (%)	Degree of methylation* (%)	Degree of esterification* FTIR (%)	Methyl content* (%)	Degree of esterification* calculated (%)	AUA %	Zeta potential	2 θ	
microwave	17.6±0.2^B	79.15±0.31^B	64.05±0.35^A	12.92±0.35^B	64.16±0.18^B	22.88±0.36^A	-14	12.56	44.44
Oven	19±0.31^C	79.62±0.08^B	63.80±0.27^A	12.91±0.21^B	60.99±0.31^A	24.05±0.54^B	-12	21.29	—
Solar	13.1±0.21^A	71.23±0.10^A	64.10±0.47^B	11.63±0.42^A	61.72±0.54^A	21.41±0.15^A	-12.4	21.1	44.4
standard	–	79.15±0.62^B	63.78±0.41^A	12.92±0.65^B	64.96±0.32^B	23.47±0.81^B	-16.38	21.5	44.59

*Mean ± SD with a significant difference at $p \leq 0.05$.

The lowest amount of pectin was extracted from orange peels dried in an oven. The degree of methylation was greater than 50%. This indicates that highly methylated pectin can be used for jam and jelly manufacturing because the ability of pectin particles to form gels depends mainly on their degree of methylation. MC of pectin was ranged from 11.63 to 12.92 %.

The use of microwave heating to reduce the extraction period induced differences in the physical changes in the orange peel tissues. During drying using microwaves, large pressure builds up inside the orange peel, breaking down the structure of the cell wall and improving the capillary-porous nature of the orange peel tissues. This phenomenon allows enhanced diffusion of the solvents in the fleshy tissue of the orange peel, improving the extraction of pectin. This result confirms the findings of **Fishman et al.** [1].

3.3. Characterization of extracted pectin

3.3.1. SEM

Fig. 1 (A) shows SEM images of pectin extracted from orange peels dried via different methods. The structure of the pectin extracted from the orange oven-dried sample remained smooth and compact compared to that of the other pectin samples. The structures of pectin from microwave and solar drying were destroyed, leaving more porous surfaces with hollow holes in their structure Fig. 1 (A). This result revealed that microwave irradiation and solar power significantly destroyed the microstructure of the orange peel and smoothed the extraction of the pectin. The mechanism of the destruction of microstructure by microwave drying treatment could be due to the rapid increasing in the temperature in the intercellular of orange peel and the pressure in the orange peels.

The microwave radiations have the ability to penetrate the food and generate heat in it. Therefore, by increasing the intensity of microwave energy, the damage in the intracellular lamella is increasing, which causes the destroying and collapse of the orange peel cell walls. The microstructure of dried orange peels was affected by microwave radiation treatment. This result revealed that microwave irradiation and solar power significantly destroyed the microstructure of the orange peel and smooth the extraction of the pectin [11].

3.3.2. FT-IR spectroscopy

The structure of pectin, including PO, PM, and PS drying methods, was analyzed by FR-IR spectroscopy as shown in Fig. 1(B). The FR-IR spectra of pectin from oven drying (PO) and pectin from solar drying (PS) have similar chromatogram, which indicates that these pectin samples contain similar functional groups in the same position. The characteristic peak shifts of 3360, 2920, and 1201 cm−1 were due to inter and intermolecular hydrogen of O-H, C-H of CH2 and CH3, and C-O-C of glycoside compounds. The peak at about 2900 cm−1 is related to the CH, CH2, and CH3 stretches of galacturonic acid methyl esters. The peak at 1740 cm−1 is the C-O stretch observed in the ester and derived from the acetyl (COCH3) group. The peak at 1630 cm−1 is related to the OH vibration band, and the bands at 1380–1445 cm−1 indicate the presence of CH3 groups [10].

