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Carbohydrate Polymers 73 (2008) 83–91
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Influence of pectin and CMC on physical stability, turbidity loss rate, cloudiness and flavor release of orange beverage emulsion during storage

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Received 18 August 2007; received in revised form 30 September 2007; accepted 5 November 2007
Available online 20 February 2008

Abstract

In the present work, the effect of type and concentration of two hydrocolloids namely pectin (1.5%, 3% and 4.5%) and CMC (0.1%, 0.3% and 0.5%) on physical stability, turbidity loss rate, cloudiness and flavor release of orange beverage emulsion was investigated during six months storage. From the turbidity loss rate results, the orange beverage emulsions containing 4.5% and 1.5% (w/w) pectin showed the highest and least storage stability, respectively. In contrast to the first two months storage, the replacement of both supplementary emulsion components resulted in a significant ($p < 0.05$) increase in turbidity loss rate of all orange beverage emulsions, thus indicating a decrease in capability of beverage emulsion to maintain the cloudiness during storage. The cloudiness of all samples significantly ($p < 0.05$) decreased during storage. The differences between the volatile release behaviors of target volatile compounds from orange beverage emulsions having different formulations indicated that the overall volatile flavor release was strongly influenced by the emulsion composition. This finding may be explained by the interactions between emulsion matrix and volatile flavor compounds. The release contents of most of target flavor compounds were significantly ($p < 0.05$) decreased during storage, especially for the aldehyde compounds studied (i.e. octanal, decanal, neral, geranial).

Keywords: Flavor release; Physical stability; Turbidity loss; Cloudiness; Beverage emulsion; Pectin; CMC; Supplementary emulsion components

1. Introduction

A food emulsion consists of a suspension of small oil droplets in an aqueous continuum (e.g., milk, salad dressings, ice cream mix) or vice versa (e.g., butter, margarine, chocolate) (Coupland & McClements, 2001). Beverage emulsions are also a unique class of emulsions differing from other food emulsions. They are oil in water emulsions that are normally prepared as a concentrate and then diluted into finished products (Tan, 1997). The beverage emulsions must have a high degree of stability in both concentrated and diluted forms (Tan, 1997; Tse & Reineccius, 1995).

Emulsions are thermodynamically unstable systems from a physicochemical point of view, rapidly or slowly separating into two immiscible phases over a period of time (Borwankar, Lobo, & Wasan, 1992) and are stabilized by improvement of their kinetic stability (Bergenstahl &

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doi:10.1016/j.carbpol.2007.11.002

Claesson, 1997; McClements, 1999), where stability may be defined as the resistance to physical changes (Mulder & Walstra, 1974). Meanwhile, the stability of an emulsion can be related to a kinetic concept (Dickinson & Stainsby, 1982), because the long-term stability of a dispersed system implies that the rate and extent of change in its structure and properties are sufficiently low in real time (Tolstoguzov, 1992).

Flavor release is complex phenomena, and several mechanisms can occur: mass transfer, matrix structural hindrance, flavor–matrix interactions, etc. (Roberts, Elmore, Langley, & Bakker, 1996). Factors controlling flavor release from foods are complicated and not well understood. Physicochemical interactions between flavor compounds and food components can affect flavor compound migration in foods. The most important factors which can influence flavor partitioning from an emulsion system are flavor binding, fat level, the rheological properties of the matrix, type and concentration of emulsifier, hydrocolloid, polysaccharide or any thickeners used to produce emulsion (McClements, 1999). There are many other published reports on the flavor release from a variety of emulsion systems (Dickinson, Evison, Gramshaw, & Schwope, 1994; Van Ruth & Roozen, 2000).

Among food hydrocolloids, pectin is one the most commonly used hydrocolloids and gelling polysaccharides in the food industry. In addition to gelling properties, high ester (HE) pectins can be used as an emulsifying agent in various applications such as flavor and vegetable oils emulsions and mayonnaise. In addition to pectin, cellulose derivatives have also gained acceptance for pharmaceutical, cosmetic, food, and packaging uses. They are obtained by replacing the hydroxyl groups with either alkyl or hydroxy-alkyl groups. Carboxymethylcellulose (CMC) is the most utilized cellulose ether. Contrary to pure cellulose, CMC is water-soluble cellulose derivative, but retains the biodegradability of its original natural macromolecule. CMC is used as a thickener, binder, stabilizer, suspending and water-retaining agent in pharmaceutical, food and other major industries (Pilizota, Subaric, & Lovric, 1996).

