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The effects of pectin and wax on the characteristics of oil-in-water (O/W) emulsions

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Abstract: The study was aimed to investigate characteristics of emulsion containing pectin, wax, maltodextrin, and carotenoid enriched flaxseed oil by means of stability, rheology, particle size, and low-resolution of time domain nuclear magnetic resonance (NMR) relaxometry measurements. Emulsions were prepared with different carotenoid enriched-flaxseed oil concentrations (6%, 9%, 12%, and 15% w/w) and ratios of maltodextrin/(pectin+wax) (3:1, 6:1, 9:1, and 12:1 g/g). Percentage separation of 12% oil 12:1 ratio of maltodextrin/(pectin+wax) (g/g), 15% oil 9:1, and 12:1 ratios of maltodextrin/(pectin+wax) (g/g) of emulsions was determined as 2.0 ± 0.5%, 4.0 ± 0.5%, and 8.0 ± 0.5%, respectively. No separation was observed in other emulsions. The rheological behavior of emulsions was best described by the power law model. When the concentration of pectin+wax in the emulsion decreased, the *n* values of the emulsions were close to 1, indicating that the fluid behavior approaches Newtonian behavior. Moreover, the emulsion viscosity was observed to increase when pectin and wax concentrations in the emulsion increased. The increase in pectin and wax concentration in emulsions with oil contents of 6% and 9% resulted in a reduction in the average particle size. However, if the oil concentration in the emulsions was 12% or more, the increase in the ratio of maltodextrin/(pectin+wax) (g/g) led to a decrease in the average particle size. NMR transverse relaxation times (T_2) of emulsions were measured and results showed that T_2 values for almost all formulations decreased when the ratio of maltodextrin/(pectin+wax) reduced.

Practical Application: Study results demonstrated that the combination of pectin and wax together with maltodextrin as a filling material could be an alternative way to improve emulsion stability. Findings of this study provided useful guidance for the future studies about the potential use of pectin, wax, and maltodextrin as wall material in encapsulation of oils or in producing edible films.

KEYWORDS
emulsion, nuclear magnetic resonance (NMR), pectin, rheology wax

1 | INTRODUCTION

Flaxseed oil is one of the richest sources of omega-3 fatty acids. It has a chemical composition constituting 9% of saturated fatty acids, 18% of monounsaturated fatty acids, and 73% of polyunsaturated fatty acids (Goyal et al., 2014). Oils with high polyunsaturated fatty acids, such as flaxseed oil, have beneficial effects as they can prevent many

diseases (Vijaimohan et al., 2006). Therefore, flaxseed oil is widely used in food and pharmaceutical industries as salad dressings or supplements due to its health-promoting effects (Goyal et al., 2014).

Emulsions can be defined as heterogeneous mixtures consisting of the droplets of a liquid dispersed in a continuous immiscible second liquid phase (Baloch & Hameed, 2005). The third component, called emulsifier, is used in the emulsions to improve the stability of the system (Dokić et al., 2012). Pectin is a carbohydrate mixture found in the wall cell of many plants and can form stable emulsions at low concentrations (Ngouémazong et al., 2015). The emulsion activity of pectin is due to its ability to reduce the interfacial tension between oil and water phases by forming a protective layer around the oil droplets to prevent them from aggregation (Leroux et al., 2003). However, earlier reports also suggested lower effect of emulsion stabilization of pectin because of the relatively thin hydrated layer unable to provide sufficient steric effects (Maravić et al., 2019; Nakauma et al., 2008). Additionally, macromolecules of pectin are inefficient as a barrier against water vapor due to their hydrophilic capacity (Baümler et al., 2013). Thus, the combination of pectin with other polysaccharides and/or lipids found to be effective in increased emulsion stability and barrier characteristics (Chalapud et al., 2018; Nakauma et al., 2008). Addition of maltodextrin to emulsions systems along with emulsifying agent results in more stable emulsion (Klinkesorn et al., 2004) as maltodextrin can exhibit certain specific stabilizing properties (Maravić et al., 2019). Waxes are esters of long-chain alcohols and fatty acids and are widely used as an edible coating material to improve the water vapor and oxygen barrier properties of food products (Bourlieu et al., 2009). Moreover, the presence of wax crystals might contribute further to the stabilization of the emulsion formed if crystals are in the continuous phase, coming into contact with the interface and adsorbing at the surface of the droplet (Li et al., 2009). Therefore, the emulsifying stability of pectin can be enhanced by the combination of polysaccharides, such as maltodextrin, and lipids, such as wax.

Low-field (LF) nuclear magnetic resonance (NMR) experiments have been utilized to characterize complex food systems, including emulsions (Van Duynhoven et al., 2002). Transverse relaxation parameters of time domain (TD) NMR were used to characterize the physical properties of emulsion systems, textural properties of gels, and physical changes in the film-forming solutions after treatment (Xia et al., 2019; Xiao, 2018). Transverse relaxation time (T_2) depends on the relaxation rate of ^{1}H protons in a transverse plane, which enables characteristics of distinct systems and formulations (Hashemi et al., 2010).

Combination of pectin and wax together with maltodextrin can be considered as suitable systems for producing edible films, coatings, or innovative wall materials for encapsulation of oils. However, there is a lack of studies about the combined effect of pectin and wax on emulsifying characteristics of the emulsion with maltodextrin as a filler. In that respect, this study aimed to investigate the characteristics of oil-in-water (O/W) emulsions containing pectin, wax, and maltodextrin by using different physical methods, such as stability, rheology, particle size distribution, and low-resolution time domain NMR experiments.