The band at 2950 cm^{-1} was referred to the methyl ester (COO-CH3) group in galacturonic acid in the skeleton of pectin. These results indicated that the structure of pectin extracted from orange peel dried using oven and solar was not changed compared to pectin extracted from orange peel dried using microwave and standard pectin. The characteristic peak at 825 cm^{-1} (α- configuration) and 930 (β-configuration) in all pectin spectrum FTIR was similar to pectin standard from citrus; this result indicated that there was no change in all configurations and they were simultaneously present in orange pectin dried by different methods.

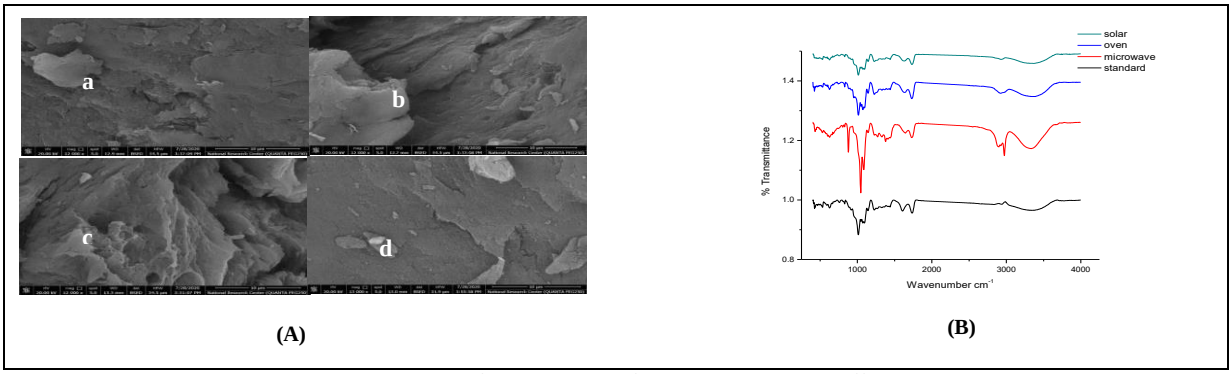

Fig.1. SEM (A) and FTIR (B) of pectin extracted from orange peel under different drying methods:
a) microwave b) oven, C) solar, and d) citrus pectin standard

3.3.3. Zeta Potential

The zeta potential (ζ) of pectin extracted by different drying methods of orange peel ranged from -12 to -14 mV and was also found to be less negative than the standard pectin (-16.83 mV) as presented in Table 1. This indicates that pectin particles extracted by different drying methods showed the lowest stability in aqueous dispersion than pectin standard.

3.3.4. XRD

The XRD pattern of the extracted pectin was obtained to obtain more information about the pectin phase (crystalline or amorphous). The XRD patterns of std., po, ps, and pm extracted from different drying methods of orange peels are presented in Table 1. Std., PM, and PS demonstrated several sharp and intense peaks at 12, 21, and 44° (2θ), which are due to the crystallinity of their structures. An amorphous structure is also observed in this PO pattern at 9.47 and 12° (2θ). Thus, it could be concluded that all the extracted pectin samples had crystalline and amorphous structures.

3.3.5. DSC of extracted pectin

The endothermic peak at 50 to 150°C refers to water evaporation for citrus pectin [21]. The endothermic peak of the extracted pectin from different dried methods of orange peel (melting temperature) is ranged from 100.5 to 128.12°C, and the heat of fusion is ranged from 233 to 291 J/g for the extracted pectin, while the exothermic peak and the heat of fusion for the pectin standard are 139.41 °C and 229.4 J/g, respectively. The endothermic peak heat of fusion was related to hydrophilic groups and reflected the ability to retain water of the pectin sample, the degree of esterification, and the galactouronic acid content of pectin samples. The sample's degradation characteristics are reflected by the exothermic peak, which are typically correlated with the composition of the sample. The heat of fusion values of pectin from different drying methods were lower than the pectin standard, which indicated that drying methods induced a decrease in DE and made pectin particles absorb more water. Therefore, more energy was required to completely remove water because the exothermic temperature of pectin particles was increased from 237.65°C for pectin stander to 253.92°C for pectin extracted from orange peel dried using the solar method (the exothermic phenomenon was attributed to water evaporation), while the endothermic temperature was 250.3 and 249.29°C for microwave and oven drying methods, respectively as presented in Fig. 2. Thus, pectin with high temperature resistance could be favourite in the food industry.