Beverage emulsions are often stabilized by Arabic gum, xanthan gum or hydrophobically modified starch. The effect of different concentration level of Arabic gum, xanthan gum and orange oil on physicochemical emulsion properties and flavor release from orange beverage emulsion has been mainly investigated in our previous studies (Mirhosseini, Tan, Hamid, & Yusof, 2007a, 2007b, 2007c; Mirhosseini, Yusof, Hamid, & Tan, 2007d). In the present study, the use of two hydrocolloids namely pectin (1.5%, 3% and 4.5%) and CMC (0.1%, 0.3% and 0.5%) as replacers for Arabic gum and xanthan gum was investigated by determining the changes in physical properties and flavor release profile of beverage emulsions during six months storage. In the present study, the emulsion properties considered were emulsion stability, turbidity loss rate and cloudiness. In addition, the other critical emulsion properties namely viscosity, fluid behavior, average particle size, polydispersity index, zeta potential, electrophoretic mobility, conductivity, size index, pH and density have also been investigated in our other studies.

2. Materials and methods

2.1. Materials

Orange volatile compounds, ethyl acetate (99%), α-pinene (99.5%), ethyl butyrate (99.7%), β-pinene (98.5), 3-carene (98.5%), myrcene (95%), limonene (99%), γ-terpinene (98.5%), octanal (98%), decanal (95%), linalool (95%), 1-octanol (95%) and citral (95%) (neral and geranial) were supplied by Fluka (Buch, Switzerland). Arabic gum (food grade) was provided by Colloides Naturels International Co. (Rouen, France). Xanthan gum was donated by CP Kelco (Chicago, USA). CMC was provided by Suzhou Elifa Chemical Co. Ltd. (Suzhou, Jiangshu, China). Citric acid, sodium benzoate and potassium sorbate (p.a. $\geqslant$ 95%) were purchased from Fisher Scientific (Pittsburgh, PA). Valencia cold pressed orange oil and an extra slow set, high methoxy pectin (GRINDSTED™ Pectin CF 120) were provided by Danisco (Danisco Cultor, Aarhus, Denmark).

2.2. Preparation of orange beverage emulsion

In the present study, an orange beverage emulsion having the basic emulsion formulation composed of Arabic gum (20% w/w), xanthan gum (0.3% w/w), orange oil (14% w/w), sodium benzoate (0.1% w/w), potassium sorbate (0.1% w/w), citric acid (0.4% w/w) and deionized water was prepared as a control sample (without supplementary components). In other emulsion formulations, different concentration levels of two supplementary emulsion components namely pectin (1.5%, 3% and 4.5% w/w) or CMC (0.1%, 0.3% and 0.5% w/w) were used as replacer for Arabic gum and xanthan gum, respectively. The proposed concentration levels of two supplementary emulsion components were considered as low, medium and high concentration levels of independent variables in the present study. To prepare the continuous phase, sodium benzoate, potassium sorbate and citric acid were dispersed in deionized water (60 °C) using a high-speed blender (Waring blender 32BL80, New Hartford, USA). While mixing the mixture, Arabic gum was gradually added to the deionized water (60 °C) and mixed for 3 min to facilitate hydration. The Arabic gum solution was kept overnight at room temperature to fully hydrate (Buffo, Reineccius, & Oehlert, 2001).

To prepare the continuous phase, xanthan gum solution was also prepared separately by dissolving xanthan gum in deionized water and then mixed with Arabic gum or pectin solution by using the high-speed blender. While mixing the continuous phase, the cold pressed orange oil was gradually added as the dispersed phase into the continuous phase to provide an initial coarse emulsion. The pre-emulsion was subjected to pre-homogenization using a high shear homogenizer (Silverson L4R, Buckinghamshire, UK) for 1 min and then passed through a high-pressure homogenizer (APV, Crawley, UK) for three passes (30, 28 and 25 MPa) (Mirhosseini et al., 2007a, 2007b, 2007c).

2.3. Analytical methods

2.3.1. Emulsion stability

For emulsion stability test, 15 ml of a prepared beverage emulsion was transferred into 20 ml test tube and stored for 2 weeks at room temperature (25 ± 1 °C). Emulsion stability index (ESI) was calculated as percentage of the initial emulsion height (HE), height of cream layer (HC) and height of the sedimentation phase (HS): $\mathrm{ESI} = 100 \times (\mathrm{HE} - (\mathrm{HC} + \mathrm{HS}))/\mathrm{HE}$. Monitoring test was performed in duplicate samples. The higher emulsion stability was demonstrated by the larger ESI value. The measurement of physical stability test was performed once per two months during storage. Samples were taken at regular time intervals.

