

RHEOLOGICAL AND THERMAL BEHAVIOR OF POLYPROPYLENE- KAOLIN COMPOSITES

(Reologi dan Sifat Thermal Komposit Polipropilena-Kaolin)

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Abstract

Kaolin's effect on rheological behaviour of polypropylene-kaolin composites was investigated. The research found that not only the kaolin content influence the rheological behaviour but also the compounding using internal mixer and twin screw extruder. In details, viscosity and shear stress increased with addition of kaolin content. These characteristics also exhibited higher in polypropylene-kaolin composite suspensions compounded using twin screw extruder than using internal mixer. Chain scission was assumed to occur and affect the melt properties. Further justification characterized by Differential Scanning Calorimeter (DSC) showed that the effect of kaolin and loading content were more evident on the onset melting temperature and crystallinity. Besides, due to the different cooling operation in both processes, the effect of compounding on melting characteristic was conspicuous.

Keywords: Polypropylene-kaolin composite, twin screw extruder, brabender internal mixer, melt rheology, capillary rheometer, and MFI.

Abstrak

Kesan kaolin terhadap tingkahlaku rheologi komposit polipropilena-kaolin telah dikaji. Kajian ini mendapati bahawa bukan sahaja kandungan kaolin yang mempengaruhi tingkahlaku reologi tetapi juga pengkompaunan yang menggunakan mesin pencampur dalaman dan skru ekstruder berkembar. Secara terperinci, kelikatan dan tegasan ricih telah meningkat dengan penambahan kandungan kaolin. Ciri-ciri ini juga menunjukkan suspensi polipropilena-kaolin komposit yang dikompaunkan oleh skru ekstruder berkembar adalah lebih tinggi daripada menggunakan mesin pencampur dalaman. Kepisahan rantaian diandaikan berlaku dan menjejaskan sifat-sifat leburan. Justifikasi selanjutnya dicirikan oleh kalorimetri pengimbas pembezaan (DSC) menunjukkan bahawa kesan kaolin dan kandungan terbukti pada peleburan suhu awal dan penghabluran. Selain itu, akibat daripada operasi penyejukan yang berbeza dalam kedua-dua proses, kesan pengkompaunan pada sifat keleburan adalah senang dilihat.

Kata kunci: Komposit Polipropilena-Kaolin, Skru Extruder Berkembar, Mesin Pencampur Brabender, Rheologi Keleburan, Kapilari Reometer, dan MFI.

Introduction

The use of kaolin in polymer composites has attracted industrial interest due to low contamination of toxic element. As other commercial inorganic fillers, kaolin enables to improve thermal endurance, fire resistance, mechanical properties and dimensional stability of a product. Kaolin consist of 1:1 layer lattices (silica-alumina), platy particle shape and particle size down to 0.2 μm . Due to its unique structure, many researcher believes kaolin has specified functionality in polymer composites such as improve process-ability, product's physical and mechanical performances. Like other general filler, presence of kaolin increases the composite viscosity. Research done by Rahim et al. [1] reported viscosity of polypropylene increased with increasing in kaolin loading since kaolin hindered the polymer suspensions movement. High content of kaolin loading not only result in high viscosity but also caused lower mechanical properties. This is due to filler agglomeration. This circumstance was surmounted by the addition of compatibilizer but still unsatisfactory at high kaolin loading contents [1-3].

Compounding process has an important role to control composite's properties. During compounding, the equipment generates heat and shear which significantly gives an effect on polymer molecular weight and structure. Other than matrix condition, compounding process affected distribution and dispersion of fillers which also give major influences to the composite's properties [4-5]. Focus in this article is to comprehend the effect of filler loading and compounding process on rheological properties of PP/kaolin composite. The most common melt blending of twin screw extruder and internal mixer were selected to study the effect of compounding. The evaluation was based on rheological properties of composite measured by using melt flow index (MFI) and capillary rheometer. Melting transition characteristic was studied by using differential scanning calorimeter.

Materials and Methods

Materials and Sample Preparation

Polypropylene co-polymer grade TitanPro SM340 with melt flow index 4g/10min at 230°C (ASTM D1238) supplied by Titan polypropylene Polymer (M) Sdn. Bhd. Kaolin was provided by Sigma-Aldrich with catalog K7375 and linear formula of $\sim\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Polypropylene grafted Maleic Anhydride (PPgMA) was supplied by Uniroyal Chemical.