The different degradation temperatures of pectin are commonly thought to be due to its different chemical structures, as shown by FTIR. Higher DE and GalA contents can improve the thermal stability of pectin samples. According to the abovementioned results, PS had relatively good thermal stability compared to the other pectin samples and could be used as an additive for food products such as cakes, breads, and pastries that are processed at high temperatures.

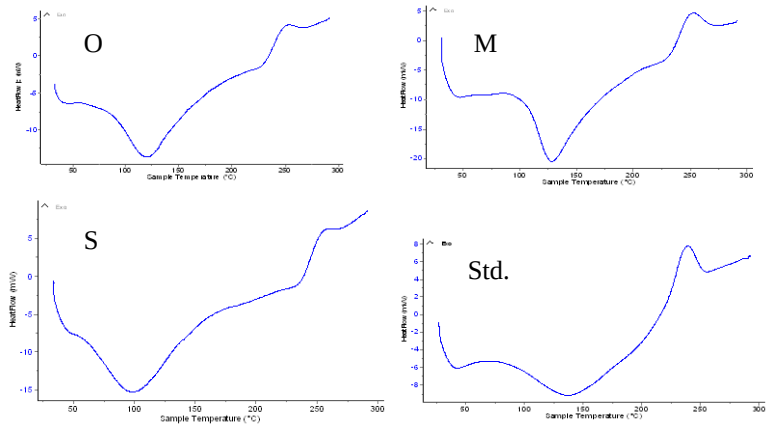

Fig.2. DSC of pectin extracted from orange peel dried using different methods, oven (o), microwave (M), solar(S) and pectin standard (Std).

3.4. Characterization of chocolate spread

3.4.1. Color of chocolate

In terms of quality and customer awareness, color is the most essential feature of chocolate spread [22]. Chromatic properties such as luminosity (L*), saturation (C*), whiteness index (WI), a*, and b* (chromaticity coordinates) were measured in this study. In general, consumers are more accepting of chocolate spreads with a higher L* color and smoother appearance. The color characteristics of the chocolate spreads fortified with different pectin are shown in Table 2. Chocolate spread substituted with pectin from solar drying caused a significant decrease in a* values ($P < 0.05$) and little effect on L* and b* values ($P<0.05$) compared to the chocolate control negative sample (CN) (Table 2). The chocolate spread substituted with pectin from oven dried orange peel had the highest browning index (6.50). This browning reaction was caused as a result of non-enzymatic browning reactions (Millard), during chocolate spread processing; sugar in milk interacts with protein (amino acids) and change the color characteristics of the chocolate spread product.

Additionally, the higher saturation (H*) values for spreads prepared with pectin from oven drying were due to higher temperatures performed during processing. The chroma C* values were influenced by replacing pectin from different drying methods in chocolate samples, causing an increase in color intensity, except for the chocolate containing pectin from solar drying. The hue angle values h◦ ranged from 7.1 to 10.39, and the formulations PS and CP presented the lowest H*. In general, the chocolates spread differ in their physical and particle size distribution, having an impact on the appearance and light scattering coefficients. There is a negligible change in a* and b* values of chocolate spread substituted with pectin. There was a negligible difference in the WI index for all chocolate spreads compared to the control sample. This result may be due to a decrease in the Millard reaction during chocolate spread processing and therefore a reduction in the ratio of chocolate spread darkening [23].

Table 2. Color characteristics of chocolate spread substituted with extracted pectin.