2.3.2. Turbidity loss rate

Turbidity loss rate is an indicator to determine the emulsion cloud stability (emulsion breakage) under accelerated (diluted form) condition. It was monitored by measuring the absorbance (loss rate of turbidity) at 500 nm by means of a UV–visible spectrophotometer (Spectronic Genesys™ 10, GENEQ Inc., Montreal, Canada). The beverage emulsions were diluted to 0.25% (w/w) in a 10% sugar solution and stored in 1 L plastic bottles at room temperature before the absorbance reading. Absorbance vs. time data for each sample was fitted to a first-order model (Labuza, Nelson, & Nelson, 1991):

$$\ln A = \ln A_0 - k_1 t \tag{1}$$

where t is the time, A the absorbance at time t, A_0 the absorbance at time 0 and k_1 the first-order rate constant. In this study, k_1 (first-order rate constant) was calculated as the loss rate of turbidity to evaluate emulsion shelf life. The beverage emulsion involving the smaller k_1 value indicated the lower loss rate of turbidity, thus indicating the higher emulsion stability than the emulsion having the larger k_1 value. The procedure for the determination of turbidity loss rate has been described in detail by previous researchers (Buffo et al., 2001). The readings were taken twice daily until absorbance fell to 10% of the initial absorbance value. For data analysis, the absorbance values were the average of three consecutive readings. The loss rate of turbidity of orange beverage emulsions was measured once per two months at regular time intervals during 6 months storage.

2.3.3. Cloudiness

The orange beverage emulsions were diluted (2.5:1000) for the measurement of cloudiness. The measurements were carried out by using a UV–visible spectrophotometer (Spectronic Genesys™ 10, GENEQ Inc., Montreal, Canada). Spectra were obtained over the wavelength range of 190–1100 nm. Cloudiness was also calculated from the absorbance at 660 nm (Garti, Aserin, & Azaria, 1991). Wavelength accuracy of the instrument was found to be approximately ±1.0 nm with wavelength repeatability equal to ±0.5 nm.

2.3.4. HS-SPME analysis

The SPME device, SPME fiber assortment kit No. 4, 20 ml glass vial, teflon coated rubber septa and aluminum caps were supplied by Supelco Inc. (Bellefonte, USA). As shown in our previous study (Mirhosseini et al., 2007d), the extraction procedure using a CAR/PDMS fiber provided the highest extraction efficiency for orange beverage emulsion. In the present study, 10 g concentrate orange beverage emulsion was transferred into a 20 ml serum vial. Subsequently, the vial was sealed with a teflon-lined septa and screw cap that was immersed in a thermostated water-bath (25 °C). After 10 min equilibrium time period, the SPME fiber coated with CAR/PDMS (75 mm, carboxen/polydimethylsiloxane) was manually exposed to the sample headspace for 45 min at 25 °C under stirring mode to reach the equilibrium condition. Consequently, the fiber was immediately inserted into the injector for thermal desorption at 250 °C for 8 min. Each experiment was carried out in duplicate, and the average of two individual sampling was reported for data analysis. Samples were taken at regular time intervals (once per two months) during six months storage.

2.4. Instruments

As mentioned in our previous study (Mirhosseini et al., 2007d), the volatile flavor compounds of Valencia cold pressed orange oil were initially identified by using a Hewlett–Packard 6890N GC system (Wilmington, DE) equipped with Time-of-Flight Mass Spectrometer (TOF-MS, Pegasus III, Leco Corp., St. Joseph, MI, USA). The volatile flavor compounds of orange beverage emulsions were then analyzed by a Hewlett–Packard 6890 GC equipped with a flame ionization detector (FID) and a DB-Wax column (J&W Science, i.d. = 0.25 mm, length = 30 m, film thickness = 0.25 μm, Supelco, MA). The GC injection port was equipped with a 0.75 mm i.d. liner (Supelco) to minimize peak broadening. For GC-FID analyses, the injection was performed for 5 min at 250 °C in the splitless mode. Oven temperature was programmed at 45 °C for 5 min, then ramped to 51 °C at 1 °C/min and held for 5 min at 51 °C then increased to 160 °C at 5 °C/min and finally raised to 250 °C at 12 °C/min and held for 15 min at the final temperature. Helium was used as the carrier gas. Detector temperature was set at 270 C. The experimental conditions have been described in detail in our previous study (Mirhosseini et al., 2007d).

2.5. Statistical analysis

Experiments were performed according to a completely randomized design (CRD). The individual significance probability of each independent variable is shown by *p*-value. The *p*-value provides an objective measure of the strength of evidence which the data supplies in favor of the null hypothesis. The term with higher *p*-value ($p > .05$) was statistically considered to be non-significant ($p > .05$) on the response variable and vise versa. All data were subjected to analysis of variance (ANOVA) using the Minitab v. 13.2 statistical package (Minitab Inc., PA, USA). Least significant difference (LSD) tests were used to compare differences among means.