2 | MATERIALS AND METHODS

2.1 | Materials

Flaxseed was supplied from the local market and pressed by using a cold press oil machine (Karaerler, NF 100, Ankara, Turkey) for producing the cold-pressed flaxseed oil. Then, flaxseed oil was enriched with carotenoids using microwave-assisted extraction technique to produce enriched-flaxseed oil (CEFO). Microwave-assisted carotenoid extraction was performed according to Elik et al. (2020). The total carotenoid content of CEFO was 397.10 ± 0.8 μg β-carotene equivalent/g oil. CEFO was subjected to the high temperature (80°C) for only 5 min during the homogenization. According to our previous study (Elik et al., 2021), this duration did not cause any degradation of carotenoids. Moreover, the final concentration of carotenoids in the emulsions depended on the oil concentration (6–15%) of the emulsion. Final carotenoid concentration in emulsion varied from 23.83 to 59.57 μg β-carotene equivalent/100 g emulsion.

Low methoxylated pectin (LMP) (Yantai Andre Pectin Co. Ltd., China, type APA 210), sunflower wax (SFW) (Koster Keunen Holland, B.V., melting point: 74–77), and maltodextrin (MD) (Roquette, Lestrem, France, Dextrose equivalent [DE]: 6) were used in emulsion preparation.

2.2 | Emulsion preparation

LMP and MD were mixed with distilled water and stirred at 300 rpm for 30 min at 80°C in order to dissolve LMP and MD completely and to overcome problems for further mixing with wax. Solid SFW was weighed in a beaker and melted at 80°C, while LMP-MD solution was prepared. SFW was mixed with CEFO and then, LMP-MD solution and SFW-CEFO mixture were homogenized using a high shear homogenizator (IKA, T18 Digital Ultra-Turrax) at 25,000 rpm for 5 min at 80°C to prevent the crystallization of wax. The emulsions were cooled down to room temperature (20±1°C) before further analysis.

TABLE 1 The experimental design of the emulsion formulation

CEFO concentration in emulsion (%)	MD/(LMP+SFW) (g/g)	MD (g)	LMP (g)	SFW (g)	Water (g)
6	3:1	18.00	4.00	2.00	70
	6:1	20.57	2.28	1.14	70
	9:1	21.60	1.60	0.80	70
	12:1	22.15	1.23	0.62	70
9	3:1	15.75	3.50	1.75	70
	6:1	18.00	2.00	1.00	70
	9:1	18.90	1.40	0.70	70
	12:1	19.38	1.08	0.54	70
12	3:1	13.50	3.00	1.50	70
	6:1	15.43	1.71	0.86	70
	9:1	16.20	1.20	0.60	70
	12:1	16.62	0.92	0.46	70
15	3:1	11.25	2.50	1.25	70
	6:1	12.86	1.43	0.71	70
	9:1	13.50	1.00	0.50	70
	12:1	13.85	0.77	0.38	70

Abbreviations: LMP, low methoxylated pectin; MD, maltodextrin; SFW, sunflower wax.

The experimental design for the emulsification process is given in Table 1. The amount of solids (LMP + SFW + MD) and CEFO in emulsion were kept constant at 30%. Various LMP/SFW ratios were studied and it was found that 2:1 (LMP/SFW) ratio was the best in terms of stable emulsion formation. Increased ratio of LMP/SFW resulted in flocculation, while decreased ratio caused separation. Therefore, LMP and SFW ratio was kept constant as 2:1 (g/g) in all runs. Various oil concentrations (6–15%) were studied. The oil content kept as 15% maximum in final emulsion and it was referring to 50% of the water free part, which is suitable in case of further coating studies. In addition, various ratios (3:1–12:1) of MD/(LMP+SFW) were studied to observe the effect of high (3:1) and low (12:1) concentrations of pectin and wax to maltodextrin on emulsion properties, while the oil content was kept constant.

2.3 | Stability of emulsion

Immediately after the emulsion preparation, 25-ml aliquots of each sample were transferred to graduated cylinders, sealed, stored at room temperature for 24 h, and the volume of the upper phase was measured after 24 h. The stability was measured by the percentage of separation using following equation:

$$\%\text{Separation} = [(H_1) / (H_0)] \times 100, \quad (1)$$

where H_1 is height of the upper phase and H_0 is initial height of emulsion.

2.4 | Rheological measurements

The rheological behavior of the emulsions was determined in the shear rate range of 0–200 s^{-1} during 60 s at 20°C by using Haake Rheostress RS1 (Karlsruhe, Germany) equipped with TCP/P Peltier temperature controller unit. A plate-plate sensor (diameter 3.5 cm; gap 1 mm) was used throughout the measurements. The shear rate versus shear stress data was analyzed with a Power law model (RheoWin 3, Haake) according to the following equations:

$$\tau = K\dot{y}^{\cdot n}, \quad (2)$$

where τ is the shear stress (Pa), $\dot{y}$ is the shear rate (s^{-1}), K is the consistency index ($Pa.s^n$), and n is the flow behavior index. Apparent viscosity was calculated at 50 s^{-1} of shear rate.