Chocolate samples	ΔL*	Δa*	Δb*	ΔE	C*	H*	WI*	BI*
CN	23.94 ± 0.1^{A}	11.24 ± 0.23^{B}	1.21 ± 0.31^{A}	26.741 ± 0.45^{B}	11.305 ± 0.21^{A}	9.253 ± 0.5^{C}	23.494 ± 0.1^{B}	6.215 ± 0.24^{A}
CP	24.24 ± 0.05^{B}	11.21 ± 0.17^{B}	1.36 ± 0.51^{B}	27.005 ± 0.18^{C}	11.292 ± 0.32^{A}	8.202 ± 0.2^{B}	23.727 ± 0.25^{B}	6.245 ± 0.58^{B}
o	24.12 ± 0.04^{B}	12.09 ± 0.5^{C}	1.16 ± 0.12^{A}	26.929 ± 0.14^{B}	12.146 ± 0.14^{B}	$10.390\pm.18^{C}$	23.104 ± 0.35^{A}	6.500 ± 0.21^{B}
M	24.36 ± 0.7^{B}	11.42 ± 0.3^{B}	1.16 ± 0.14^{A}	26.825 ± 0.6^{B}	11.479 ± 0.17^{A}	9.811 ± 0.36^{C}	23.403 ± 0.17^{B}	6.153 ± 0.31^{A}
S	24.51 ± 0.09^{B}	10.8 ± 0.02^{A}	1.5 ± 0.36^{B}	26.474 ± 0.7^{A}	10.904 ± 0.6^{A}	7.154 ± 0.52^{A}	23.154 ± 0.36^{A}	6.110 ± 0.52^{A}

*Mean ± SD with a significant difference at $p \leq 0.05$.

3.4.2. Texture profile of chocolate

The most important factor in determining sensory acceptance of a chocolate spread product is the texture, also affected by its processing and composition. Spreadability is the force needed to make the chocolate spread flow across a surface, whereas firmness is the maximum force needed for deformation. [26]. Based on the results proved in Table 3, the chocolate spread control positive and chocolate substituted with pectin from solar drying method had the higher firmness and spreadability (0.7 N and 1.37 N.mm, respectively) than other chocolate samples. This was in agreement with the results obtained from the rheological behavior (Table 3), [27] verifying that the chocolate spread control positive and chocolate substituted with pectin from solar was firmer and more elastic. Three theories can be used to explain this phenomenon: First, noted that replacing palm oil with oleo-gels (less stiff fats) decreased the firmness of chocolates, demonstrating that the hardness of chocolate spreads is positively connected with the stiffness of the solid fat phase. Second, revealed that hardness and spreadability are inversely correlated with fat droplet size, i.e., the stronger the droplet-droplet contact, the smaller the droplet size. This would increase the textural robustness of the chocolate matrix by reducing the

mobility of solid particles [18]**.** Third, due to the softening impact of free water in chocolate spreads, a strong negative association between a_w and textural characteristics (firmness and spreadability) was discovered in the study by **Acan et al.** [26]. Spreadability is a relative to consistency and can be defined as the energy requisite spreading the chocolate spread product with a knife tool. The control negative sample had a work of shear value (spreadability) of 1.31 N mm, whereas the other chocolate spread samples was ranged from 1.10 to 1.37 N. mm (Table 3). The firmness of chocolate spread substituted with pectin from orange peel oven and microwave drying methods was decreased (0.6).

Table 3. Flow behavior and texture profile of chocolate spread substituted with pectin from different drying orange peel.

