

**RHEOLOGICAL METHOD FOR DETERMINATION OF CRITICAL  
CONCENTRATION OF PECTIN DISPERSION – A REVIEW**

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**Abstract**

Pectin critical concentration is a parameter that determines the effectiveness of pectin as a thickening and gelling agent. A lower critical concentration indicates the ease of a particular hydrocolloid to thicken the solution or form gel. From the industrial point of view, this is of interest as it entails a lower production cost. This review examines the critical advantages and limitations of various methods in determining the rheological-based critical concentration of pectin. The methods discussed in this work were based on dynamic viscosity flow pattern ( $\eta$ ) plotted against shear rate ( $\dot{\gamma}$ ), apparent viscosity ( $\eta_{app}$ ), zero shear viscosity ( $\eta_0$ ), and consistency index ( $K$ ) plotted against concentration ( $c$ ), and specific viscosity ( $\eta_{sp}$ ) plotted against the dimensionless number ( $c[\eta]$ ). Empirically, these methods have been shown to successfully predict critical concentrations of pectin. However, models that can be used generally for each type of pectin flow are (1)  $\eta_0$  plotted against  $c$  and (2)  $\eta_{sp}$  plotted against  $c[\eta]$ . Conclusively, this review provides information for industries and researchers to select a suitable method for analyzing the critical concentration of pectin where variations might be present due to different sources and methods for extraction.

**Keywords:** critical concentration, pectin, rheology, viscosity

**Introduction**

Pectin is a hydrocolloid often used by the food and pharmaceutical industries as a gelling agent (Pan *et al.*, 2021), emulsifier (Zhang *et al.*, 2020), stabilizer, and thickener (Agudelo *et al.*, 2014; Yapo, 2011; Erçelebi and Ibanoglu, 2009; Codex, 2018). The demand for pectin production shows an increasing number. This could be seen from the global pectin production in 2009 of 30000 tonnes/year then

increased to 60000 tons/year in 2015 (Ciriminna *et al.*, 2016). Pectin is one of the most widely used hydrocolloids because pectin provides not only functional (Sitanggang *et al.*, 2010; Sakoei-Vayghan *et al.*, 2020) but also health benefits (Figuroa and Genovese, 2018; Tan and Nie, 2020; Muñoz-Almagro *et al.*, 2020; Liu *et al.*, 2020).

The use of hydrocolloids in the food industry is closely related to the rheological properties and appearance of the product (Laguna *et al.*, 2020; Funami *et al.*, 2012). The long-chain polymer structure in hydrocolloids is water-soluble and can swell in it, thus could potentially change the rheological properties of the solution (Li and Nie, 2016). One of the essential parameters that determine the functional quality of pectin is the critical concentration ( $c^*$ ) (Rodrigues *et al.*, 2020). If the viscosity can only represent coil interaction or coils-solvent interaction when it is deformed, the critical concentration not only defines the conditions of the interaction but also the concentration at which the interaction between the coils begins. The interaction between the coils occurs due to the total volume occupied by the polymer, which almost fills the total volume of the solution (Sayah *et al.*, 2016). The easier the coils interact, the lower the critical concentration produced. The critical concentration may reflect characteristics that are not visible in pectin. Indirectly, the critical concentration is the appearance of the molecular particles and the appearance of the interaction between internal and external factors present in the solution. Knowledge of critical concentration is important in analyzing flow dynamics (Rodrigues *et al.*, 2020), transportation of pipeline systems in the industry, and as a reference for using the amount of pectin concentration to achieve a certain degree of viscosity.

In general, polymers are in the form of long coils that can interact with solvents and interact with each other at certain concentrations, so the determination of the critical concentration of pectin can also be applied to other polymers, even though they have different rheological properties. Determination of critical concentration has variations in methods, due to differences in sample sources and preparation methods, types, and specifications of instrument used. One of the fatal problems in predicting critical concentration is the assumption that all predictive methods can be used for every type of pectin. Not all methods can be used for all types of pectin because each material has specific flow behavior that is influenced by intrinsic and extrinsic factors. This is based on Newton's viscosity law which states that there are two kinds of flow, Newtonian and non-Newtonian (George and Qureshi, 2013). Flow behavior has an enormous effect on viscosity which has an impact on critical concentrations. When the prediction model used does not match the flow behavior, it will be difficult to produce accurate information. Each existing method will have advantages and disadvantages. There are many studies related to critical concentrations, particularly on pectin, but the information related to existing methods is still scattered and has not been compared with one another. In addition, existing studies do not clearly explain the reasons for using the chosen method, even though the precision of the method is important to generate predictions that are close to the true value. To date, there is no review article that discusses the

various methods of determining critical concentration specifically for pectin. Based on the background described, the purpose of this review is to explain various methods of determining critical concentration. The content of this review includes the description of critical concentration, analytical methods for determining the critical concentration, and the critical issue in each method. This review can be used as a piece of information for researchers and industrial practitioners to choose a suitable critical concentration prediction method, especially for pectin.

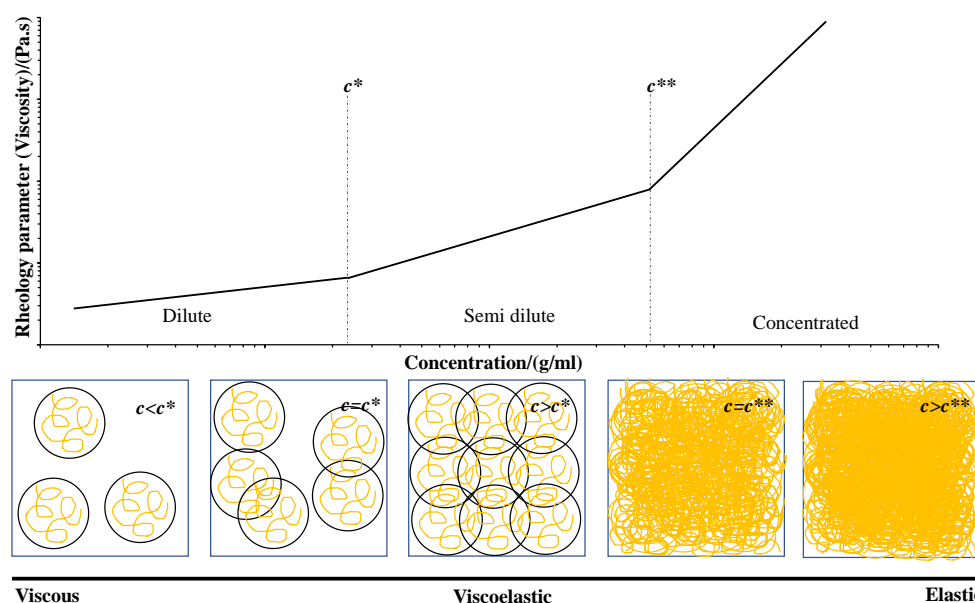
### **The critical concentration of pectin**