2.5 | Particle size measurements

Particle size analysis was performed using a particle size analysis device (Model LA-950, Horiba, Tokyo, Japan). Briefly, a small amount of sample was dispersed in water using a magnetic stirrer and each measurement was

monitored until successive readings became constant. The mean particle size of the emulsions was evaluated as the volume mean diameter (D_{43}) given in Equation 3:

$$D_{43} = \left(\sum_i z_i {D_i}^4\right) / \left(\sum_i z_i {D_i}^3\right), \quad (3)$$

where n_i is the number of droplets of diameter (d_i).

2.6 | NMR relaxation time measurements

T_2 relaxation times of all emulsions were measured using an NMR system equipped with a permanent magnet of 0.5 T (Spin Core, Gainesville, FL, USA), having a 10 mm diameter radio frequency (r.f.) coil. CPMG (Carr-Purcell-Meiboom-Gill) sequence was used to measure T_2 times. CPMG experiments were performed using a repetition delay of 3 s, echo time (TE) of 1200 ms, 32 scans, and number of echoes changing between 7000 and 11,000 depending on the sample. T_2 relaxation times were calculated by using the formula:

$$S = M_0 \left(e^{-\mathrm{TE/T2}}\right), \quad (4)$$

where S denotes signal and M_0 is the initial net magnetization.

2.7 | Statistical analysis

Statistical comparison of emulsions prepared in different formulations was analyzed by one-way ANOVA followed by a post-hoc Tukey test. Data were analyzed using SPSS statistical software, version 22.0 (SPSS Inc., Chicago, IL, USA). All analyses were performed in triplicate and averaged. Results are expressed as mean ± standard deviation (SD). The difference between the means was determined at 5% significance level.

3 | RESULTS AND DISCUSSION

3.1 | Emulsion stability

Emulsion stability refers to the ability of emulsions to resist changes in their physicochemical properties over time (Hu et al., 2017). The influences of individual factors on the stability of the emulsions were obtained by observing % separation of the emulsions after 24 h. There were 16 emulsions with various combinations of oil, pectin, maltodextrin, and wax (Table 1). The stability study revealed that most of the emulsions were kinetically stable after 24 h. The formation of a small separation layer was observed only in three emulsions. Percentage separation in these three emulsions for 12% CEFO 12: 1, 15% CEFO 9: 1, and 12: 1 (ratios refer to MD/[LMP+SFW]) was determined as 2.0±0.5%, 4.0±0.5%, and 8.0±0.5%, respectively. As it is seen, at lower concentrations of CEFO (6% and 9%), there was no phase separation. However, increased CEFO concentration resulted in phase separation at a limited level only in some of the emulsions.

Pectin is able to stabilize the emulsions by adsorbing onto the oil–droplet interface, thus providing a physical barrier to coalescence (Leroux et al., 2003). However, pectin concentration is very important in terms of providing the emulsion stability as only a modest proportion of the pectin used as emulsifier adsorbs on the droplets (Akhtar et al., 2002). In the present study, one of the major factors which lead to phase separation of some emulsions might be an insufficient amount of pectin. Low quantity (less than 1 wt%) of added LMP is found to destabilize the emulsions, leading to the formation of oil droplets on the emulsions. In other words, the higher amount of LMP in the emulsion diminished phase separation. This is mainly attributed to the specifically higher increase of continuous phase viscosity (Table 2). Similarly, a study investigating emulsion stabilizing properties of depolymerized pectin, oil in water emulsions containing 20% rapeseed oil showed excellent long-term stability at 4 wt% pectin concentration due to forming a relatively viscous emulsion. However, when concentration of pectin decreased from 4% to 1 wt%, it has been reported that there was very extensive serum separation (Akhtar et al., 2002).

Besides LMP, a lower concentration of SFW was observed to cause phase separation in the emulsions containing 12% and 15% CEFO. SFW was completely melted as the emulsification process was carried out at 80°C and therefore, crystals cannot diffuse through the droplets causing coalescence. In the following cooling process, the wax crystallizes near the oil/water interface, which prevents the droplet coalescence and stabilizes the droplets. So, the emulsion stability might also be enhanced with higher SFW concentration along with LMP. A study conducted by Li et al. (2009) has been reported that increasing wax concentration in the emulsion, particularly prepared at high temperature (85°C), significantly improved emulsion stability.

The emulsifying properties of pectin only may not always be sufficient to obtain stable emulsion (Maravić et al., 2019). Preliminary studies also showed that considerable phase separation was observed in all emulsions prepared with only pectin and wax (data not shown). Therefore, MD was included in emulsion system. MD was contributed to the stability of emulsions, which contain 6% and

TABLE 2 Flow behavior (rheological) properties and apparent viscosity values at 50 s^{-1}, temperature = 20°C