Treatments	Consistency (K) coefficient **dynes.S^n/cm^2**	Flow behaviour **N-Index**	R^2	Apparent viscosity (centi poise) **η_a at 10.2 S^{-1}**	Firmness (N)	Springiness (mm)	Cohesiveness	Gumminess (N)	Spreadability (N*mm)
CP	0.568	5.608	0.99	9.873	0.7	1.83	0.74	0.45	1.37
CN	0.774	5.294	0.99	6.831	0.8	1.33	0.78	0.23	1.31
O	0.447	7.592	0.98	16.984	0.6	1.18	0.83	0.25	1.29
M	0.637	5.294	0.99	8.310	0.6	2.15	0.22	0.04	1.10
S	0.483	7.741	0.98	16.026	0.7	1.93	0.46	0.23	1.37

*Mean ± SD with a significant difference at $p \leq 0.05$.

3.4.3. Rheology of chocolate spread

3.4.3.1 Viscosity of chocolate spread

The measurement of viscosity is a very vital test of the food product's behaviour, ensuring the quality of food products. As shown in Fig. 3, the viscosity of the chocolate spread substituted with pectin extracted from oven dried peels (O) was the highest viscosity compared to all tested chocolate spread samples, followed it the chocolate spread substituted with pectin from solar drying (S), and then chocolate from microwave drying, and the lowest one was the chocolate spread control sample. The increased viscosity of the chocolate spread samples could be attributed to a strong network and interaction between pectin and the other ingredients (cocoa powder, oil, and sugar). Also, it may be due to the high quantities of galacturonic acid residues on a pectin surface, which results in greater repulsive forces between the galacturonic acids units; hence, increased the viscosity in polymers causes them to expand and reside in more hydrodynamic space, and it could generate a continuous phase of particulate suspension and other solid contents that could disrupt this continuous phase and decrease the viscosity. This performance is similar to that of other surfactants agents, which interact with lipid particles in the bulk phase and attraction cocoa butter off their surfaces, making chocolate spread products more viscous, more stretched, stronger, and less susceptible to flow and disruption. [24] (Fig. 3).

As shown in Fig. 3, the slope of shear stress lines decreased with the increase in shear rate. As a general trend, the apparent viscosity of chocolate spread samples decreased with an increase in shear rate for all chocolate spread formulations. The flow behaviour index (n) of chocolate spread samples changed between 5.294 and 7.74. The consistency coefficient (K) value of the chocolate spread control negative, at 0.774 dynes.Sn/cm and the other chocolate spread samples was between 0.447 to 0.637 dynes.Sn/cm. K value improved with the addition of pectin from the microwave as a fat substitute in chocolate spread but decreased with the addition of pectin from the oven and solar drying methods. The pectin particles from oven and solar drying methods with an irregular surface may affect the flow behaviour of chocolate spread. This result agrees with Bonarius et al. [25].