Pectin has many hydroxyl groups (-OH), which can increase the affinity to bind water molecules. It can produce colloid dispersion which affects the rheological properties of the food system, both flow behavior and solid behavior. One of the most important parameters in the study of dispersion rheology of pectin is viscosity (Einhorn-stoll, 2018; Saha and Bhattacharya, 2010). Viscosity is a physical property of the fluid which describes the resistance to flow and is calculated as a ratio of shear stress and shear rate ( $\eta=\tau/\dot{\gamma}$ ) (Kasapis and Bannikova, 2016). Generally, an increase in concentration will be accompanied by an increase in viscosity (Zhang *et al.*, 2016).

The basic critical concentration concept of polymer is a transition point from dilute ( $c < c^*$ ), semi-dilute ( $c^* < c < c^{**}$ ), and concentrated dispersion ( $c^{**} < c$ ), which can be known from the slope change of rheological parameter value (*i.e.* viscosity, see Figure 1) (Benchabane and Bekkour, 2008; Rao, 2007).

There are two critical concentration terms in polymer, overlapping critical concentration ( $c^*$ ) and entanglement critical concentration ( $c^{**}$ ) (John *et al.*, 2019). Kale *et al.* (2015) showed that there is a negative correlation between viscosity and critical concentration. At low concentrations, polymer coils have a tenuous radius, are independent, and do not interact with each other so that the coils can move freely which makes the viscosity relatively low (Kale *et al.*, 2015). In this condition, it can be said that the solution is dilute ( $c < c^*$ ). Dilute solution study is used to understand the basic properties of the polymers like polysaccharides (*i.e.* conformation, molecular weight, molecular weight distribution, and interaction properties) (Rao, 2007). The overlapping critical concentration is a narrow concentration range of solution ( $c = c^*$ ), in which polymer coils start to interact and form overlapping coils. When the concentration of polymer in a solution is above  $c^*$ , the viscosity can increase sharply if there is an addition of polymer (Vinogradov and Titkova, 1968; Saha and Bhattacharya, 2010; Cui, 2005). The increase of concentration above the  $c^*$  point causes the polymer to enter the semi-dilute regime ( $c > c^*$ ). In the semi-dilute regime, there are physical interactions (mutual penetration and entanglement) between coils that are near to each other (Kale *et al.*, 2015; Rao, 2007; Rodrigues *et al.*, 2020). Dispersion will enter a transition state from dilute to concentrated ( $c = c^{**}$ ), in which the polymer chains formed a network or entanglement, as concentration increases. Indirectly, the information on the range of dilute to semi-dilute regions can describe

conditions of the product at a higher concentration level. In optimizing product production, lower concentration conditions will be preferred because they can reduce the cost burden. Based on this, there is a strong reason why the studies of polysaccharide dispersions reported, especially for food applications, are mostly reported dilute and semi-dilute regimes ( $c < c^* < c$ ) (Cui, 2005; Benchabane and Bekkour, 2008).



**Figure 1.** The viscosity of polymer dispersion as a function of concentration in the dilute, semi dilute, and concentrated regime as well as a schematic overview of its constituent polymer interactions (modified from Rayner *et al.* (2016)).

Especially for pectin dispersion, it behaves as a Newtonian fluid when the concentration is below  $c^*$ , and as the concentration rises above  $c^*$  such non-Newtonian (shear-thinning) flow behavior is observed (Methacanon *et al.*, 2014; Endress *et al.*, 1996; Lopes *et al.*, 2014). This condition also applies generally to the other hydrocolloids (Li and Nie, 2016). A study by Kontogiorgos *et al.* (2012) showed the property of okra pectin is Newtonian in low concentration ( $c < \sim 1\%$  ( $m/V$ ) or  $c < c^*$ ) and it has shear-thinning behavior in the high concentration ( $c > \sim 1\%$  ( $m/V$ ) or  $c > c^*$ ). The knowledge of the flow behavior of pectin is very important to obtain the desired product viscosity without changing other product attributes (Morales-Contreras *et al.*, 2020). The information on the critical concentration of pectin is indirectly linked to the ability of pectin to form a gel. When the concentration is higher than  $c^*$ , a number of chains are sufficient to form a junction zone and three-dimensional networks to form a gel with a stronger consistency (Colodel *et al.*, 2019). The lower value for  $c^*$  of pectin shows a lower concentration needed to form a gel.

### Factors affecting critical concentration

In the literature (Table 1), it has been shown that different sources and methods of pectin extraction can result in different  $c^*$  values.

**Table 1.** Critical concentration of pectin in several studies.

Source	Solvent	Extraction process DM/DE	$c^*$ % (m/V)	References
Citrus	0.1 M NaCl at pH 7.0	DM 72 %	0.13 <sup>a*</sup>	Axelos <i>et al.</i> (1989)
		DM 53 %	0.15 <sup>a*</sup>	Axelos <i>et al.</i> (1989)
		DM 45 %	0.19 <sup>a*</sup>	Axelos <i>et al.</i> (1989)
		DM 38 %	0.17 <sup>a*</sup>	Axelos <i>et al.</i> (1989)
		DM 30 %	0.17 <sup>a*</sup>	Axelos <i>et al.</i> (1989)
Okra ( <i>Abelmoschu s esculentus</i> )	0.1 M NaCl at pH 7.0	Hot buffer soluble solids (HBSS)	0.83 <sup>b*</sup>	Kontogiorgos <i>et al.</i> (2012)
		Diluted alkali- soluble solid (DASS)	1.23 <sup>b*</sup>	Kontogiorgos <i>et al.</i> (2012)
Pomelo ( <i>Citrus maxima</i> )	Deionized water	DE 58 %	0.55	Methacanon <i>et al.</i> (2014)
		pH 7.0 in Sorensen's phosphate buffer	pH 2 DM 40 % 0.37 <sup>b*</sup>	Alba <i>et al.</i> (2015)
Okra ( <i>Abelmoschus esculentus L.</i> )	pH 3.0 citric buffers in 0.1 M NaCl	pH 3 DM 40 %	0.45 <sup>b*</sup>	Alba <i>et al.</i> (2015)
		pH 7 DM 24.4 %	0.15 <sup>b*</sup>	Alba <i>et al.</i> (2015)
Lemon juice waste ( <i>Citrus limon L.</i> )	0.1–20 g·L <sup>-1</sup> citric buffer pH 3.5	pH 3 DM 24.4 %	0.44 <sup>b*</sup>	Alba <i>et al.</i> (2015)
		Lemon albedo DM 59.3 %	0.30 <sup>b*</sup>	Dimopoulou <i>et al.</i> (2019)
		Lemon core parts and membranes DM 51.4 %	0.06 <sup>b*</sup>	Dimopoulou <i>et al.</i> (2019)
Apple ( <i>Blanca de Asturias</i> )	Deionized water	Lemon extract DM 46.9 %	0.05 <sup>b*</sup>	Dimopoulou <i>et al.</i> (2019)
		DM 63 %	1.50	Morales-Contreras <i>et al.</i> (2020)
Riang ( <i>Parkia timoriana</i> (DC.) Merr.) pod	Deionized water	Riang pod husk DE 66.2 %	1.2	Buathongjan <i>et al.</i> (2020)
		Riang pod powder DE 66.3 %	1.5	