CEFO concentration in emulsion (%)	MD/(LMP+SFW) (g/g)	Power law model			Apparent viscosity(Pa.s)
		K (Pa.s^n)	n	R^2	
6	3:1	7.7853 ± 0.0858	0.7723 ± 0.0025	0.9984	3.1939 ± 0.0043[a]
	6:1	1.4971 ± 0.0312	0.8892 ± 0.0046	0.9992	0.9702 ± 0.0028[b]
	9:1	0.6310 ± 0.0254	0.9582 ± 0.0084	0.9998	0.5355± 0.0039[c]
	12:1	0.3869 ± 0.0079	0.9933 ± 0.0031	0.9995	0.3769 ± 0.0031[d]
9	3:1	5.1902 ± 0.0054	0.8137 ± 0.0002	0.9990	2.5037 ± 0.0005[a]
	6:1	1.2767 ± 0.0208	0.9238 ± 0.0004	0.9995	0.9476 ± 0.0170[b]
	9:1	0.2854 ± 0.0022	1.0617 ± 0.0019	0.9993	0.3632 ± 0.0001[c]
	12:1	0.2711 ± 0.0108	1.0023 ± 0.0103	0.9995	0.2733 ± 0.0001[d]
12	3:1	2.2092 ± 0.0069	0.8851 ± 0.0001	0.9996	1.4093 ± 0.0052[a]
	6:1	0.3936 ± 0.0082	1.0353 ± 0.0039	0.9988	0.4518 ± 0.0025[b]
	9:1	0.1740 ± 0.0042	1.0933 ± 0.0039	0.9986	0.2505 ± 0.0022[c]
	12:1	0.1471 ± 0.0139	1.0470 ± 0.0198	0.9963	0.1764 ± 0.0030[d]
15	3:1	1.0113 ± 0.0004	0.9511 ± 0.0003	0.9996	0.8352 ± 0.0013[a]
	6:1	0.2178 ± 0.0059	1.0659 ± 0.0045	0.9988	0.2817 ± 0.0027[b]
	9:1	0.1476 ± 0.0036	1.0016 ± 0.0048	0.9983	0.1485 ± 0.0008[c]
	12:1	0.0872 ± 0.0043	0.9995 ± 0.0107	0.9926	0.0869 ± 0.0007[d]

All the given values are means of three ($n = 3$) determinations ± SD.
[a,b,c,d]Means within a row with different letters for each oil concentration are significantly different ($p < 0.05$).
Abbreviations: LMP, low methoxylated pectin; MD, maltodextrin; SFW, sunflower wax.

9% CEFO. In the emulsions containing 12% and 15% CEFO, however, an increase in MD/(LMP+SFW) ratio (increase in concentration of MD) was not contributed further to the emulsion stabilization. This probably results from that the phase-separated emulsions had lower total water soluble solids (LMP and MD) and the higher concentration of MD was not able to provide the emulsion stabilization alone due to the lower LMP content in the emulsions. It has been reported in the literature that in emulsions containing MD as stabilizers, a sufficient amount of emulsifying agent is required for the production of a stable emulsion because MD is not particularly surface-active (Klinkesorn et al., 2004). Therefore, the combination of LMP and SFW at defined ratios plays an important role in the formation of stable emulsions together with MD as a filling material.

3.2 | Rheological properties of emulsion

Figure 1 shows the rheograms of the flow behavior properties of emulsions prepared in different formulations. It can be seen that the shear stress of the emulsions increases with increasing shear rate. A power law model was used to explain the rheological behavior of the emulsions. The coefficients of determination of the model were found to be very high (0.9926–0.9998). The *K* (consistency coefficient) and *n* (flow behavior index) values of the emulsions at different formulations were calculated by the power law model (Table 2). The *K* and *n* values of the emulsions obtained from 16 different runs are shown in Table 2. The *K* values obtained were between 7.7853 and 0.0872 and *n* values ranged between 0.7723 and 1.0933.

For all CEFO concentration, emulsion with 3:1 MD/(LMP+SFW) ratio had the smallest *n* value, which means that the degree of pseudoplasticity or shear thinning ability of emulsions was the highest. But when MD/(LMP+SFW) ratio increased, the *n* values of the emulsions were close to 1, indicating that the fluid behavior approaches Newtonian behavior. This may be attributed that the higher concentration of LMP led to a reduced collision frequency, reducing the mobility of oil droplets. These results are in agreement with those of other workers who have also observed an increase in pseudoplasticity with an increase in pectin concentration (Baümler et al., 2013; Muhammad et al., 2014). Moreover, pseudoplastic behavior of the emulsions may have promoted by the higher concentration of SFW (along with LMP) due to exhibiting a typical shear-thinning flow of the emulsions which contain wax (Li et al., 2009). However, for a constant CEFO level, the increase in MD ratio led to emulsions to approach Newtonian flow behavior. This was not an unexpected result, since the study conducted by Udomrati et al. (2013) reported that the emulsions which