3. Results and discussion

3.1. Emulsion stability

As shown in Fig. 1, the stability of all orange beverage emulsions was significantly ($p < 0.05$) decreased during storage period. In general, the use of pectin was observed to be more effective on physical stability than CMC except for the emulsion containing 1.5% (w/w) pectin (Fig. 1). The emulsion stabilizing effect of pectin may be explained by the positive effect of pectin on viscosity, pseudoplastic behavior and/or negatively charged ζ-potential (repulsive forces). In fact, pectin is basically an anionic polysaccharide which consists of a linear chain of α-D-galacturonic acid with 1–4 linkages with high molecular weight (~110,000–150,000). This chain is regularly interrupted by some rhamnogalacturonan segments which combine galacturonic acid residues and A-L-rhamnopyranose by a 1–2 linkage which is called esterification (Schols & Voragen, 1996). The presence of a negatively charged polysaccharide (i.e., pectin) can enhance the electrostatic repulsive forces between emulsion droplets. In this case, the similarly negatively charged emulsion droplets repel each other followed by retard the aggregation and flocculation. A hypothesis by Endreß and Rentschler (1999) showed that high acetyl content in the chemical structure of pectin could enhance the hydrophobicity of pectin followed by increase the emulsion stability of pectin-based emulsions. On the other hand, the presence of hydroxyproline rich protein in pectin could also be responsible for emulsion stabilizing effect induced by pectin.

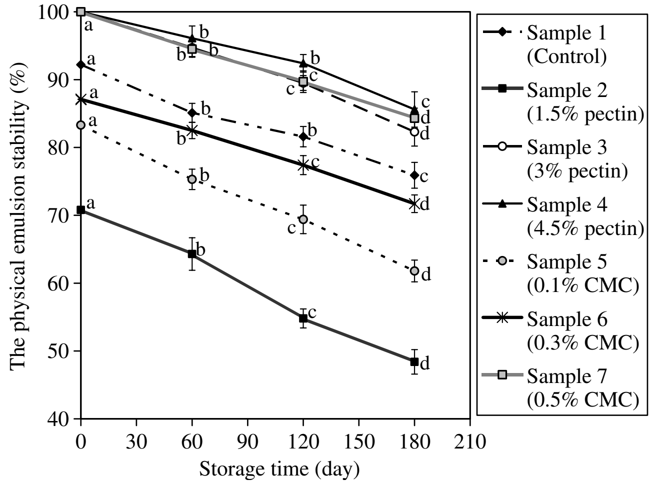

Fig. 1. The changes of physical stability during storage period as function of pectin and CMC concentration.

The slope of the stability curves appeared to be constant in most cases (Fig. 1). The magnitude of curve slopes also exhibited that the stability of beverage emulsion increased with the increase of pectin or CMC concentration. As shown in Fig. 1, the physical stability of pectin-based beverage emulsion was directly proportional to the concentration of pectin. The direct relationship between pectin concentration and emulsion stability has also been pointed out in previous study (Leroux, Langendorff, Schick, Vaishnav, & Mazoyer, 2003). They explained that the emulsifying properties of pectin were most probably due to the protein residues present within the pectin. The authors demonstrated that pectin could be used to produce stable emulsions in the same manner as Arabic gum but at much lower dosage.

By comparing all beverage emulsions, it was found that the substitution of 20% Arabic gum with 3% or 4% (w/w) pectin significantly ($p < 0.05$) improved the physical stability as compared to the control sample having the basic emulsion formulation. Akhtar, Dickinson, Mazoyer, and Langendorff (2002) have also observed that the creaming stability of the pectin-based emulsion improved with increasing pectin content up to 12% (w/w). They also demonstrated that at high pectin concentration, the improved creaming stability was affected substantially by the contribution of the hydrocolloid to the viscosity of the continuous aqueous phase.

The results indicated that the replacement of 0.3% (w/w) xanthan gum with 0.5% (w/w) CMC resulted in a significant ($p < 0.05$) increase in storage stability as compared to the control sample. Previous researchers (Kika, Korlos, & Kiosseoglou, 2007) have also reported that the addition of CMC to the whey protein-based emulsion improved the physical stability. The observation may be explained by the electrostatic repulsion induced by the presence of CMC in the emulsion formulation. On the other hand, CMC is an anionic polysaccharide with a heterogeneous molecular structure consisting both of amphipathic anhydrous glucopyranose (AHG; hydrophilic equatorial sides and a hydrophobic axial plane) and hydrophilic CM units. The presence of both hydrophilic and hydrophobic fractions in CMC structure induces a powerful emulsifying or stabilizing role in the emulsions and colloidal systems. Because of its effective structure, the CMC molecules adsorb to the surface of the droplets produced during homogenization where they form a protective coating that prevents them from aggregating, flocculating and/or coalescing. In addition, the adsorbed CMC can reduce the oil–water interfacial tension, thereby facilitating the further disruption of lipid droplets during homogenization.

3.2. Turbidity loss rate

Fig. 2 represents the capability of emulsion to maintain the turbidity under accelerated condition like an emulsion-based product (i.e. carbonated beverage) during storage. As a rule, the lower degree of turbidity loss rate reflects more capability of emulsion to maintain the cloudiness and higher emulsion cloud stability. In general, the loss rate of turbidity was reversely proportional to the concentration of pectin or CMC. All diluted beverage emulsions except for the ones having 1.5% (w/w) pectin and 0.1% (w/w) CMC were more capable of maintaining the cloudiness of beverage emulsions as compared to the control sample (Fig. 2). The results also showed that the addition of 4.5% (w/w) pectin resulted in the least loss rate of turbidity during six months storage (Fig. 2). Conversely, the highest turbidity loss rate was obtained by the addition of 0.1% (w/w) CMC to the basic emulsion formulation (Fig. 2).