a\*=notation converted from g·L<sup>-1</sup> to % (m/V), b\*=notation converted from g·dL<sup>-1</sup> to % (m/V), DM=degree of methoxylation, DE=degree of esterification

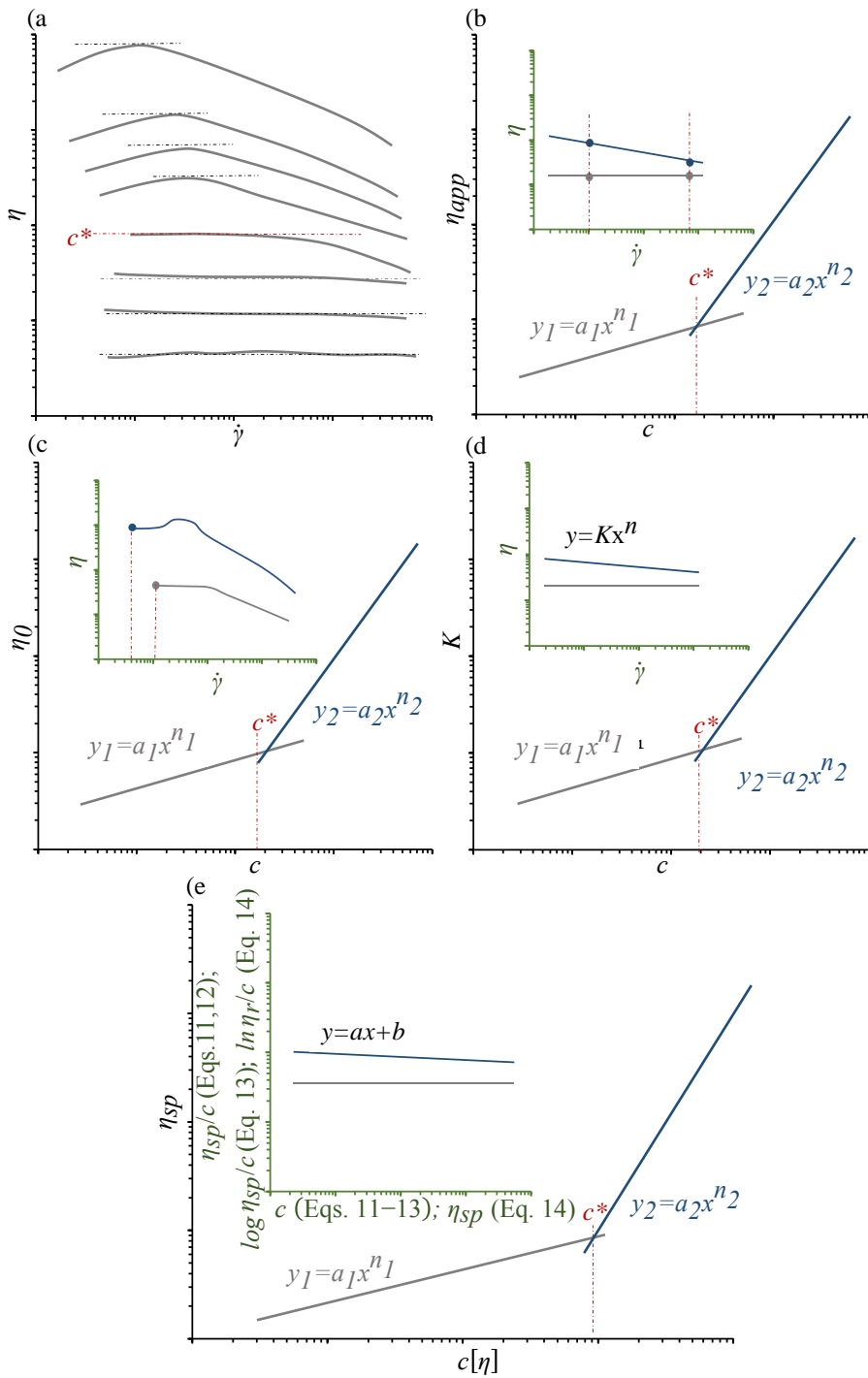
Generally, the intrinsic factors which affect the critical concentration of pectin are the degree of esterification (DE) (Schmidt *et al.*, 2015; Monsoor *et al.*, 2001; Sundar Raj *et al.*, 2012; Narasimman and Sethuraman, 2016; Morris and

Binhamad, 2020), acetyl groups (Kpodo *et al.*, 2018), degree of polymerization (DP), protein groups (Pacheco *et al.*, 2019), distribution of carboxyl groups (Sundar Raj *et al.*, 2012), the charge of pectin molecule (Kale *et al.*, 2015; Lewicki, 2004), chemical conformation, and particle morphology (Morris and Ralet, 2012; Einhorn-stoll, 2018; Einhorn-Stoll *et al.*, 2012). Some studies showed that an increase in molecular weight (Jin-hua *et al.*, 2008; Schmidt *et al.*, 2015; Kale *et al.*, 2015; Fu *et al.*, 2010), branch chains (Ngouémazong *et al.*, 2012; Wang *et al.*, 2021), and neutral sugar groups (Constenla and Lozano, 2003; Morris and Ralet, 2012) has a direct effect on the decreasing of critical concentration.