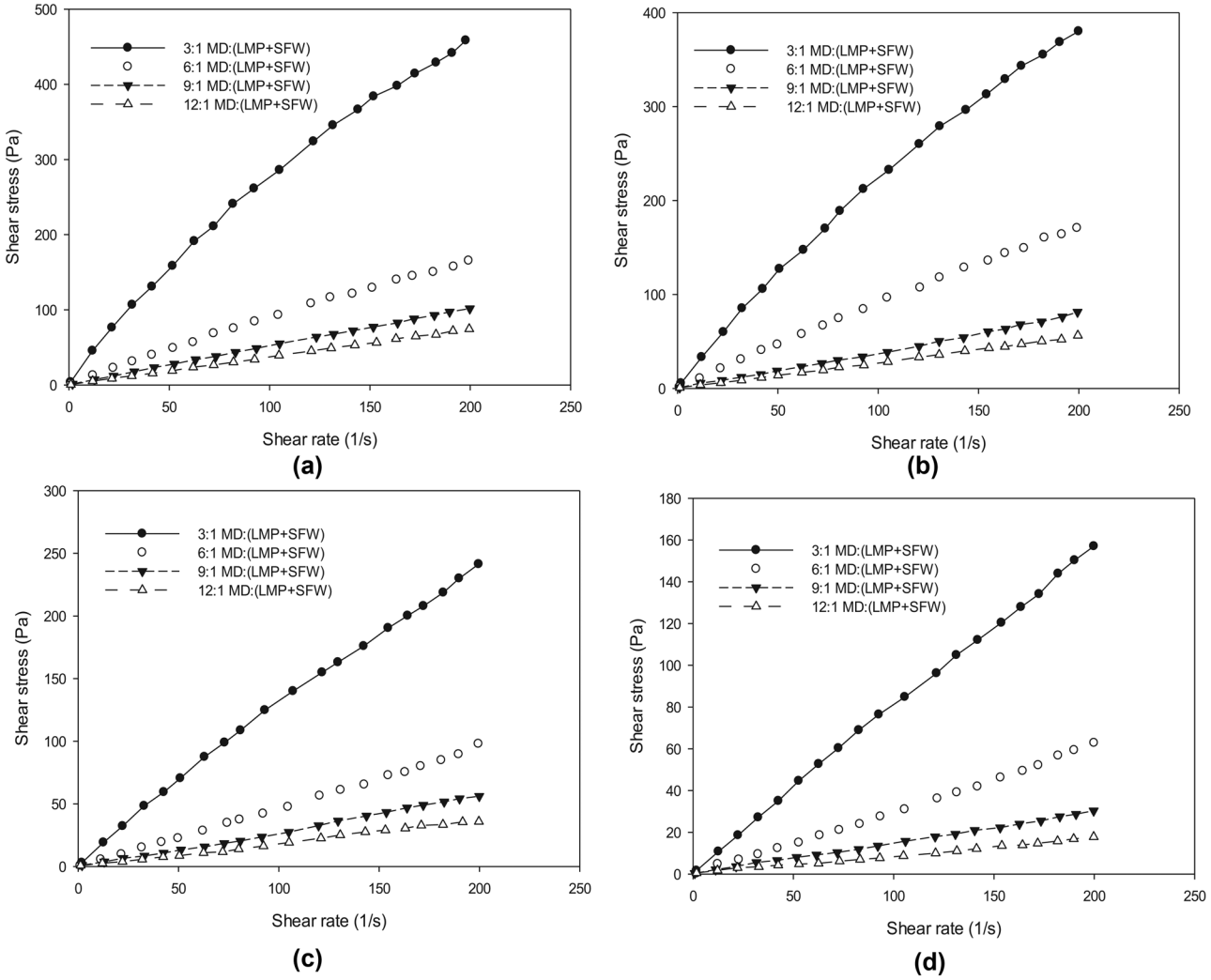

FIGURE 1 Flow behavior rheograms of emulsions at constant temperature: (a) 6% oil concentration; (b) 9% oil concentration; (c) 12% oil concentration; and (d) 15% oil concentration

contain maltodextrin at different concentrations (5–35%) exhibited Newtonian flow behavior.

Apparent viscosities of emulsions at a specified shear rate (50 s^{-1}) were in the range of 0.0869–3.1939 Pa.s. Lower emulsion viscosities were observed with the increase in CEFO concentration. This could be explained with the lower amount of LMP present in the emulsions formed with higher CEFO concentration, for the same total solid content, resulting in a significantly less pronounced thickening effect and thus in less viscous emulsions. Tonon et al. (2011) also verified a decrease of viscosity with the increase in the mass ratio of oil for the same total solid content.

The results also showed that the increase in LMP + SFW concentration in the emulsions containing 6% CEFO led to a significant increase in apparent viscosity. Approximately a three-fold rise in pectin concentration (1.23–4 g) caused about an eight-fold increase in the apparent viscosity of the emulsions (0.3769–3.1939 Pa.s). The emulsions that contained 9%, 12%, and 15% CEFO also showed similar behavior. This is probably due to the fact that increasing the content of LMP increases the viscosity of the emulsion. Similarly, Baümler et al. (2013) and Chalapud et al. (2018) have been reported that an increase in pectin concentration resulted in a significant increase in apparent viscosity. In addition to LMP, an increase in SFW concentration might have led to more pronounced increase in viscosity. As mentioned above, wax starts to crystallize near the oil/water interface during the cooling process following the emulsification. The crystallization of wax may increase emulsion viscosity. These results are in agreement with those of other workers who have also observed an increase in the emulsion viscosity when wax concentration increases (Li et al., 2009). On the contrary, the increase in MD ratio in the emulsions at a constant CEFO level was observed to cause a decrease in apparent viscosity. This decrease in viscosity is basically because of a lower content of LMP+SFW

