Rheology of Sunflower, Citrus and Apple Low Methoxyl Pectin

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Abstract: Pectin is a hydrocolloid which widely used to form a specific desired texture and viscosity of food products. Therefore, it is important to observe the rheological characteristics of pectin. There are three sources of commercial pectin commonly used in the food industry i.e. sunflower, citrus, and apple. These three pectins were characterized rheologically in this study using MCR 92 Rheometer (Anton Paar, GmbH, Germany). The sunflower pectin had the highest viscosity and consistency index number (k) compared to citrus and apple pectin. The sunflower pectin exhibited shear-thinning behaviour at, especially at concentrations 2.5% and 3.0% (*i.e.*, with flow behaviour index number (n) was less than 1.0). The higher the pectin concentration, the lower n value obtained with the increased k value. The information found in this study is considered useful for consumers, industry, and researchers especially when pectin is used to modify the rheological properties of food products.

1 INTRODUCTION

Pectin is a natural food additive which can be used as a gelling agent, emulsifier, stabiliser, and thickening agent (Yapo, 2011). The potential of pectin is closely related to its chemical characteristics. Commonly, the pectin structure consists of main chain *(1→4)–β-D-GalA* (galacturonic acid) which is partly esterified by methyl alcohol or acetic acid at the carboxylate acid side (Round et al., 2010). Pectin has varied molecular weights (MWs), ranging from 60 to 130,000 g mol^{-1}. The molecular weight of pectin depends on the number of glucose-side and esterification level of methyl (Khan et al., 2012). Commercial pectin, in general, has at least 65% galacturonic acid content (May, 1990). There are two types of commercial pectin that commonly used: High Methoxyl Pectin (HMP) and Low Methoxyl Pectin (LMP). Degree of esterification (DE) number for HMP is more than 50 %, while LMP is less than 50% (De Oliveira et al., 2015; Sundar Raj et al., 2012). LMP produced from orange and apple is a derivative of its HMP (Fertonani et al., 2009; Morales-Contreras et al., 2020). Meanwhile, LMP produced from sunflower seed is naturally formed (Iglesias & Lozano, 2004; Miyamoto & Chang, 1992). Different kinds of pectin have different properties due to variation of structure in methyl ester chain located along the main chain. Naturally, DE number of each pectin is different for different resources (plant species), plant maturity, and cell wall properties (Round et al., 2010). Varied pectin properties might also be due to differences in extraction methods and post-extraction treatments (Constenla & Lozano, 2003).

Water-soluble pectin has potential as a thickening or stabiliser agent for water-based food products (Razak et al., 2018). The thickening process is the transition condition from free flow behaviour molecules (dilute) to binding molecules in a network (Saha & Bhattacharya, 2010). Each pectin has different concentrations to reach certain rheological consistency, which is related to the chemical structure of each pectin (Alba et al., 2015; Axelos et al., 1989; Dimopoulou et al., 2019; Morales-Contreras et al., 2020). The mechanism of pectin as a thickening agent is closely related to viscosity. Hydrocolloid molecules flow freely at a dilute solution and show no thickening properties. Meanwhile, at viscous solution, molecules interact with each other, and the flow is limited (Saha & Bhattacharya, 2010).

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Table 1: Properties of pectin.

	Sunflower (M)	Citrus (C)	Apple (A)
Degree of esterification (%DE)	31.2	29.34	27.6
Degree of amidation (%DA)	0	19.2	22.6
Galacturonic acid (%GA)	85.45	88.7	65

The thickening process of pectin is also related to the ability of pectin to form a gel, emulsify and stabilise (Ngouémazong et al., 2015). Gel forming capacity in LMP is not dependent on the glucose content of the product, and not pH-sensitive, the same as HMP. Based on the previous study by Yang *et al.* (2018), LMP could form a gel ranging from acidic (pH 3.5) to saline condition (pH 9.5), by the addition of divalent cation such as calcium. One of the main purposes of pectin used in the food product is to form a specific food texture, which makes rheological study important. Prior to product formulation, it is crucial to know the rheological characteristics of pectin. Raw material selection is a crucial factor to make the desired product. The important rheological parameters, especially in the liquid system, are flow behaviour index (n) and consistency index (k). It is generally known that the greater the concentration and viscosity of pectin, the higher the shear thinning properties. However, the effect of concentration is unique for each pectin. Therefore, the purpose of this study was to investigate the effect concentration and source of LMP (*i.e.* sunflower, citrus, and apple) on the rheological properties of pectin solution. This study can be used as a source of information to choose suitable pectin source for certain food product formulation.