Dispersant, which is an external factor, affects the critical concentration obtained. Generally, the solvent used as a dispersing medium is deionized water (Morales-Contreras *et al.*, 2020; Methacanon *et al.*, 2014) and sodium chloride solution (*e.g.*, 0.1 M NaCl) (Alba *et al.*, 2015; Axelos *et al.*, 1989; Kontogiorgos *et al.*, 2012). The purpose of using deionized water is to minimize the effect of ions, which can increase viscosity, especially for Low Methoxyl Pectin (LMP) (Yang *et al.*, 2018). Whereas the use of NaCl is to maintain constant ion strength (Sayah *et al.*, 2016). Another critical factor is the preparation of pectin dispersion. Pectin is a polymer with less hydrophilic characteristics compared to other carbohydrate-based hydrocolloids due to the presence of hydrophobic groups (Einhorn-stoll, 2018), such as the methyl ester group (Monsoor *et al.*, 2001; Sundar Raj *et al.*, 2012; Narasimman and Sethuraman, 2016; Schmidt *et al.*, 2015) and the acetyl group (Kpodo *et al.*, 2018). Therefore, previously reported studies on critical concentration measurements were carried out by overnight stirring to obtain homogenous pectin dispersion (Axelos *et al.*, 1989; Kontogiorgos *et al.*, 2012; Alba *et al.*, 2015; Dimopoulou *et al.*, 2019; Morales-Contreras *et al.*, 2020; Methacanon *et al.*, 2014). Generally, the extrinsic factor that affects critical concentration associated with the condition of the environment such as ionic strength (Colodel *et al.*, 2019), pH (Alba *et al.*, 2015), temperature (Cui, 2005), the presence of other dissolved substances (Constenla and Lozano, 2003; Singh and Heldman, 2009; Zhong and Daubert, 2013; Cullen, 2012; Morris and Binhamad, 2020), and mechanical energy (*e.g.* stirring intensity) (Einhorn-stoll, 2018). However, these factors affect not only critical concentration but also the kinetics of polymer dissolution (Miller-Chou and Koenig, 2003).

### **Critical analysis of critical concentration models**

The concept of critical concentration determination based on rheological properties assumes that there is no steric interaction and friction in the coils (Clasen *et al.*, 2006). Hereby, the critical concentration is based on the correlation between viscosity and polymer concentration (Figure 1 and Figure 2).



**Figure 1.** Various models to predict critical concentration (a)  $\eta$  vs.  $\dot{\gamma}$ , (b)  $\eta_{app}$  vs.  $c$ , (c)  $\eta_0$  vs.  $c$ , (d)  $K$  vs.  $c$ , and (e)  $\eta_{sp}$  vs.  $c[\eta]$ .

The viscosity can be represented by different embodiments, such as dynamic viscosity ( $\eta$ ), apparent viscosity ( $\eta_{app}$ ), zero shear viscosity ( $\eta_0$ ), consistency index ( $K$ ), and specific viscosity ( $\eta_{sp}$ ) (Figure 2).

Generally, the range of pectin concentration to determine  $c^*$  is 0.1-3 % ( $m/V$ ) (Morales-Contreras *et al.*, 2020; Methacanon *et al.*, 2014). One must be aware that the more dilute the solution, the more the sensitivity of the instrument is needed to measure the viscosity (Rodrigues *et al.*, 2020). The concentrations of pectin dispersion must represent dilute and semi-dilute regimes. There should be at least three concentration points for each region. In general, the viscosity increases along with the increase in concentration. The higher the concentration, the viscosity will increase differently depending on the internal properties of the polymer. By this, two different regimes separated by different slope values can be observed (Morris *et al.*, 1981; Yang and Yuan, 2018). The critical concentration can be thus, determined based on the transition point when the viscosity change drastically or at the intersection point between two lines that represent dilute regime and semi-dilute regime (Kale *et al.*, 2015).

#### **Dynamic viscosity pattern**

Dynamic viscosity pattern is a collection of viscosity values from the ratio of shear stress and shear rate in Newton's viscosity law as defined in Equation 1.

$$\eta_{app} = \frac{\tau}{\dot{\gamma}_i} \quad (1)$$

The prediction of critical concentration using dynamic viscosity flow pattern is by having a viscosity as a function of shear rate (Figure 2a). As mentioned above, the increase in pectin concentration can shift the flow behavior of pectin suspension. At low concentration ( $c < c^*$ ), the flow behavior is Newtonian, in which the shear rate effect is very small or negligible because the viscosity does not show a significant change. However, when the concentration has entered critical concentration or more ( $c > c^*$ ), the flow behavior changes to a little shear thinning and becomes very strong in shear-thinning properties. In this condition, it will appear that the viscosity will depend on the shear rate. The shear-thinning condition is *due to* the re-entanglement rate being slower than the entanglement rate (Arora *et al.*, 2016). Flow pattern that shows a transition pattern can be used to predict the critical concentration (Benchabane and Bekkour, 2008). This method can be used as a preliminary method because this seems to be a simple one, but it can be tough since one must precisely obtain the critical concentration through the pattern obtained. In this method, the transition line cannot be extrapolated to obtain a more detailed critical concentration point. Hereby, this method is rarely used to predict critical concentration. Benchabane and Bekkour (2008) reported successful prediction of a critical concentration of carboxymethyl cellulose (CMC) using this method. The results were validated by zero shear viscosity and specific viscosity. Although Methacanon *et al.* (2014) and Pancarz *et al.* (2020) could obtain the dynamic viscosity pattern for pectin dispersion, especially at the Newtonian plateau regime, they still predicted  $c^*$  using a zero shear rate. The accuracy of dynamic



viscosity flow pattern-based critical concentration determination is highly dependent on the concentration interval employed.

### **Apparent viscosity**

Apparent viscosity ( $\eta_{app}$ ) is viscosity measured at a certain shear rate ( $\dot{\gamma}_i$ ) following Equation 1 (Rodríguez de Castro and Agnaou, 2019). If the flow behavior is Newtonian, the number of apparent viscosity obtained will be the same in different shear rate values (Morris *et al.*, 1981). Meanwhile, when the flow behavior is non-Newtonian, the apparent viscosity deviates following shear rate values. Based on this, the changes in viscosity can be observed for shear-thinning (pseudoplastic fluid) and shear-thickening (dilatant fluid) (Funk and Dinger, 1994). It must be noted that extrapolation must not be performed to calculate apparent viscosity whenever the measurement settings are beyond the instrument quantification capacity. This was also reported by Funk and Dinger (1994) in which the number obtained from mathematical extrapolation is not mechanically reliable in the fluid. Rodríguez de Castro and Agnaou (2019), there is a tendency for different flow patterns along with different shear rate values for certain polymers.