As compared to the control sample, the use of pectin or CMC led to significant ($p < 0.05$) decrease in the index of turbidity loss rate in most cases during first two months of storage. Subsequently, the turbidity loss rate of all diluted samples exhibited an increase, thus indicating a decrease in capability of emulsions to maintain the cloudiness leading to reduce the cloud stability during last four months of storage (Fig. 2). The slope of turbidity loss curves indicated that the changes in turbidity loss rate of pectin-based beverage emulsions was less than that of CMC-based beverage emulsions (Fig. 2). Thus, the addition of pectin was found to be more effective in order to decrease the turbidity loss rate, thus indicating more capability of pectin to keep the desirable cloudiness during storage. As for CMC-based beverage emulsions, the capability of emulsions to maintain the cloudiness significantly ($p < 0.05$) improved with increasing the concentration of CMC (Fig. 2). Genovese and Lozano (2001) reported that the stabilizing effect of CMC in cloudy apple juice was basically due to its electronegativity.

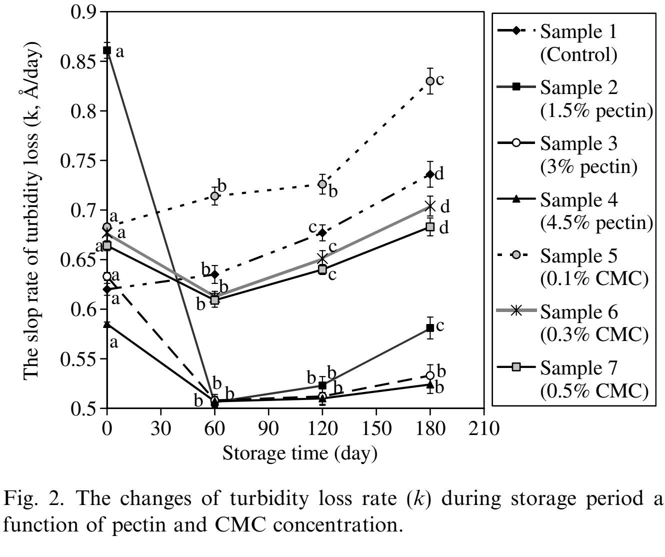

Fig. 2. The changes of turbidity loss rate (*k*) during storage period as function of pectin and CMC concentration.

As demonstrated by Buffo and co-workers (2001), the balance of Van der Waals (attractive), electrostatic (repulsive) and polymeric steric (repulsive) are the main droplet interactions playing a role in the determination of stability of dilute beverage emulsions. The magnitude of repulsive interactions and forces (as barrier energy) between emulsion droplets play a positive role in emulsion stability. On the other hand, the increases in average droplet size and polydispersity index caused over the time due to the mechanisms such as flocculation, coalescence and aggregation are the other reasons responsible for the turbidity loss during storage. In the present study, the addition of different type and concentration of hydrocolloids to the beverage emulsion formulation caused different layer thickness in the interface area of the emulsion systems. This may contribute to different turbidity loss rate during storage. On the other hand, electrostatic repulsion potential can be decreased by a reduction of interface layer thickness over the storage time. Thus, according to the DLVO theory, there is a significant reduction or even disappearance of the energy barrier for retarding the flocculation. The resulting potential falls into the droplets flocculation, the enhancement of creaming velocity and ultimately the loss of turbidity (Friberg, Goubran, & Kayali, 1990). In the present study, the positive role of pectin in preventing the droplet aggregation and/or maintaining the repulsive forces between emulsion droplets during storage appeared to be more effective than CMC in most cases. Thus, it might be concluded that the time of storage caused more negative impact on the emulsifying role of CMC as compared to pectin.

3.3. Cloudiness

The results indicated that the initial cloudiness of orange beverage emulsion increased when the concentration of pectin or CMC was increased (Fig. 3). As expected, the cloudiness of all beverage emulsions significantly ($p < 0.05$) decreased during six months storage depending on the type and concentration of hydrocolloid as well as storage time (Fig. 3). This observation may be due to the changes in average droplet size induced by the aggregation of oil droplets as well as the changes in the refractive index of oil phase and aqueous phase. Our primary results exhibited that pectin-based beverage emulsions had a lager average droplet size and smaller polydispersity index as compared with control sample and CMC-based beverage emulsions (data not shown). The results indicated that pectin-based beverage emulsions except for the one containing 1.5% (w/w) pectin showed a less variability in terms of average droplet size and polydispersity index than control sample and CMC-based beverage emulsions during six months storage (data not shown). These change patterns could be related to the observation that the loss rate of