2 MATERIALS AND METHODS

2.1 Materials

The three sources of pectin used in this study were sunflower, citrus and apple with the specifications as indicated in Table 1. The pectins were purchased from Hunan Zhengdi Biological Resources Development Co., Ltd., China. The solvent used was deionised water.

2.2 Preparation of Pectin Solution

Pectin from each source was dissolved in 100 mL deionised waters, stirred overnight at room temperature. For each, there were eight concentrations prepared (*i.e.*, 0.1, 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 % (w/v)).

2.3 Viscosity Measurements

The flow properties of prepared pectin samples were measured by using MCR 92 Rheometer (Anton Paar, GmbH, Germany); with geometric cone and plate (diameter = 50 mm and angle = 2 °). A sample of 5.0 mL was applied on the surface of the plate with a 0.1 mm gap between plates. The instrument was operated at shear rates of 0.01 - 1000 s^{-1} and temperature of 25 °C (Kontogiorgos et al., 2012). The data points were set as 51 points, logarithmic ramp duration, 10 s initial time and 1 s final time. The data set value was at a shear rate variable, logarithmic ramp profile, 0.01 s initial time and 1000 s final time. Flow curve analysis was done using RheoCompass^{TM} software, and the measurement of each sample was repeated twice.

The information obtained were shear rate, shear stress, and viscosity of the samples used to determine flow behaviour. Experimental data were fitted using the power-law model (Equation 1), where τ is shear stress (Pa), ($\dot{\gamma}$) is the shear rate (s^{-1}), n is the dimensionless flow behaviour index value and k is the consistency index (Pa.s^n). Slope of flow behaviour curve plotted as log τ vs log $\dot{\gamma}$ shows the flow behaviour index (n). The results show Newtonian typical flow when $n = 1$, shear-thinning if $0 < n < 1$ and shear thickening fluid if $n > 1$ (Rao, 2007; Steffe, 1996).

$$\tau = K\,\dot{\gamma}^{n} \qquad (1)$$

2.4 Statistical Analysis

The experimental design of this study was factorial completely randomised design (CRD), and all tests were repeated in duplo ($N = 2$). Statistical research was carried out using two-way variance analysis (ANOVA) to evaluate significant differences between mean values, and continued by Duncan test.

3 RESULT AND DISCUSSION

3.1 Flow Curve Behaviour

The rheological properties indicate the ability of pectin to fulfil a specific role in modifying the food texture. One of the important parameters in rheological studies of pectin as a thickening agent is viscosity (Saha & Bhattacharya, 2010). The data of pectin viscosity as function of shear rate measured at different concentrations are shown in Figure 1. It was found that increased concentration leads to the increasing flow resistance in sunflower (M), citrus (C) and apple (A) pectin, as indicated by higher value of viscosity. This condition could be attributed to the interaction between dispersed solids which caused limited movement of water (Saha & Bhattacharya, 2010; Vinogradov & Titkova, 1968).