The determination of  $c^*$  using apparent viscosity can be carried out by plotting apparent viscosity as a function of concentration, this method shows in Figure 2b. The measurement of apparent viscosity is based on the interaction within polymer chains, which depended on the molecular weight (Yang and Yuan, 2018). This condition makes apparent viscosity an indirect representation of material molecular weight. The apparent viscosity-based critical concentration determination can be adjusted with specific shear rate values (inset of Figure 2b) and makes this method more feasible. The measurement of apparent viscosity is relatively fast due to one-point measurement. The apparent viscosity-based critical concentration determination is considered a simple method as it needs only a rotary viscometer to measure viscosity value at one specific shear rate. Cited as an example, a shear rate of  $50 \text{ s}^{-1}$  is used as a representative condition in describing the mastication and swallowing process based on NDD (National Dysphagia Diet) standard (Popa Nita *et al.*, 2013). The value of apparent viscosity in Newtonian or slightly shear-thinning flow will give a more representative critical concentration value because the viscosity values are relatively the same at different shear rates. Similar or relatively close viscosity values at different shear rates will give critical concentration values with minimal deviation.

Several factors are considered when determining the  $c^*$  value using apparent viscosity that is the instrument used and the flow of behavior information. During the measurement, the instrument must achieve the targeted shear rate to omit any extrapolation taking place. When a rotary viscometer is used, one must have the estimated viscosity value of the fluid beforehand. Cardoso de Castro *et al.* (2016) showed that measuring viscosities above  $5000 \text{ mPa}\cdot\text{s}$  using Brookfield rotary viscometer resulted in less accurate values compared to rheometer because rotary viscometer has a limited range of shear rate and less accurate value of actual angular velocity. In addition to the instrument capacity, the flow behavior index ( $n$ ) is also the highlighted factor for determining the  $c^*$  value, especially for shear

thickening or shear-thinning fluid. Pectin dispersion shows shear thinning behavior at elevated concentrations. With this, the flow behavior index of the suspension must be measured instead of apparent viscosity because of the limitation that cannot represent all of the flow regimes. Therefore, apparent viscosity-based critical concentration study of pectin dispersion is still limited. Pectin dispersion usually exhibits Newtonian behavior at low shear rates but can drastically change as the shear rate increases (Chan *et al.*, 2017). One of the studies on pectin that used apparent viscosity as a parameter to determine critical concentration is a study by Ström, Schuster, and Meng (2014). In this study, the shear rate used was  $10 \text{ s}^{-1}$ , but the flow properties of the pectin tested were unknown. Besides that, several studies reported successful critical concentration determinations using apparent viscosity. Liu *et al.* (2014) investigated the critical concentration of several polyacrylamide types (PAM) at a shear rate of  $7.34 \text{ s}^{-1}$ , where it was known that the flow properties possessed by PAM were slightly shear thinning in the concentration range used to measure critical concentrations. Another study is in an article written by (Yang and Yuan, 2018) on polyimide precursor-polyamic acid (PAA), but it did not show the shear rate and material flow properties.

#### **Zero shear viscosity**

Polymer dispersion shows shear-thinning flow behavior in general (Morris *et al.*, 1981). Pectin shows Newtonian behavior at low concentration ( $\sim c < c^*$ ) and shear thinning behavior at high concentration ( $\sim c > c^*$ ) (Methacanon *et al.*, 2014; Endress *et al.*, 1996). The decrease of viscosity at dilute solution along with the increase of shear is negligible since the polymer coils have structural elongation and the flow has the same direction. The shear-thinning characteristic will be more visible in the concentrated solution ( $\sim c = c^*$  or  $\sim c > c^*$ ) because of the increased interpenetration of polymer coils in the solution due to dynamic entanglement, this depends on the conditions of the pectin used. Such Newtonian flow behavior occurs at a low shear rate (close to zero) because the entanglements in the concentrated solution are disrupted and replaced by the formation of new entanglements in the same or different coils without changing the number of entanglements. That is why the decrease of viscosity will not occur (Lam *et al.*, 2015). The inset of Figure 2c shows that an increase in shear rate will decrease viscosity. The regime with the highest (apparent) viscosity, the asymptotic point at the lowest shear rate produces the plateau area or Newtonian region labeled as zero shear viscosity ( $\eta_0$ ) (Chhabra and Uhlherr, 1979; Morris *et al.*, 1981; Pancarz *et al.*, 2020).

As a unique molecular representation, zero shear viscosity can be used as a reference to determine the critical concentration (Figure 2c) (Rayner *et al.*, 2016). Zero shear viscosity depends on the chemical type, temperature, molecular weight, number of branch chains, solution concentration, solvent, and instrument sensitivity (Morris *et al.*, 1981; Lam *et al.*, 2015). In general, zero shear viscosity is dependent on molecular weight. The greater the molecular weight, the higher the zero shear viscosity. Likewise, the higher the concentration, the higher the zero shear viscosity value (Larson and Desai, 2015). Pectin has a wide range of zero

shear viscosity in dilute solution and becomes narrower with the increase of concentration (Sousa *et al.*, 2015; Methacanon *et al.*, 2014). Hereby, the Newtonian regime might be taken to determine zero shear viscosity, and thus for the prediction of critical concentration. The challenge for determining zero shear viscosity is to have a highly sensitive instrument that can operate at shear rates as low as possible (Clasen *et al.*, 2006). This is because polymers with high molecular weight are susceptible to shear forces so that the flow properties of zero shear viscosity are challenging to detect by the tool (Wolf, 2020). Meanwhile, pectin is a polymer that has a big molecular weight (Sayah *et al.*, 2016; Chen *et al.*, 2015). The commercial pectin molecular weight range is approximately  $1.9 \cdot 10^5 \pm 3 \cdot 10^4$  g/mol -  $1.95 \cdot 10^5 \pm 5 \cdot 10^3$  g/mol (Sayah *et al.*, 2016), so it is possible that the instrument cannot detect the zero shear viscosity. Therefore, there is a prediction model for zero shear viscosity, which has been validated for several polymers at Equation 2. Equation 2 is the most used equation for all polymer conditions. In Equation 2, it was assumed that the solvent in pectin is not directly involved in the test process, where the solution viscosity ( $\eta$ ) is divided by the solvent viscosity ( $\eta_\infty$ ) (Equation 3), labeled as relative viscosity ( $\eta_r$ ). The values of  $\beta$ ,  $\alpha$ , and  $\gamma$  are system's specific hydrodynamic parameters of polymer. The value of  $\alpha$  can be assumed to be zero, but this will depend on the type of polymer used. Concentration ( $c$ ) is the relationship between mass ( $m$ ) divided by volume ( $v$ ) ( $c=m/V$ ). The value of  $\tilde{c}$  is assumed to have the same value as the coil overlap parameter (Equation 4) (Wolf, 2020), even though the value of  $\tilde{c}$  does not represent the change in the dimension of the polymer coil molecularly (Wolf, 2015). Wolf (2020) reported that Equation 2 produced an error of 5% in all toluene/polystyrene concentrations, while at low concentrations ( $c < 0.01$  g/ml) the resulting error value is 15%. However, Equation 2 has not been used in determining the prediction of zero shear viscosity pectin.