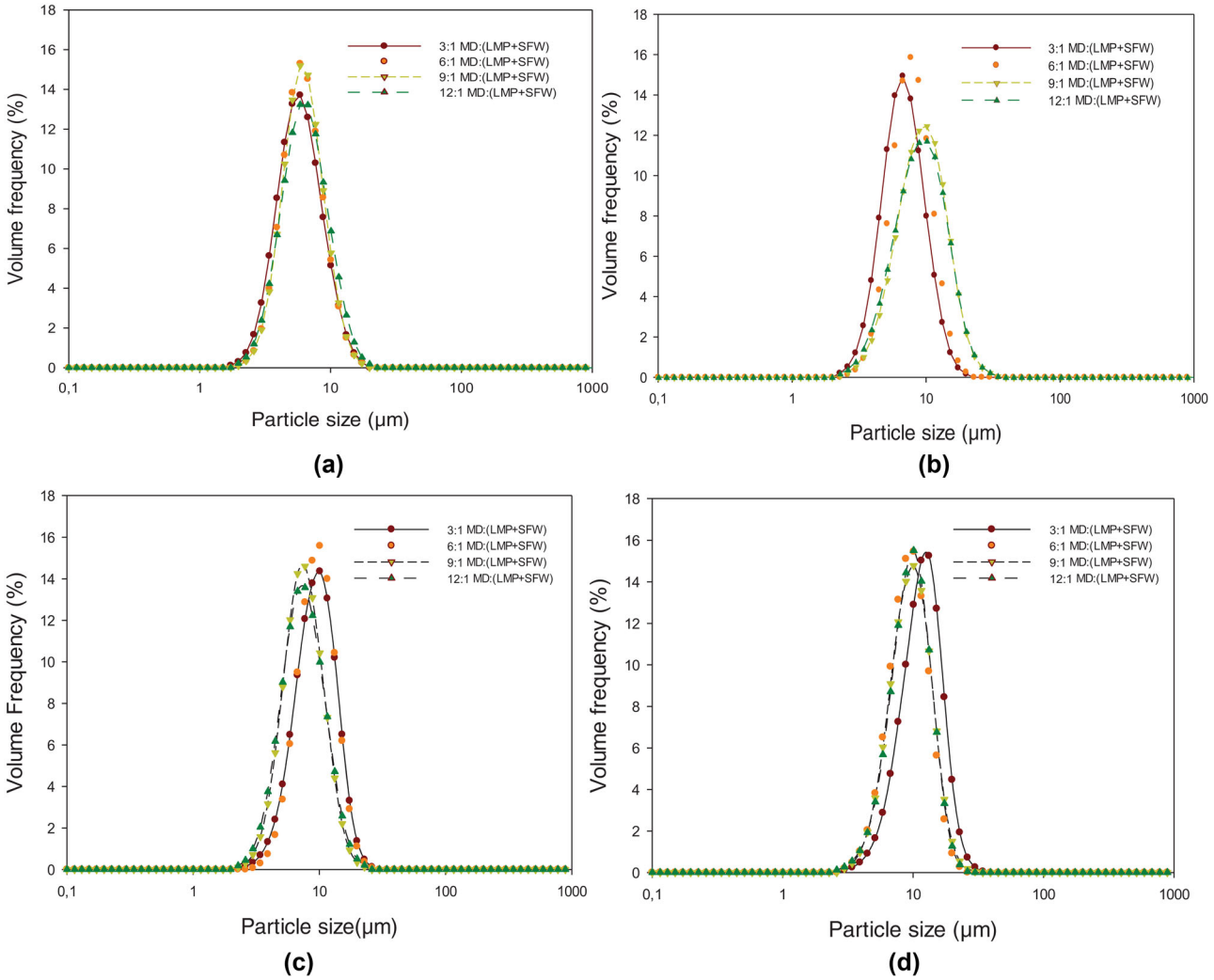

FIGURE 2 Particle size distributions of the emulsions: (a) 6% oil concentration; (b) 9% oil concentration; (c) 12% oil concentration; and (d) 15% oil concentration

with increasing ratio of MD in the emulsions. Even if the total soluble solid is constant in the emulsion, the decrease in the amounts of emulsion stabilizing components, LMP and SFW, might be the main reason for this decrease in the viscosity. So, the water binding and the gel formation abilities of pectin and crystallization effect of wax are the main contributors to the viscosity of the emulsion.

3.3 | Emulsion particle (droplet) size analysis

The droplet size and droplet size distribution of the dispersed phase in the emulsion are important parameters which are directly related to the emulsification process and provide information on emulsion stability. Generally, small droplet size and narrow monomodal droplet size distribution indicate that the emulsion is more stable (Guo et al., 2014). The droplet size distribution of the emulsions was determined to evaluate the extent of emulsion droplet flocculation. It can be seen from Figure 2 that there is no considerable visible difference between the droplet size distribution of emulsions prepared with different CEFO concentration and MD/(LMP+SFW) proportions. All emulsions showed very narrow and uniform droplet size distributions. Results indicated that there was no extensive aggregation between the oil droplets for all emulsions.

The average particle size values ($D_{4,3}$) of the emulsions prepared at different concentrations are given in Table 3. According to the results, the average particle sizes of the emulsions varied in the range of 5.85 and 11.35 μm. At low CEFO concentrations (6% and 9%), it was observed that the average particle size increased with increasing MD/(LMP + SFW) (g/g) ratio. In other words, the increase in LMP +

TABLE 3 Average particle size of emulsions prepared in different formulations

CEFO concentration in emulsion (%)	MD/(LMP+SFW) (g/g)	$D_{[4.3]}$ (μm)
6	3:1	5.85 ± 0.02^{a}
	6:1	6.07 ± 0.13^{ab}
	9:1	6.11 ± 0.17^{ab}
	12:1	6.32 ± 0.12^{b}
9	3:1	6.74 ± 0.04^{a}
	6:1	7.62 ± 0.08^{b}
	9:1	9.32 ± 0.22^{c}
	12:1	9.21 ± 0.15^{c}
12	3:1	9.19 ± 0.18^{b}
	6:1	9.27 ± 0.03^{b}
	9:1	7.41 ± 0.13^{a}
	12:1	7.42 ± 0.37^{a}
15	3:1	11.35 ± 0.26^{b}
	6:1	9.01 ± 0.17^{a}
	9:1	9.41 ± 0.31^{a}
	12:1	9.39 ± 0.32^{a}

All the given values are means of three ($n = 3$) determinations ± SD.