PP/kaolin composites were prepared via internal mixer (Brabender) and twin screw extruder (Lab Tech), and the recipe was shown in Table 1. Compounding in internal mixer was carried out at 190°C and 50min⁻¹ rotor speed for 6 minutes. Polypropylene was preheated for 2 minutes, further by the addition of kaolin. The compounds were taken out and cooled in ambient atmosphere. After that, compounds were crashed into small pieces before rheological test. Same processing temperature was used on twin screw extruder with screw speed 50rpm. Extrudates were cooled by water bath and pelletized right afterward. Twin screw extruder model Benchop 16-40 has 16 mm screw diameter and 40 L/D screw ratio with inter-mesh co-rotational design.

Table 1. PP/Kaolin composite formulation

Sample nomination		Polypropylene	Kaolin loading	PPgMA Content
Internal mixer	Twin screw extruder	(wt%)	(wt%)	(phr)
IM0	TSE0	100	0	0
IM5	TSE5	95	5	2
IM10	TSE10	90	10	2
IM15	TSE15	85	15	2
IM20	TSE20	80	20	2

Capillary Rheological Test

Rheological behavior of PP/Kaolin composites was studied by using Dynisco LCR-7001 capillary rheometer according ASTM D 3835 testing standard. Viscosity and shear stress versus shear rate were reported based on the built-in software. Testing temperature was carried out at 190°C and preheats 6 minutes. Input shear rate was varies from 50s⁻¹ till 5000s⁻¹ [3].

Melt Flow Index (MFI)

MFI test was done according to ASTM D 1238. Testing temperature was carried at 190°C with 2.16kg load and preheated for 6 minutes. MFI values were calculated using formulation (equation 1) below:

$$MFI = 600W / t \quad (1)$$

where W is weight of extrudate, and t is interval time (in seconds) to collect the extrudates. Units for MFI is g/10min [3].

Differential Scanning Calorimeter (DSC)

Melting characteristic and crystallinity of PP/Kaolin composites were measured by using a TA Instrument Q-10 DSC. The samples were heated from room temperature up to 190°C with a 10°C/min of heating rate in nitrogen gas atmosphere. First DSC scan results were reported in order to reflect thermal history from different compounding equipments. Heat changes obtained from thermograms were calculated to crystalline percentage by using heat changes reference of polypropylene, $\Delta h_f^0 = 207.1 \text{ J/g}$ with equation (2) below:

$$\text{Crystallinity} = \frac{\Delta h_f}{\Delta h_f^0} \times 100\% \quad (2)$$

where, Δh_f is the enthalpy of melt transition in polypropylene [6].

Results and Discussion

Rheological Properties of PP/Kaolin Composites

Figure 1 illustrates MFI values of PP/kaolin composites with different kaolin contents from both compounding processes. It was found that, MFI values dropped gradually with increase in kaolin content. The effect of kaolin particles was as expected by causing a relative increase in the polymer's melt viscosity and reduction the output. This is in agreement with Rahim et al. (2011) founding. The main reason is that kaolin particles hindered the fluency of polypropylene flow [3]. The more the loading of kaolin, the high the obstruction are the lower MFI results. In comparison between two compounding processes, sample from twin screw extruder displayed slightly lower MFI values than those from internal mixer. The difference was in a range of $0.1 \pm 0.05 \text{ g/10min}$. However, the distinction became smaller after 10 wt% of kaolin loading. It could be assumed that the effect of different compounding process was insignificant and covered by the high kaolin content effect. It is noted that MFI is only reflecting the rheological properties of PP/Kaolin composites at low shear rate. The rheological behaviour at high stress rate was examined from capillary rheometer testing.