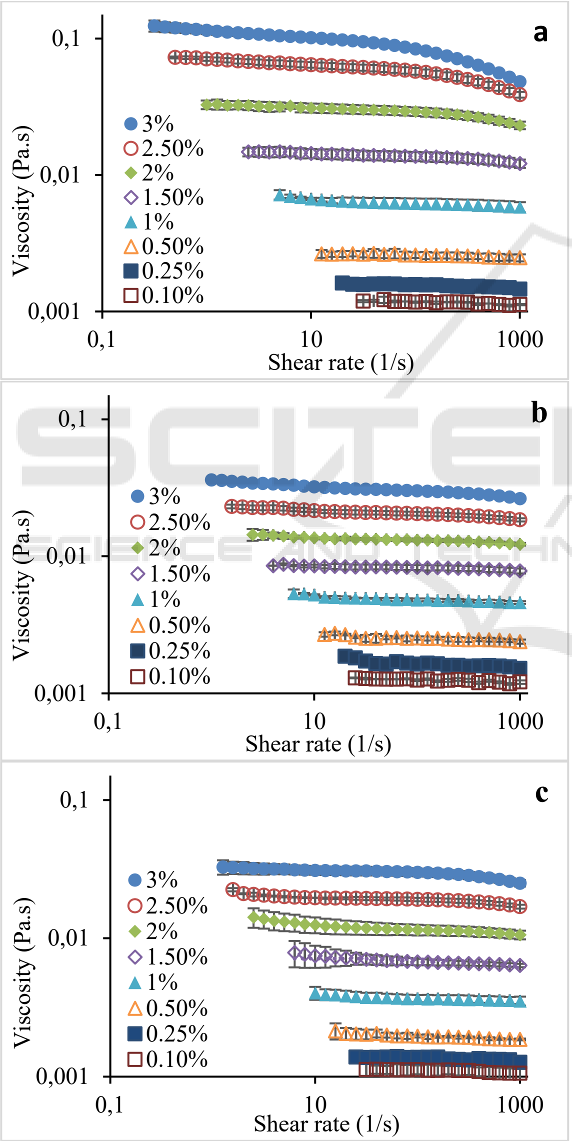

Figure 1: Viscosity of pection solution as function of shear rate for (a) sunflower, (b) citrus and (c) apple.

In general, at low shear rates, there is a plateau or Newtonian flow of the pectin. When the shear rate increases, or after passing the critical shear rate, the viscosity starts to decrease or displays shear thinning behaviour. At high concentrations, the Newtonian flow region is shorter than at low concentrations. The lower the concentration, the longer the Newtonian flow region and could extend to the highest shear rate. At low concentrations, the dominant flow pattern is Newtonian and there is no indication of viscosity decrease under high shear rate conditions. At low concentrations, pectin has Newtonian properties, shown by the constant viscosity as the shear rate increases. This condition can be linked to the fact that of coil disentanglement due to shear forces is lower than the rate of coil re-entanglement in all shear rate range. Therefore, the shear force has no significant effect on the decrease in viscosity. This condition is similar to the study conducted by Li *et al.* (2013), Chan *et al.* (2017) and Kalegowda *et al.* (2017), where at low shear rates, pectin shows a Newtonian flow pattern and become shear thinning at higher shear rates. The ability of the coil to reconfigure a network can be based on the ability of pectin to form hydrogen bonds. LMP at low concentrations have more probability to form hydrogen bonds and consequently increasing re-entanglement rate of the coil and thus, viscosity decrease was not observed.

3.2 Pectin Rheological Parameters

Quantitatively, Newtonian and non-Newtonian flow patterns can be described using the power-law model (Equation 1), extracted from the relationship between shear rate and shear stress (Figure 2). Power law model is widely used in viscosity modelling in food processing during handling, heating, or cooling (Rao, 2007; Steffe, 1996). Coefficient of determination obtained from the relationship between shear rate and shear stress are shown in Table 2. The results showed that the power-law model describes the flow behaviour of all three pectin types. This is indicated by the coefficient of determination which is close to one. The results provided confidence in extracting the fitting parameters (*n* and *K*) from the model for further analysis.