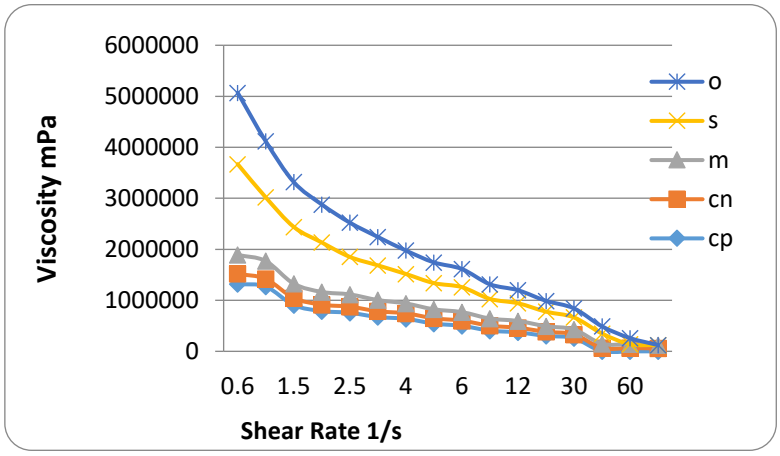

Fig. 3. Viscosity of chocolate spread substituted with extracted pectin

3.5. Sensory evaluation

The mean scores of the sensory properties of chocolate spread substituted with pectin extracted from different drying methods of orange peels (Fig. 4) show that chocolate spread with pectin extracted from microwaves is the most acceptable among the solar, oven, control negative, or control positive samples and was found to be significantly greater at $p < 0.05$ in comparison with all the chocolate samples. Replacement of fat with pectin from microwave-dried orange peel as a fat substitute led to a resultant increase in chocolate smoothness that was significantly greater than that of the control. The panel assessed the characteristics of the chocolate spread samples (taste, texture, flavor, smoothing, and overall acceptability). The flavor of all the chocolate spread samples ranged from 7 to 8.6%, and the flavor of the chocolate with pectin from the microwave-dried peel samples received the highest score.

Other chocolate samples (oven, solar, control negative, and control positive) were less preferred, but the difference was not significant ($P<0.05$). The sensory evaluation of the chocolate spread samples indicated that the chocolate spread (control positive) had a lower taste and smoothness. The spreads prepared with pectin from the microwave as a fat substitute of 50% fat showed improved smoothness, with a score of 8.8 (Fig. 4). This result is comparable to that of **Furlán et al.** [23], who concluded that the manufacture of low-calorie chocolate by replacing fat and sugar with polysaccharides resulted in better organoleptic properties.

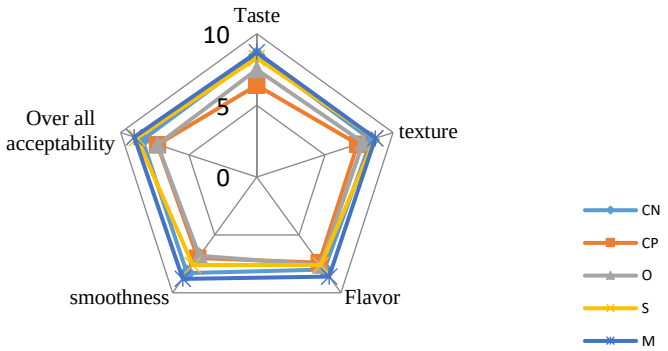

Fig. 4. Sensory evaluation of chocolate spread substituted with extracted pectin. CN (control negative, CP (control positive) O (oven), S (solar), M (microwave).

Chocolate substituted with pectin from the microwave had a greater chocolate flavor score (8.6), which was significantly greater at $P<0.05$ than that of all the chocolate samples. Replacement of fat with pectin from microwave-dried orange peel as a fat substitute led to a resultant increase in chocolate smoothness that was significantly greater than that of the control. These results may be due to the role of pectin as a carbohydrate-based fat substitute in the formation of a gel matrix that mimics fat by binding water with other ingredients and providing softness and a preferred mouthfeel [28, 29].

4. Conclusions

The present study characterized and developed pectin from different dried orange peels as a new functional fat substitute for chocolate spread products. In addition, compared to the control chocolate spread, the substitution of fat with pectin from orange peels increased the viscosity and spreadability of the chocolate spread. Sensory findings indicated that pectin can substitute 50% of the total fat of chocolate spread without affecting chocolate characteristics (appearance, flavor, taste and overall acceptability scores). Additionally, a significantly higher smoothness value was obtained for low-fat chocolate spread with pectin from microwave drying. The results suggest that pectin from orange waste can be used as a fat substitute in chocolate spread products, thus allowing the production of potentially healthier food items. This study indicated that chocolate spread formulated with pectin as a fat substitute can be successfully presented on the market as low-fat chocolate spreads.

5. Data availability

The data will be made available upon request.

6. Conflicts of interest

There are no conflicts to declare.

7. Funding

The work team is truly thankful to the National Research Centre, which funded the project (grantee no. 12010407) to allow for the potential to complete this research as a part of this project.

8. Ethics approval and consent to participate

All procedures performed in studies involving human. Ethical approval certificate number: (20 036).

9. Acknowledgments

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