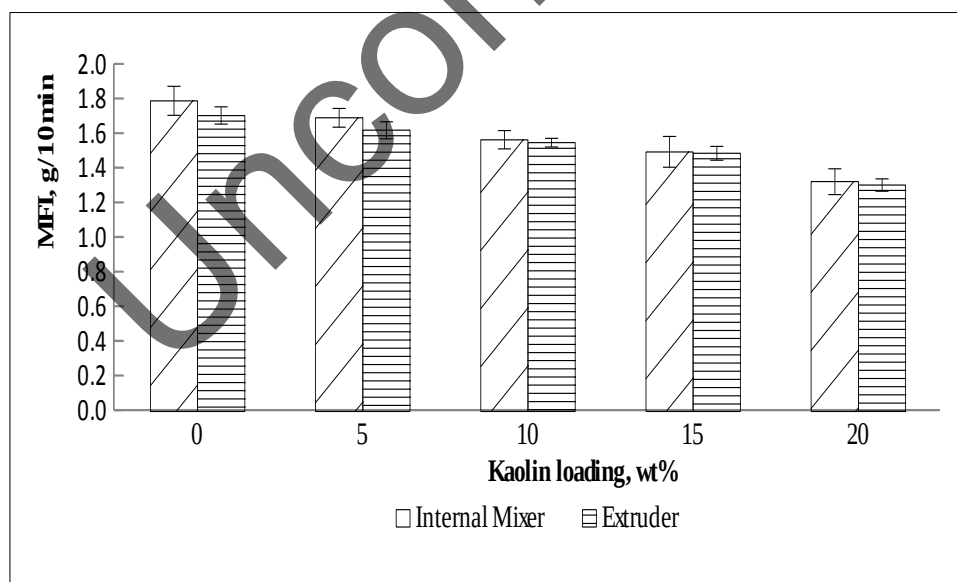


Figure 1. MFI values of PP/Kaolin composites

As inferred, PP/kaolin composites exhibit non-Newtonian pseudo-plastic behavior (Figure 2). It could be said that Kaolin does not interfere or cause any significant change in pseudo-plastic behaviour of PP/kaolin composites from polypropylene control. As un-interactive filler to polypropylene, the incorporation of kaolin only led the PP

composite suspension in relatively higher viscosity at all shear rates. Similar effect also can be found in titanium-oxide and nano- CaCO_3 [7-8]. Due to the polymer structure, polypropylene is considered as a kind of low intermolecular forces. Increase in shear rate confers and exalts chain mobility of polypropylene so that the polymer chains align along the stress direction. Directionally induced polypropylene chain exhibits low frictional force between the wall-melt interfaces causing increase in melt's velocity hence decrease in viscosity [2].

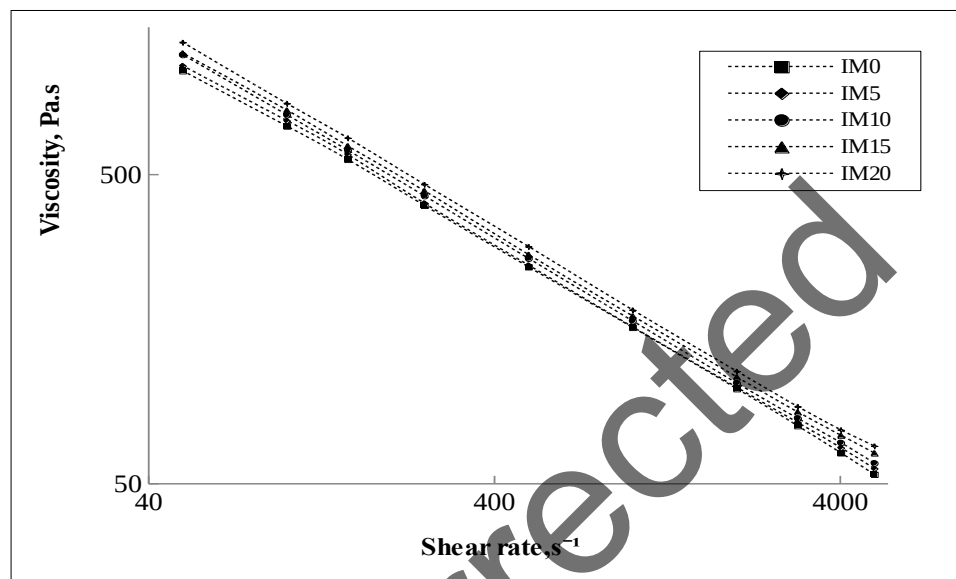


Figure 2. Viscosity against shear rate of PP/Kaolin composites compound via internal mixer

Similar effect of kaolin on PP/Kaolin composite's shear stress was observed. Figure 3 shows that higher shear stress obtained for polypropylene composite suspension with increase in kaolin weight percentage. Such factors as immobility of kaolin, shelf-attraction of kaolin molecular, low interaction between kaolin and polypropylene caused difficulties for polypropylene chain to carry and move along [3]. This particular difference turned to be more obviously with increase in shear rate due to higher mobility of polypropylene polymer chains.