$$\ln \eta_r^o = \frac{\tilde{c} + \alpha \tilde{c}^2}{1 + \beta \tilde{c} + \gamma \tilde{c}^2} \quad (2)$$

$$\ln \eta = \frac{\ln \eta}{\eta_\infty} = \ln \eta_r \quad (3)$$

$$\tilde{c} = c[\eta] \quad (4)$$

In pectin, zero shear viscosity is affected by its branch structure. The greater the number of branch chains, the higher the zero shear viscosity. On the other hand, linear chains tend to have lower zero shear viscosity. In the semi-dilute state, the presence of branches will affect zero shear viscosity if the molecular weight is considerable. This condition will depend on the type of polymer used. However, the zero shear viscosity value shows a value inversely proportional to the intrinsic viscosity value (Hwang and Kokini, 1992). This causes the lower the zero shear viscosity of the polymer, the lower the critical concentration value of the polymer (Takahashi *et al.*, 1986).

### **Consistency index**

The flow consistency index value ( $K$ ) will be obtained based on the flow characterization by using the power law (Equation 5) or Herschel Bulkley equation (Equation 6). As shown at the inset of Figure 2d, there are at least three viscosity points at different shear rates needed in order to obtain consistency index value. The consistency index ( $K$ ) shows the dependence on concentration (Arora *et al.*, 2016) and can be used to determine critical concentrations. The higher the pectin concentration, the higher the  $K$  value, because the number of coils blocking the flow is getting more significant. Figure 2d shows the graph model used in the prediction of critical concentration using a consistency index value. Kale *et al.* (2015) have demonstrated the utilization of consistency index value for measuring the same  $c^*$  as in the general method. Morales-Contreras *et al.* (2020) reported the prediction of  $c^*$  value in apple pomace pectin based on the consistency index value. Existing studies only use the consistency index parameter when the flow behavior ( $n$ ) of the material was Newtonian or slight shear thinning. The consistency index value represents the overall flow resistance properties at various shear rate measurements, thus the consistency index is the mean viscosity percentage (Pang *et al.*, 2020). The unit of the consistency index value is affected by the unit of flow behavior index exponential ( $n$ ) from the shear rate (Equations 5 and 6), so the consistency index value method would be best used on samples that exhibit Newtonian flow or slight shear thinning behavior.

$$\tau = K\dot{\gamma}^n \quad (5)$$

$$\tau = K\dot{\gamma}^n + \tau_0 \quad (6)$$

### **Specific viscosity and coil overlap parameter**

One of the frequently used methods to determine critical concentration is by plotting specific viscosity ( $\eta_{sp}$ ) as a function of the degree of space-occupancy dimensionless number ( $c[\eta]$ ) or degree of space-occupancy (Axelos *et al.*, 1989; Alba *et al.*, 2015; Dimopoulou *et al.*, 2019). Specific viscosity ( $\eta_{sp}$ ) is such an incremental increase of viscosity due to the presence of polymer in the solution. Normalization of specific viscosity to concentration ( $\eta_{sp}/c$ ) indicates the additional viscosity per unit polymer concentration. Then, the extrapolation of  $\eta_{sp}/c$  to zero concentration is used to determine intrinsic viscosity  $[\eta]$  (Dufresne, 2013). Intrinsic viscosity value is defined as the capability of the polymer to increase viscosity (Sayah *et al.*, 2016). Intrinsic viscosity represents the hydrodynamic volume, thus depicting the molecular weight and hydrodynamic polymer radius (Dufresne, 2013; Yoo *et al.*, 2006). Pectin with higher intrinsic viscosity will have a higher solution viscosity because the level of intermolecular interactions will be more significant. However, this condition is significantly influenced by the condition of the branch chain (Hwang and Kokini, 1992).

In order to determine the intrinsic viscosity, it is necessary to determine relative viscosity ( $\eta_r$ ), specific viscosity ( $\eta_{sp}$ ), and reduction viscosity ( $\eta_{red}$ ). In general, a capillary viscometer is the most common instrument used in determining these parameters. It is a simple instrument but has good repeatability. There are several

types of glass capillary viscometer, such as Ostwald, suspended level, and reverse flow type for an opaque solution. These three viscometers have some categorical classes with different kinematic viscosity ranges ( $\text{mm}^2 \cdot \text{s}^{-1}$ ). Ostwald viscometer can be used for transparent pectin, with a kinematic viscosity range of 0.2 - 20.000  $\text{mm}^2 \cdot \text{s}^{-1}$  (Gupta, 2014). The most important thing that affects the accuracy of this method is the reading of the upper and lower meniscus. In principle, the capillary viscometer measures the time for the fluid to flow over a certain distance. Relative viscosity ( $\eta_r$ ), specific viscosity ( $\eta_{sp}$ ), and reduction viscosity ( $\eta_{red}$ ) are calculated using Equations 7, 8, and 9, where  $t$  is the time when solution drop from viscometer,  $t_0$  is the time when solvent drop from viscometer,  $\rho$  is solution density ( $\text{g} \cdot \text{cm}^{-3}$ ), and  $\rho_0$  is solvent density ( $\text{g} \cdot \text{cm}^{-3}$ ).