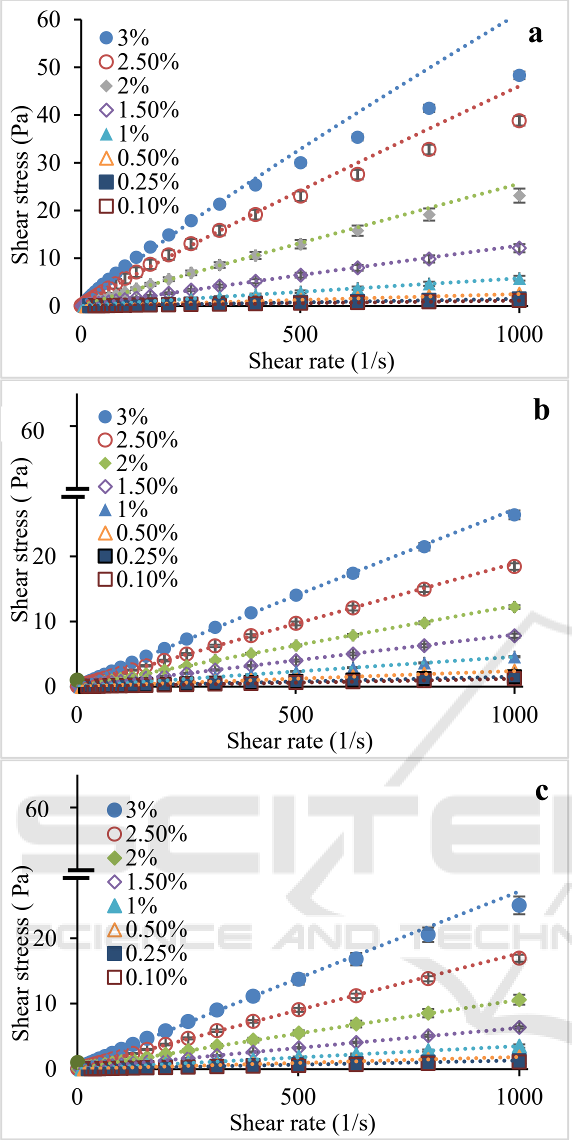

Figure 2: Flow curves of pectin solutions ((a) sunflower, (b) citrus, and (c) apple)) measured at different concentrations. Dotted lines are Power Law Model used to describe the experimental data.

Figure 3 shows the effect of concentration of the flow behaviour index (Figure 3a) and consistency index (Figure 3b) of pectin solution. Flow behaviour indexes (*n*) at various LMP concentrations decreased as pectin concentration increased. A behaviour of typical Newtonian-to-slightly shear thinning was observed, as shown by the value of n <1. Based on two-way ANOVA, it was known that the concentration of pectin and their interactions had a significant effect on *n* value. Pectin solutions showed more shear thinning behaviour at higher concentration. For example, at concentrations of 2.5% and 3.0 % for sunflower pectin, showed the smallest flow behaviour index value which was significantly different from other concentrations. Whereas at low concentrations, the results showed that *n* values close to one (less shear thinning). Pectin solution practically has Newtonian characteristics when the concentration was below 1% w/v.

Table 2: Coefficient of determination (R^2) of linear regressing between shear rate and shear stress for sunflower, citrus and apple pectin.

Conc. (%)	*Coefficient of determination (R^2)*		
	Sunflower	Citrus	Apple
3	0.9985	1	0.9998
2.5	0.9993	1	0.9999
2	0.9997	1	0.9999
1.5	0.9999	1	0.9999
1	0.9999	0.9999	0.9999
0.5	1	0.9999	0.9999
0.25	0.9999	0.9996	0.9998
0.1	0.9999	0.9999	0.9999

Other study by Kontogiorgos *et al.* (2012) showed similar observation. Okra pectin showed Newtonian properties at a concentration below 1% w/v, and when the concentration increased, it exhibited shear-thinning properties. Whereas in the study of okra fruit pectin DE 58% by Methacanon *et al.* (2013) showed Newtonian flow behaviour at concentrations below 0.4% w/v. Based on the type of pectin used, sun flower pectin (M) had the lowest *n* value and was significantly different from the other two pectin sources. At 3% concentration, *n* value of sunflower pectin showed the lowest value (0.9021) or displayed more shear-thinning behaviour than the other two pectin sources ($p < 0.05$). The overall *n* values for all pectin were close to one: M (0.9021- 0.9838), C (0.9608 - 0.9855), and A (0.9599- 0.9817). The shear-thinning behaviour of pectin solutions can be linked to the inter-polymer chain. At high shear rate, the formation rate of polymer entanglements is smaller than the breaking rate. This causes the number of cross-link bonds between polymers to decrease. Moreover, the breakdown of previously formed polymer-polymer hydrogen bonds reduces the final polymer dimension. Thereby, the water or solvent can easily flow out of the entangled polymer coils (Thirawong et al., 2008). On the other side, the aggregation that occurs between pectin polymers is due to the formation of polymer-polymer hydrogen bonds. This eventually leads to the formation of a stable network that can trap water, leading to the increase of viscosity (Karimi et al., 2016).