In order to compare the effect of compounding process, rheological behaviour of polypropylene control and polypropylene composite with 15wt% kaolin from two process were plotted and showed in Figure 4 (representing viscosity) and Figure 5 (shear stress) respectively. Samples from internal mixer have lower viscosity compared to twin screw extruder, for both polypropylene control and its composite. In fact, polypropylene was compounded for 6 minutes in internal mixer, while about 1 minute in twin screw extruder at same temperature, hence, higher heat generation at internal mixer is expected. It could be inferred that thermal degradation occurred in internal mixer, which imparted chain scission of polypropylene chains [15]. Shorter polymer chain will had easier alignment and therefore if exhibited lower viscosity. Another possibility is the chain scission happened during sample preparation for capillary rheometer characterization. Samples from internal mixer were crushed and trimmed into small pieces compared to palletizing of twin screw extruder.

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Differences of viscosity between IM0 and TSE0 became insignificant at high shear rate. It could be said the scission in internal mixer was quite minor and acceptance for PP control. Moreover, due to the uni-direction alignment of PP chain; the flow mechanism and flow-ability are almost alike causing by high speed of testing piston. On the other hand, presence of kaolin intensified the effect of processing and the difference was still present obviously on PP/Kaolin composite's viscosity even at high shear rate (zoom in part in Figure 4). The possible explanation is

kaolin was generated and amplified PP chain scission in internal mixer. Kaolin was added into melt polymer after 2 minutes. It required a higher torque to disperse the cool kaolin, hence inducing a high shear in melt suspension polypropylene in internal mixer chamber, which could accelerate the chain scission phenomenon (for 4 minutes after addition of kaolin). In contrast, kaolin and polypropylene were mixed in advanced, the rotation and conveyance of twin screw within 1 minute could minimize the chain scission. Therefore, TSE15 exhibited higher viscosity compared to IM15 for all share rates.

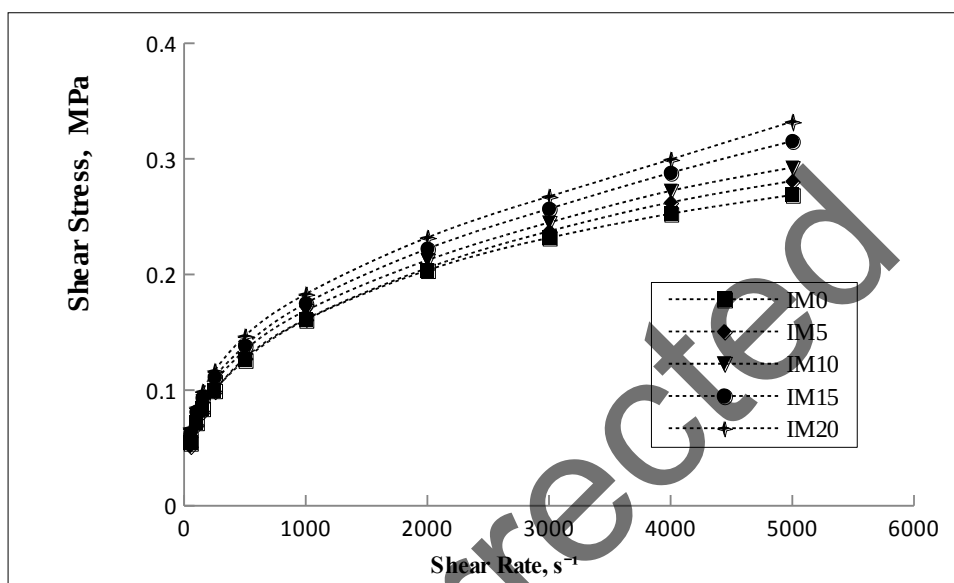


Figure 3. Shear stress against shear rate of PP/Kaolin composites compound via internal mixer