[a,b,c]Means within a row with different letters for each oil concentration are significantly different ($p < 0.05$).

Abbreviations: LMP, low methoxylated pectin; MD, maltodextrin; SFW, sunflower wax.

SFW concentration in emulsions with CEFO contents of 6% and 9% resulted in a reduction in the average particle size. This is probably attributed that the pectin enhances droplet stabilizing mechanism at its higher concentration. This increase in average particle size, when MD/(LMP + SFW) (g/g) ratio increases, is not significant at 6% CEFO concentration, but is more pronounced in emulsions containing 9% CEFO. It has been reported in previous studies that the average particle size decreases with increasing the pectin concentration (Akhtar et al., 2002; Chalapud et al., 2018). However, if CEFO concentration in the emulsions was 12% or more, the increase in MD/(LMP + SFW) (g/g) ratio led to a decrease in the average particle size. Pectin and maltodextrin are water trapping components. When the oil concentration increases, the amount of water soluble solids (pectin and maltodextrin) decreases (from 23.38% to 13.75%). The decrease in water trapping components and the increase in nonpolar component concentration (SFW + CEFO) might have caused the oil droplets to form large particles more readily. Therefore, at higher CEFO concentrations (12% and 15%), the increase in the total amount of solids (LMP + MD) rather than the effect of pectin alone leads to the formation of more stable emulsions, decreasing the average particle sizes.

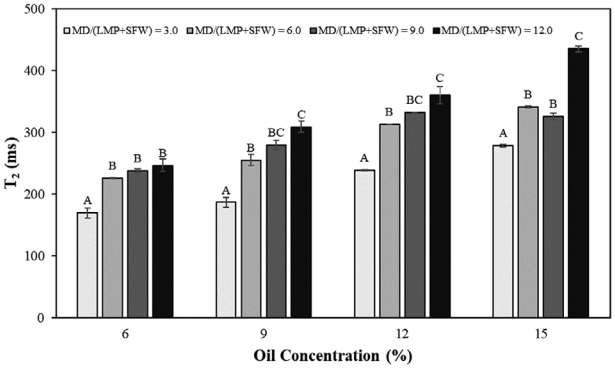

FIGURE 3 T_2 profiles of emulsions. Different letters denote the significant changes between T_2's at each oil concentration ($p < 0.05$). Errors are represented as standard errors

3.4 | NMR relaxation time experiments

NMR measurements indicated that changes in both MD/(LMP+SFW) and oil ratios affected the transverse relaxation behaviors of the emulsion systems (Figure 3). First, decreasing MD/(LMP+SFW) ratio resulted in shorter T_2 values for almost all formulations (169.53–278.91 ms) ($p < 0.05$). At each CEFO content, samples with 3:1 MD/(LMP+SFW) ratio had consistently the shortest T_2's ($p < 0.05$). T_2 of CEFO was measured around 140 ms, which was several order of magnitude shorter than the T_2 of water (Hashemi et al., 2010). Thus, a decrease in T_2 for a constant CEFO level originated mainly from the more homogeneous distribution of oil phase within the emulsions (Mariette, 2009). Especially for 6% and 9% CEFO concentrations, higher LMP content promoted smaller particle size (Table 3) and more pseudoplastic behavior (Table 2) in the emulsions. LMP was able to show its emulsifying abilities at these CEFO concentrations since lower particle size distribution and enhanced pseudoplastic flow behavior were associated with more stable o/w emulsions (Tabilo-Munizaga & Barbosa-Canovas, 2005). LMP was previously described as a thickening agent and an emulsifier (Wan et al., 2019). Different LMP concentrations created distinct characteristics in various emulsion systems (Wang et al., 2018). Therefore, LMP concentration was effective in our study. At 3:1 MD/(LMP+SFW) ratio, LMP exerted an interfacial activity on oil droplets and oil droplets became smaller. The presence of MD contributed to the homogeneous dispersion of these small oil droplets within the continuous water phase. Since shorter T_2 possessing oil droplets were evenly distributed within the system, fast relaxation of oil protons decreased the overall T_2 of the 3:1 emulsions. For higher MD/(LMP+SFW) ratios, samples attained longer T_2's at each CEFO concentration ($p < 0.05$). Lowering the LMP amount diminished the interfacial activities of LMP molecules and produced

more unstable systems as can be observed in particle size results (Table 3). Consistency index values of such emulsion types reached closer to one which implied a less pseudoplastic behavior at lower LMP concentrations ($p < 0.05$) (Sahin & Sumnu, 2006). As shown in Table 2, apparent viscosity values of these samples also decreased proving the less efficient incorporation of oil droplets in the continuous phase of the system. In this case, continuous water phase predominated the system and produced longer T_2's ($p < 0.05$).