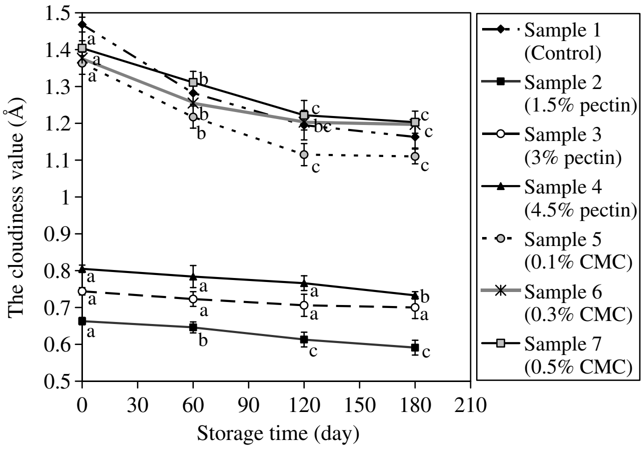

Fig. 3. The changes of cloudiness during storage period as function of pectin and CMC concentrations.

cloudiness in pectin-based beverage emulsions was less intense than control sample and CMC-based beverage emulsions. Ray, Johnson, and Sollivan (1983) and Dłużewska, Stobiecka, and Maszewska, (2006) also reported that the loss of turbidity of emulsions and beverages in the period of storage. Ray et al. (1983) described that this phenomenon may be due to the aggregation of oil droplets and the changes in refractive index of oil phase and aqueous phase. Dłużewska et al. (2006) also explained that the decrease in turbidity of beverage emulsion could be related to the change in refractive index of disperse phase.

As shown in Fig. 3, the addition of pectin to the emulsion formulation was found to be more effective than CMC in order to decrease the loss rate of cloudiness. The slope of cloudiness curves indicated that pectin-based beverage emulsions showed significantly ($p < 0.05$) less loss rate of cloudiness than the other beverage emulsions; while the CMC-based beverage emulsions exhibited a significantly ($p < 0.05$) higher degree of cloudiness as compared to the ones containing pectin during storage (Fig. 3). According to previous researchers (Neirynck et al., 2007), the absorbance of whey protein–pectin emulsion was also directly proportional to the pectin concentration. They explained that the transmission decreased inversely proportional to the pectin content, which points to the fact that pectin slightly increased the turbidity. Genovese and Lozano (2001) also reported the positive effect of CMC on cloudiness of apple juice. The authors illustrated that the addition of 0.4–0.5% CMC to cloudy apple juice resulted in stable turbidity for extended storage periods. Abd-El-Salam, Mahran, Haggag, Mahfouz, and Zaglol (1991) also demonstrated that the addition of CMC (0.05%) increased slightly the turbidity of fermented permeate and natural fruit juices.

3.4. Release pattern of volatile flavor compounds

The results showed that among 14 target volatile flavor compounds studied, the release behavior of β-pinene and 1-octanol was not clearly detectable during six months of storage. This observation may be contributed to their small initial quantity and/or a negative effect of viscosity on the release of these flavor compounds. All beverage emulsions except for the one containing 0.5% (w/w) CMC showed a significant ($p < 0.05$) decrease in the release content of ethyl acetate during first two months of storage. The results indicated that a change in release pattern of ethyl acetate was greatly influenced by type of hydrocolloid added to the emulsion formulation. For instance, the pectin-based emulsions showed a tendency towards an increase in the release content of ethyl acetate during six months of storage. Conversely, the release content was significantly ($p < 0.05$) decreased during last two months of storage. In CMC-based beverage emulsions, the release content of ethyl acetate was greatly influenced by storage time. In these emulsions, it slightly decreased during first two months storage. Subsequently, a significant ($p < 0.05$) increase in the release content was observed during three to four months of storage. Finally, the release content of ethyl acetate greatly decreased ($p < 0.05$) during last two months of storage.

In term of α-pinene, all orange beverage emulsion showed totally different release behavior from each other. The beverage emulsion containing 1.5% (w/w) pectin and the one having 0.5% (w/w) CMC followed a relatively close release pattern in term of α-pinene. This observation showed that the release pattern of α-pinene was not clearly governed neither by emulsion composition nor storage time.

In all beverage emulsions except for the one containing 3% (w/w) pectin, the release content of ethyl butyrate similarly decreased ($p < 0.05$) during the last two months of storage (Fig. 4a). The same as control sample, a decrease in the release content of ethyl butyrate was observed in the beverage emulsions containing 4.5% (w/w) pectin and 0.1% (w/w) CMC during six months of storage (Fig. 4a). Whereas, the beverage emulsion with 3% (w/w) pectin exhibited a significant ($p < 0.05$) increase in the release content of ethyl butyrate as compared with the control sample during six months of storage (Fig. 4a). The substitution of 20% (w/w) Arabic gum with 1.5% (w/w) pectin also resulted in an enhancement in the release of ethyl butyrate during first four months of storage; while the release content significantly ($p < 0.05$) decreased during the last two months of storage. Fig. 4a exhibited that the substitution of 0.3% (w/w) xanthan gum with 0.3% and 0.5% (w/w) CMC also led to the same release behavior in term of ethyl butyrate during six months of storage.