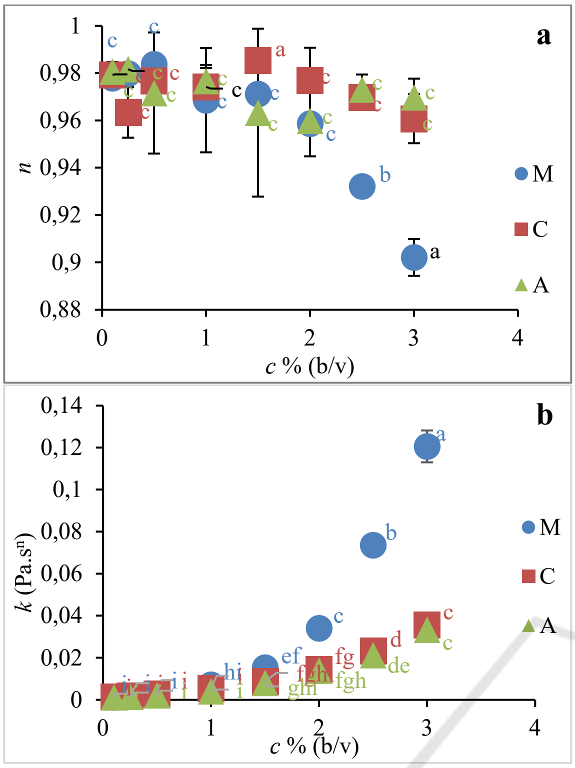

Figure 3: Flow behaviour index (***a***) and consistency index (***b***) of pectin solution.

Two-way ANOVA showed that source of pectin, concentration, and polymer interaction significantly affected the consistency index (*k*) (Figure 3b). In general, a higher concentration of pectin solution yields higher *k* value, because at higher concentration, the polymer chains overlap, so it increases competition for free water access, leading to stronger binding of the polymer chains. The overall *k* values for all sources of pectin as follows: M (0.0013 - 0.1206), C (0.0014 - 0.0357) and A (0.0012- 0.0334). Sunflower (M) pectin had the highest *k* value and was significantly different from the other two pectin sources, especially at 3% concentration (k = 0.1206 Pa.s^n) ($p < 0.05$). This result was corresponding to the viscosity profile of sunflower pectin as shown in Figure 1.

Pectin M, C and A had different degrees of esterification (DE), degrees of amidation (DA) and galacturonic acid concentrations (GA) (see Table 1). Differences in rheological properties of each source of pectin can be influenced by chemical factors, such as content of anhydrous galacturonic acid (AGA), degree of methylation (DM) or DE, molecular size, distribution of carboxyl groups, and charge of pectin molecules (Constenla & Lozano, 2003; Cullen, 2012; Singh & Heldman, 2009; Zhong & Daubert, 2013). In some cases, the viscosity can be affected by physicochemical properties and temperature of the material (Cullen, 2012; Singh & Heldman, 2009; Zhong & Daubert, 2013). Based on the chemical properties of the pectin used (Table 1), the pectin with the highest to lowest DE was M, C and A pectin. Pectin A had higher DA than pectin C, while pectin M had no DA. Based on the results, it can be shown that there was a tendency for higher DE and low DA to have a higher fluid consistency. Based on existing study, higher DE showed higher intrinsic viscosity (Morris et al., 2000; Pippen et al., 1953; Yoo et al., 2006), but this condition occurred at the same pectin source. Based on these results, it can be seen that the chemical structure of pectin sourced from sunflowers has the potential to increase viscosity higher than the other two.

The information on dynamic viscosity can provide information regarding material flow characteristics, especially to mitigate product handling during processing at food industry. In general, sunflower pectin had a higher viscosity as compared to citrus and apple pectin. Thus, it can be considered for product formulation which requires moderate-to-high viscosity level. In addition to this, one must also consider the power input or energy needed during mixing process of such highly viscous solution.

4 CONCLUSIONS

Source and concentration of pectin were shown to have influence on the rheological properties of pectin-containing solution. In general, pectin solution showed Newtonian behaviour at very low shear rate distinctly exhibited shear thinning behaviour at higher shear rate. Shear thinning behaviour of pectin solution was more pronounced at higher concentrations. Sunflower pectin had the lowest flow behaviour index and displayed vivid shear-thinning behaviour compared to other sources. Herein, sunflower pectin might be useful as an alternative thickening agent for formulating viscous food products.

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