$$\eta_r = \frac{t\rho}{t_0\rho_0} \quad (7)$$

$$\eta_{sp} = \eta_r - 1 \quad (8)$$

$$\eta_{red} = \frac{\eta_{sp}}{c} \quad (9)$$

Intrinsic viscosity in general can be determined using a capillary viscometer. However, intrinsic viscosity can also be determined using a rheometer with modified calculation. Intrinsic viscosity can be determined by single and multi-concentrations. Wang *et al.* (2015) and Chen *et al.* (2020) have demonstrated a single concentration method to determine the intrinsic viscosity of grapefruit peel pectin and citrus pectin using the Solomon-ciuta model (Equation 10). Solomon-ciuta model can be used to predict intrinsic viscosity from low to high concentration. Abdel-Azim *et al.* (1998) reported that the Solomon-ciuta model is an accurate method as compared to other single-point models. The single concentration method is simple yet though, and it can be used in any concentration of polymer observed (Rodrigues *et al.*, 2020).

$$[\eta] = \frac{\sqrt{2[\eta_{sp}] - \ln(\eta_r)}}{c} \quad (10)$$

Intrinsic viscosity determination using multi-concentration is mostly adopted in the literature and related to Huggins, Kraemer, Schulz-Blashke, and Martin's model (Equations 11-14). These models can only predict the intrinsic viscosity at low concentrations. In low concentration conditions, the coils are not overlapping. Thus, the coil capacity to increase viscosity can be well measured. Meanwhile in high concentration polymer coils are overlapping thus disturbing the measurement of pectin solution viscosity (Sayah *et al.*, 2016). At a low concentration, the deviation can occur due to macromolecule absorption at the viscometer wall, thus decreasing polymer concentration (Abdel-Azim *et al.*, 1998). The plotting results of each model (Equations 11-14), between  $\eta_{sp}/c$ ,  $\ln \eta_r/c$  and  $\log \eta_{sp}/c$  with concentration, and between  $\eta_{sp}/c$  and  $\eta_{sp}$  used to be interpolated to get a linear model equation as shown inset of Figure 2e. The interpolation of these models will

produce an intercept as an intrinsic viscosity, and the slope value from the equation of a line is a constant of the model. The model constants obtained  $k_H$ ,  $k_K$ ,  $k_{SB}$ , and  $k_M$  are Huggins, Kraemer, Schulz-Blashke, and Martin constants. Theoretically,  $k_H + k_K$  the value is equal to 0.5 and  $k_{SB}$  is about 0.3-0.4 (Axelos *et al.*, 1989; Rodrigues *et al.*, 2020; Abdel-Azim *et al.*, 1998; Morris *et al.*, 1981; Zhang *et al.*, 2016).

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \quad (11)$$

$$\frac{\ln \eta_r}{c} = [\eta] - k_K[\eta]^2 c \quad (12)$$

$$\frac{\log \eta_{sp}}{c} = \log[\eta] + k_M[\eta]c \quad (13)$$

$$\frac{\eta_{sp}}{c} = [\eta] + k_{SB}[\eta]\eta_{sp} \quad (14)$$

Coil overlap parameter ( $c[\eta]$ ) is a dimensionless number that describes a certain volume that is replaced by polymer molecules in a solution. The critical concentration can be determined by using the relationship between specific viscosity as ordinate and coil overlap parameter number ( $c[\eta]$ ) as the basis (Figure 2e) (Kontogiorgos *et al.*, 2012; Rao, 2007). Like other types of viscosity, the specific viscosity will change with a function of concentration. This method is the simplest and most used in various studies, especially for pectin (Sayah *et al.*, 2016; Pancarz *et al.*, 2020). The condition of pectin that has different flow behavior at increased concentration makes this method the best choice.

### Critical concentration determinations

Based on the various methods described, two equations will be obtained from two different regimes between dilute and semi-dilute. In general, the dilute area will produce a sloping curve, thus the slope ( $n$ ) value will be smaller than the semi-dilute area (Figure 3) (Ström *et al.*, 2014; Rayner *et al.*, 2016). In general, the slope in the dilute regime is around 1.0 ( $\mu \propto c^{-1}$ ), which can be greater or less than 1.0.

The condition in the dilute regime can be caused by a linear relationship between viscosity and concentration. Whereas in the semi-dilute regime, the resulting slope is about two to three times larger than the slope in dilute regions in general (Buathongjan *et al.*, 2020; Methacanon *et al.*, 2014; Lopez *et al.*, 2015; Rayner *et al.*, 2016; Pereira *et al.*, 2013). This condition indicates that in a semi-dilute area, the typical increase in concentration follows the power law, where the increase is unique. One of the most critical problems after determining the appropriate method is determining the critical concentration intercept. Overall, two-line equations will be obtained from the described methods (except the dynamic viscosity pattern model), as in Equations 15 and 16. Both equations are assumed to have the same axis value ordinate ( $y_1 = y_2 = y$ ) so that they can be substituted by each other as in

Equation 17, then it is linearized into Equation 18 to get Equation 19. Overall, from the two-line equations that have been obtained, Equation 20 can be used in all methods, while Equation 21 is used to predict the model using  $\eta_{sp}$  and  $c[\eta]$ .

$$y_1 = a_1 x^{n_1} \quad (15)$$

$$y_2 = a_2 x^{n_2} \quad (16)$$

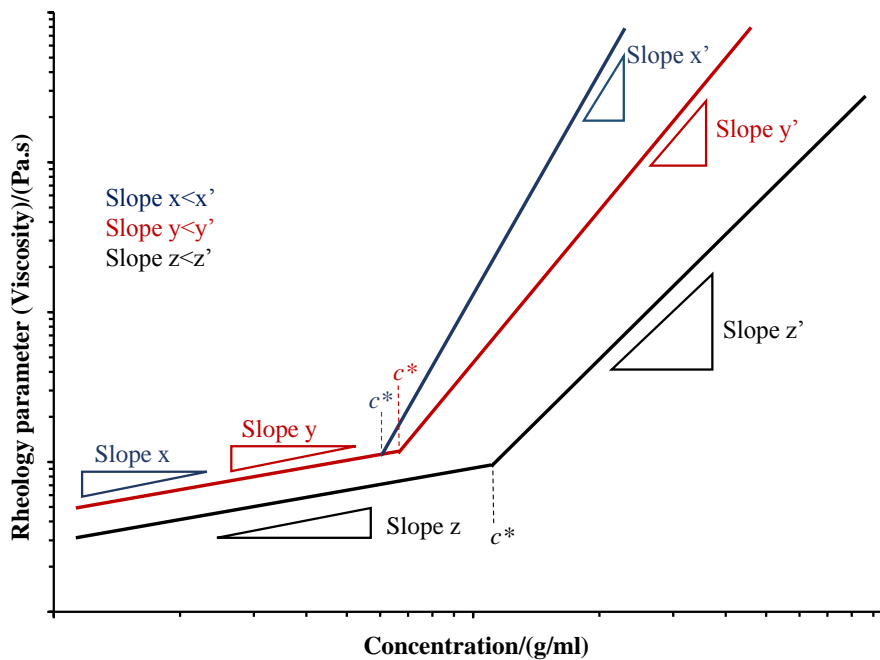
$$a_1 x^{n_1} = a_2 x^{n_2} \quad (17)$$

$$\ln a_1 n_1 \ln x = \ln a_2 n_2 \ln x \quad (18)$$

$$\ln x = \ln \frac{a_1 n_1}{a_2 n_2} \quad (19)$$

$$c^* = e^{\frac{\ln \frac{a_1 n_1}{a_2 n_2}}{n_1 - n_2}} \quad (20)$$

$$c^* = \frac{e^{\frac{\ln \frac{a_1 n_1}{a_2 n_2}}{n_1 - n_2}}}{[\eta]} \quad (21)$$