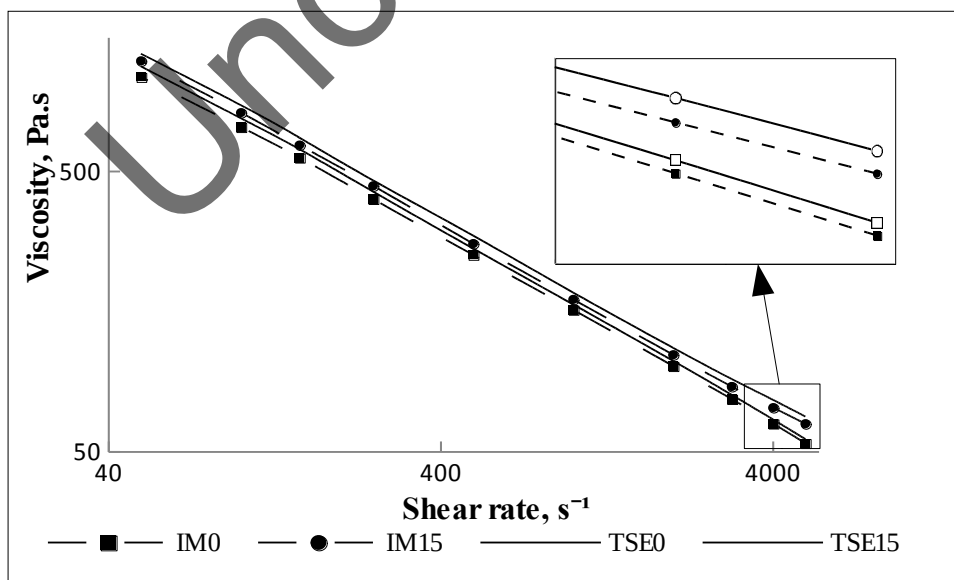


Figure 4. Effect of processing on PP/Kaolin composite's viscosity

Similar influence of compounding processes without and with kaolin was also reflected by shear stress as shown in Figure 5. Furthermore, the compounding effect was more detected on shear stress compare to viscosity, especially in high shear rate. These features are other evidences of chain scission taking place in internal mixture more than twin screw extruder. In additional, the results of capillary rheometer expressed more profound rheological behaviour compared to MFI results. It provided more details of the different effect of compounding **PP/kaolin** composites using internal mixer and twin extruder.

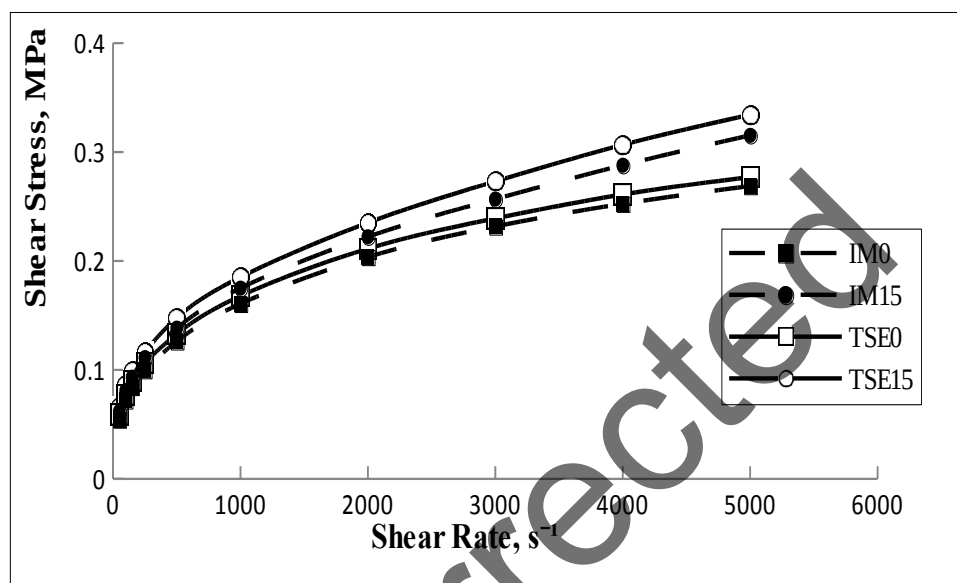


Figure 5. Effect of processing on PP/Kaolin composite's shear stress

Melt transition of PP/Kaolin composites

Table 2 reported the onset temperature, melting points and crystallinity percentage of PP/Kaolin composites. It was found that melt temperature of PP dropped $1.4 \pm 0.6^\circ\text{C}$ with addition of kaolin, but kept similar values with higher kaolin loading. The influences of kaolin content and compounding processes were only more evident for the onset temperature – as the start of melting transition and crystallinity, which will be discussed later. The decrease in melting point of **PP/kaolin** composites is a common trend. Liang and Li [9] reported the presence of inorganic phase within polymer matrix enhances heat transfer between intermolecular chains which also impart fasten melting of polymer [9]. Moreover, different crystallization led by kaolin filler resulted in defectiveness crystal, which caused the decrease in the enthalpy needed to melt the matrix [10].