In all beverage emulsions except for the emulsion containing 3% (w/w) pectin, a decrease in the release content of 3-carene was observed during the first and last two months of storage. The substitution of low concentrations of pectin (1.5% w/w) and CMC (0.1% w/w) led to a relatively same release pattern of 3-carene.

In all orange beverage emulsions except for the emulsions containing 1.5% (w/w) pectin and 0.1% (w/w) CMC, a significant ($p < 0.05$) decrease in the release con-

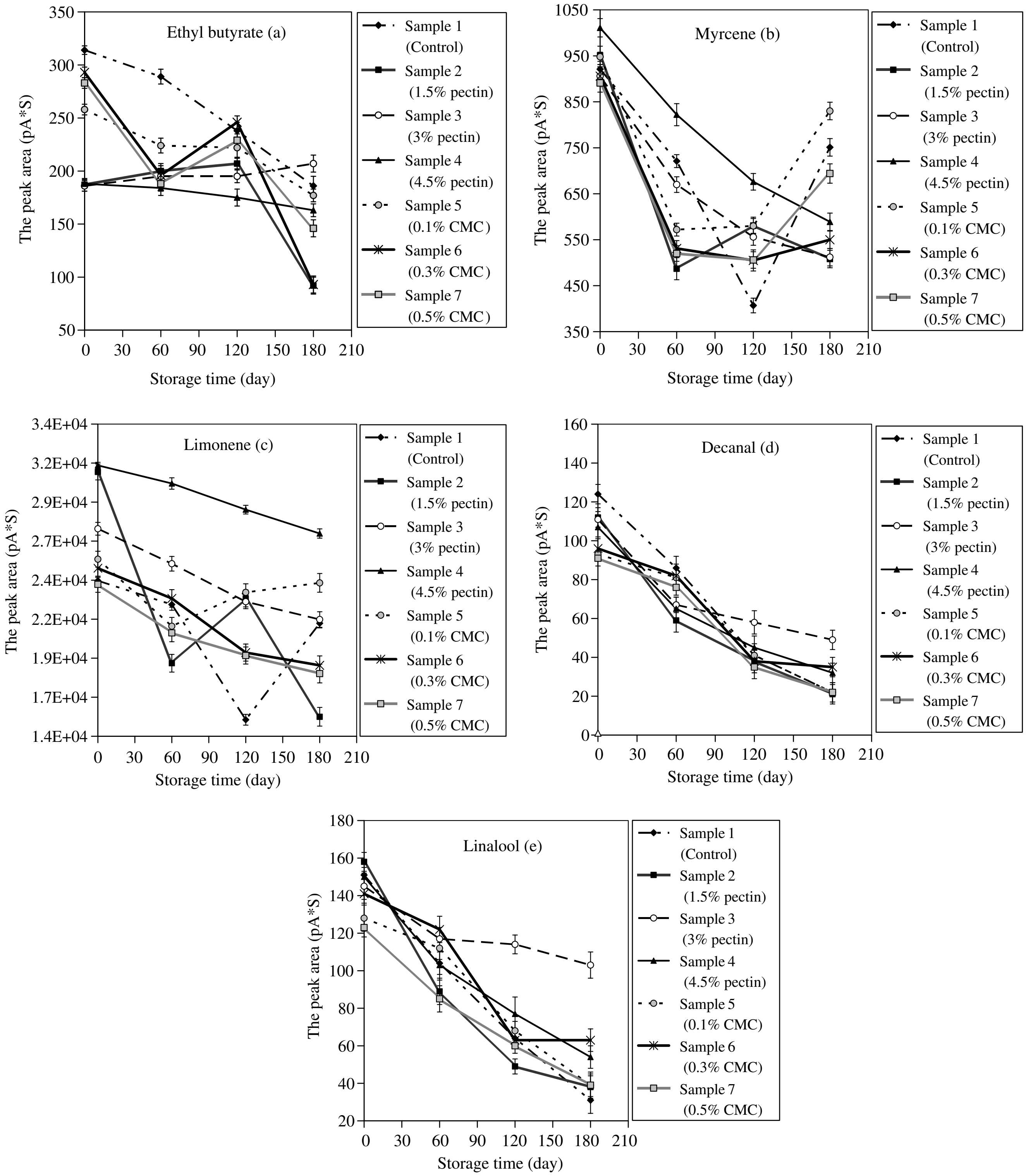

Fig. 4. The changes of release behavior of some of volatile flavor compounds during storage period as function of pectin and CMC concentrations.

tent of myrcene was observed during first four months of storage; while the release behavior of myrcene was greatly influenced by type of hydrocolloid during the last two months of storage (Fig. 4b). In pectin-based beverage emulsions, the release content of myrcene significantly ($p < 0.05$) decreased in most cases during six months of storage. However, the beverage emulsion containing 1.5% (w/w) pectin behaved slightly different from the other pectin-based beverage emulsions in term of release behavior of myrcene (Fig. 4b). Conversely, the control sample and CMC-based beverage emulsions indicated a tendency towards an increase in the release content of myrcene during the same storage period (Fig. 4b).