**Figure 3.** The illustration of the slopes to determine the critical concentration.

### Crucial considerations for model selection

Based on the analysis of the existing studies, the crucial issues that need to be considered in each method were summarized in Table 2. Overall, the dynamic viscosity pattern method can be used as a preliminary method to see the presence

of changes in viscosity increase due to changes in concentration faster. However, this method must be validated by other methods that are more suitable with the characteristics of the pectin sample. The description of the method that has been described confirms that the critical concentration can be determined using rheological parameters, such as viscosity- a parameter that follows based on the concentration function. The higher the concentration is, the higher the viscosity. But, considering the viscosity parameter alone is insufficient. The most important basic information before determining the model to be used is the flow behavior of pectin.

**Table 1.** Advantages and disadvantages of various model for determining critical polymer concentration.

Methods	Advantages	Disadvantages	Instruments	References
$\eta_{app}$ vs. $c$	<ul style="list-style-type: none"> <li>- Specific shear rate</li> <li>- Suitable for Newtonian or slight shear thinning fluid</li> <li>- Quick measurement</li> </ul>	<ul style="list-style-type: none"> <li>- Not suitable for non-Newtonian fluid</li> </ul>	<ul style="list-style-type: none"> <li>- Rotary viscometer</li> <li>- Rheometer</li> </ul>	Liu <i>et al.</i> (2014); Yang and Yuan (2018); Ström <i>et al.</i> (2014)
$\eta$ vs. $\dot{\gamma}$	<ul style="list-style-type: none"> <li>- Provide critical concentration flow</li> <li>- Direct prediction</li> </ul>	<ul style="list-style-type: none"> <li>- Requires high sensitivity instrument</li> <li>- Rough prediction</li> <li>- Need small concentration intervals</li> </ul>	Rheometer	Benchabane and Bekkour (2008)
$\eta_0$ vs. $c$	<ul style="list-style-type: none"> <li>- Molecularly representative</li> <li>- Suitable for all flow behavior</li> </ul>	<ul style="list-style-type: none"> <li>- Requires high sensitivity instrument</li> </ul>	Rheometer	Methacanon <i>et al.</i> (2014); Lam <i>et al.</i> (2015); Pancerz <i>et al.</i> (2020); Buathongjan <i>et al.</i> (2020)
$\eta_{sp}$ vs. $c$ $[\eta]$	<ul style="list-style-type: none"> <li>- Molecularly representative</li> <li>- Does not require high instrument</li> <li>- Suitable for all flow behavior</li> </ul>	<ul style="list-style-type: none"> <li>- Depend on model prediction type of intrinsic viscosity <math>[\eta]</math></li> </ul>	Capillary viscometer	Dimopoulou <i>et al.</i> (2019); Rodrigues <i>et al.</i> (2020); Sayah <i>et al.</i> (2016)
$K$ vs. $c$	<ul style="list-style-type: none"> <li>- Flow behavior representative</li> <li>- Suitable for Newtonian and slight shear thinning</li> </ul>	<ul style="list-style-type: none"> <li>- Not suitable for shear thinning and shear thickening fluid</li> </ul>	<ul style="list-style-type: none"> <li>- Rotary viscometer</li> <li>- Rheometer</li> </ul>	Morales-Contreras <i>et al.</i> (2020)



Because of the non-Newtonian flow properties of pectin, the resulting viscosity is influenced by the shear rate used. In general, pectin has Newtonian to shear-thinning flow behavior (Wang *et al.*, 2021; Chen *et al.*, 2020; Chen *et al.*, 2021), so the best method to predict the critical concentration of pectin is a method that can be used for all flow behavior. The best method in general that can be used for various kinds of flow behavior and molecular representative of materials are methods that use the relationship of 1) zero shear viscosity ( $\eta_0$ ) and concentration ( $c$ ), and 2) specific viscosity ( $\eta_{sp}$ ) and a dimensionless number ( $c[\eta]$ ). Because of the representation of the viscosity conditions without being affected by shear forces, the use of zero shear viscosity can be considered as an accurate method. Similar to a method that uses a specific viscosity ( $\eta_{sp}$ ) and a dimensionless number ( $c[\eta]$ ), where the resulting viscosity value is assumed to have no additional shear forces from the outside, or it can be ignored because it does not cause significant changes. These methods can demonstrate the internal capability of the actual viscosity increase level of the material being tested and can be used as alternatives to characterize the overlapping critical concentration. All the methods described can be used to determine any fluid with shear-thinning and Newtonian flow behavior, without exception. There is also a chance that these methods can be used for other polymers by looking at the condition of the sample.

### Conclusions

Critical concentration is the concentration that becomes the point of transition between two different fluid regimes, representing the interactions between the coils in solution. There are two types of critical concentrations, the critical overlap concentration ( $c^*$ ) and the critical entanglement concentration ( $c^{**}$ ), but the most used is critical overlap concentration. There are five (5) methods that are commonly used to determine critical concentration based on the rheological approach. The dynamic viscosity pattern method is considered a preliminary method that needs validation by other methods. The apparent viscosity ( $\eta_{app}$ ) and consistency index ( $K$ ) method can only be used on Newtonian flow properties or less shear-thinning fluid. Specific viscosity and coil overlap parameters ( $\eta_{sp}$  and  $c[\eta]$ ), and zero shear viscosity ( $\eta_0$  and concentration) methods are the most representative approaches to evaluate critical overlap concentration for pectin under various flow behaviors. The methods that use apparent viscosity parameters ( $\eta_{app}$  and concentration) and consistency index value ( $K$  and concentration) are strongly influenced by the flow behavior.

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