Table 2. Onset temperature, Melting point, and Crystallinity of PP/Kaolin Composites

Kaolin Loading, wt%	Onset temperature, °C		Melting Point, °C		Crystallinity, %	
	IM	TSE	IM	TSE	IM	TSE
0	157.2	157.9	166.3	165.7	63.8	57.5
5	156.3	156.7	164.8	164.9	64.5	59.6
10	156.4	157.1	164.4	164.3	67.9	62.4
15	154.9	155.7	164.5	164.3	60.1	55.5
20	154.5	155.2	164.4	164.9	56.4	48.4

IM= Internal Mixer, TSE= Twin Screw Extruder

To comprehend effect of kaolin and compounding processes on PP/Kaolin composite's melt transition, the onset temperature and crystallinity was plotted in Figure 6. The onset temperature showed a slight reduction with kaolin content as well as in internal mixer compared to twin screw extruder. These results were well agreement with rheological behaviour, and chain scission of PP into lower molecular weight due to kaolin and compounding processes were responsible for these [11].

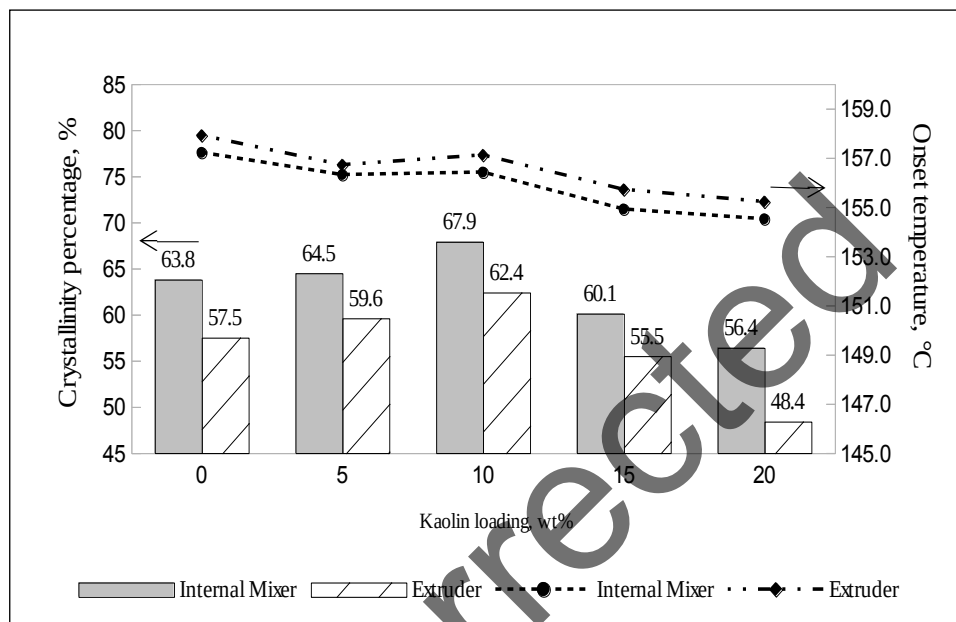


Figure 6. Crystallinity percentage and melt onset temperature of PP/kaolin composites

Nucleating effect of kaolin on PP was only found at 5 wt% and 10 wt% of kaolin loading, in which kaolin particles act as nuclei within PP matrix during cooling, and initiate the crystallization. The nucleating effect of kaolin could be originated from its high thermal conductivity, which accelerated exothermal crystallization process. In contrast, higher kaolin loading induce excess nuclei and impeded with each other during crystal growth therefore causing lower crystallinity [12-13]. In addition, crystallinity is proportional to crystallization activation energy of the composites which was reported by Ariffin et al. [14]. By using Kissinger method, 10wt% kaolin loaded PP/kaolin composite was found having the lowest crystallization activation energy, therefore it has highest crystallinity. In comparison, PP/kaolin composites prepared by internal mixer possessed higher crystallinity than those prepared by twin screw extruder. The differences were around 3~7%. The most appreciable origination came from the distinct cooling processes. The cooling process of internal mixer was carried out in ambient while extrudates were cooling down in water bath for twin screw extruder process.

Conclusion

Kaolin increase viscosity and shear stress of PP/Kaolin composite. This effect turned to be significant at high kaolin loading, and especially at high testing shear rate. For melting characteristic, the optimum kaolin content in polypropylene was 10% in weight, where kaolin could act as nucleating agent. The further addition of kaolin would reduce polymer's crystallinity. Besides, the addition of kaolin caused the composite's melting point decrease but maintain at higher kaolin loading. In comparison, twin screw extruder shows better compounding result compare to internal mixer. The drawbacks in internal mixer were claimed to chain scission of polypropylene, which became more obviously with the incorporation of kaolin.

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