As shown in Fig. 4c, the release content of limonene significantly ($p < 0.05$) decreased in most cases during storage. The decrease of limonene content may be explained by the reason that limonene might be broken down to α- or β-terpineol through an acid catalyzed hydration (Clark & Chamblee, 1992). In the beverage emulsions containing medium and high concentrations of pectin (3% and 4.5% w/w) and CMC (0.3% and 0.5% w/w), the release content of limonene significantly ($p < 0.05$) decreased during six months of storage. Conversely, two beverage emulsions containing low concentration of pectin (1.5% w/w) and low content of CMC (0.1% w/w) behaved totally different from the other beverage emulsions (Fig. 4c). Subsequently, the release content of limonene significantly ($p < 0.05$) increased during the last two months of storage (Fig. 4c).

The results indicated that the release of γ-terpinene followed a decrease behavior in the control sample during six months of storage. This observation seemed to be in parallel with the decrease in emulsion stability and turbidity during storage (Figs. 1 and 3). The same decrease pattern was observed by the other beverage emulsions except for the emulsions containing 1.5% (w/w) and 0.3% (w/w) CMC. The control sample also showed a significant ($p < 0.05$) decrease in the release content of octanal during the first four months of storage; while an increase in the release of octanal was shown in the control sample during the last two months of storage.

The release content of octanal also showed a decrease in all beverage emulsions during six months of storage. Previous study (Petersen, Tender, & Poll, 1998) also reported the loss of octanal during storage of commercial orange at high temperature. They explained that octanal presumably was oxidized to the corresponding acid. This observation also appeared to be correlated to the reduction in stability and turbidity of beverage emulsions during storage. The changes in the release content of octanal were more intensive during the first four months than the last two months of storage. There was a tendency towards a decrease in the release content of decanal during storage period. As shown in Fig. 4d, the replacement of pectin or CMC did not change the release pattern of decanal as compared with the control sample.

The release content of linalool exhibited a significant ($p < 0.05$) decrease in the control sample during storage period. The substitution of pectin or CMC did not significantly ($p > 0.05$) influence the release pattern of linalool as compared to the control sample during six months storage (Fig. 4e). The decrease in linalool content may be related to its conversion to α-terpineol through a series of steps including a ring closure (Nagy, Rouse, & Lee, 1989). Previous researchers (Petersen et al., 1998) also observed a loss of linalool during storage of commercial orange.

The same observation as decanal and linalool, a significant ($p < 0.05$) decrease in the release content of neral was also shown in the control sample. The addition of pectin or CMC did not significantly ($p > 0.05$) affect the release behavior of neral in all cases except for the emulsion containing 1.5% (w/w) pectin. In term of geranial, all beverage emulsions exhibited the same release pattern as neral, thus indicating a close correlation between the chemical classes of flavor compounds and their release pattern during storage. All orange beverage emulsions except for the emulsion containing 1.5% (w/w) pectin showed a significant ($p < 0.05$) decrease in the release content of geranial during storage period. In term of total flavor compounds, all orange beverage emulsions also exhibited the same release pattern as that of limonene. This may be explained by the reason that limonene was composed of >94% of total flavor compounds of Valencia cold pressed orange oil.

4. Conclusions

The present study demonstrated that the substitution of 20% Arabic gum with high pectin concentration (3% or 4% w/w) resulted in a better storage stability, thus ensuring the adequacy of pectin as a potential replacer for Arabic gum in the formulation of orange beverage emulsion. The results indicated that turbidity loss rate decreased with increasing the concentration of pectin or CMC, thus reflecting a direct relationship between pectin or CMC concentration and their capability to maintain the cloudiness during storage. The CMC-based beverage emulsions exhibited a higher degree of cloudiness as compared to the ones containing pectin. From the flavor release results, the release pattern of target volatile flavor compounds was significantly ($p < 0.05$) affected by the type and/or concentration of hydrocolloid as well as storage time depending on the chemical class of target volatile flavor compound. In most cases, the release content of aldehyde compounds studied (i.e. octanal, decanal, neral and geranial) significantly ($p < 0.05$) decreased during storage. The results exhibited that a decrease in the release content of aldehyde volatile compounds appeared to be in parallel with the decrease in emulsion stability and turbidity.

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