Pearson correlation coefficient analysis was performed between relaxation times and other physical parameters studied in the study (particle size, stability, and rheological parameters) of the samples. Results showed that there were significant correlations between T_2 and rheological parameters at 6%, 9%, and 12% CEFO concentrations. First at 6% CEFO, there were strong negative correlations between T_2 and K ($r = -0.993$, $p < 0.05$) as well as T_2 and apparent viscosity ($r = -0.998$, $p < 0.05$). Specific to this CEFO concentration (6%), T_2 and n showed a strong positive correlation ($r = 0.978$, $p < 0.05$). The strong significant negative correlation trend between T_2 and K, n values continued at 9% and 12% CEFO concentrations. Correlation coefficient values between T_2 and K were $r = -0.961$ and $r = -0.956$ ($p < 0.05$) at 9% and 12% CEFO, respectively. Additionally, very similar strong negative correlation values were also detected between T_2 and apparent viscosity values of the samples namely, $r = -0.979$ at 9% CEFO and $r = -0.978$ at 12% CEFO ($p < 0.05$). No significant correlation was found between other parameters ($p > 0.05$).

Another factor that induced more stable emulsions at 3:1 MD/(LMP+SFW) was the high amount of SFW presence in the system. Since molten SFW solidified in the emulsion, presence of these solid particles led to shorter T_2. Closely packed molecular structures of solid materials enabled a more efficient energy transfer between neighboring spins and contributed to shorter transverse relaxations (Marigheto et al., 2007). Moreover, hydrophobic nature of SFW made it easier for its molecules to interact with CEFO in the dispersed phase (Lee, 1999). Impurities and insoluble species in the dispersed oil phase were described as an emulsion stabilizing factor since these particles prevented the oil droplets from ripening and consequent coalescence (Meinders & van Vliet, 2004). At the highest amount, SFW particles were effective to maintain a stable CEFO distribution within the emulsions and these samples attained short T_2's.

CEFO concentration had also crucial impacts on emulsion characteristics and T_2 values. Although CEFO has a very short T_2 compared to water, increasing CEFO concentration revealed longer T_2 values (Figure 3) ($p < 0.05$). Primary reason behind this trend was the decrease in the amount of water soluble solids (LMP and MD) from 23.38% to 13.75% as CEFO concentration increased from 6% to 15%. The amount of water constituting the signal coming from continuous phase was constant throughout the experiments but exchange of water soluble solids with CEFO promoted longer T_2's ($p < 0.05$). In such emulsion or gel systems, continuous phase predominates the overall monoexponential transverse relaxation (Ozel et al., 2017). Longer T_2's at higher CEFO concentrations suggested that T_2 decreasing effect of CEFO diminished due to insufficient incorporation of CEFO droplets within the continuous phase (Vermeir et al., 2014). Rheological measurements were also compatible with T_2 results since especially at 12% and 15% CEFO concentrations, emulsions had more Newtonian character and much lower apparent viscosities (Table 2). In previous studies, MD was used to enhance the physical stability of o/w emulsions because of its viscosity increasing effect of the continuous phase (Kibici & Kahveci, 2019). MD provided a considerable viscosity for high LMP containing samples at 6% and 9% CEFO. However, MD was not able to regulate the viscosity of the samples with 12% and 15% CEFO due to further dilution of its concentration. Increasing oil concentrations also promoted unstable o/w emulsions for some studies having MD as the additional polysaccharide to control emulsion viscosity (Karaca et al., 2013). Obviously, for 12% and 15% CEFO concentrations, MD and LMP concentrations were not enough to maintain emulsion viscosity and cover the oil droplet surfaces, respectively. Consequently, 12:1 MD/(LMP+SFW) samples with 12% CEFO, 9:1 and 12:1 MD/(LMP+SFW) samples with 15% CEFO experienced phase separations. LMP was identified as a high charge density polymer and associated with emulsion stabilizing abilities due to repulsions between oil droplets created by negative charges of LMP on the droplet surfaces (Yuliarti et al., 2019). Under insufficient droplet coverage, weak repulsions between droplets resulted in aggregation of oil droplets and finally phase separation. The longest T_2 (326–435 ms) values were observed for these phase separated samples ($p < 0.05$). Oil and aqueous phases contributed separately to the transverse relaxations of these samples. Therefore, the signal coming from the aqueous phase easily predominated the short signal coming from separated creamy phase.

4 | CONCLUSION

This study revealed characteristics of emulsions containing pectin, wax, and maltodextrin. The results of the experiments where pectin, wax, and maltodextrin were used in the emulsification process indicated good emulsifying properties. Thus, the combination of pectin, wax, and maltodextrin could be an alternative way to improve

emulsion stability. LF NMR experiments proved that emulsion properties could also be monitored by such a noninvasive technique. Besides providing information on composition of emulsions, T_2 results showed that there was a prominent trend between T_2 values and other measured physical properties of emulsions, including particle size, rheology, and stability results. Future studies are needed to evaluate the potential use of pectin, wax, and maltodextrin as wall material in encapsulation of oils or in producing edible films.

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AUTHOR CONTRIBUTIONS

Aysel Elik: Conceptualization; Formal analysis; Investigation; Methodology; Writing-original draft; Writing-review & editing. Derya Koçak Yanik: Conceptualization; Methodology; Supervision; Writing-review & editing. Baris Ozel: Methodology; Writing-review & editing. Mecit Halil Oztop: Methodology; Resources; Supervision; Writing-review & editing. Fahrettin Göğüş: Conceptualization; Funding acquisition; Methodology; Project administration; Resources; Supervision; Writing-review & editing.

CONFLICTS OF INTEREST

All authors declare that there are no conflicts of interest.

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