Study on Effect of Filler Loading on the Flow and Swelling Behaviors of Polypropylene-Kaolin Composites Using Single-Screw Extruder

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ABSTRACT: Melt flow and extrudate swelling behavior of polypropylene-kaolin (PP-Kaolin) composites were investigated using a single-screw extruder. Kaolin was mixed with polypropylene (PP) using a heated two-roll mill at 185°C and the filler loading were varied from 5 to 30 wt %. Subsequently, flow behavior of the compounded formulations were evaluated through Melt Flow Index (MFI) measurement at various temperatures ranging from 190 to 230°C. The extrudate swelling ratio was also measured by using an image analysis instrument and software. It was proven that the MFI decreased with increasing loading of kaolin for test temperatures of 190 and 200°C. However, for temperatures exceeding 200°C, the MFI value rose slightly at 5 wt % of kaolin content then seemed to reduce as more kaolin was added. This is also detected in rheological measurement where the apparent visosity, η_{app}, appear to be lowered at 5 wt % loading of kaolin. Further increase in kaolin loading resulted in increasing value of the composites η_{app}. The swelling ratio decrease with increasing filler loading for composites below 20 wt %. However, at 30 wt % of kaolin content, the extrudate swelling ratio increased and noticeable blistered surface texture was observed on the extrudate surface. Furthermore, at this level of filler loading, shrinkage occurence due to the existence thermal gradient between the surface and the inner core of the extrudate caused void formation in the middle section of the extrudate. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 73–83, 2011

Key words: composites; polyolefins; processing; rheology; swelling

INTRODUCTION

Composite rheology and processing can be considered as one of the interest area in polymer field that have attracted many researches due to the need of developing and processing new composite materials with desired physical and mechanical properties. Many recent developments in thermoplastic materials especially polyolefins have been taken into consideration, which include altering the existing polymer properties in meeting end user performance requirement, especially in the automotive industry.[1] These alteration can be affected through changes in polymerization technique and chemistry, or by applying one of the most preferable technique, which is incorporation of wide variety of additives such as organic and inorganic fillers. Leong et al. claimed that the incorporation of fillers (10–40 wt % filler loading), specifically talc, kaolin, and calcium carbonate hinders plastic flow and increases the viscosity of polymer melt. Apart from such studies on the incorporation of fillers in polymer matrix, surface treatment of fillers have also been carried out extensively to offer better compounding and processing facilitation by enhancing filler dispersions and decreasing the melt viscosity.[2–7]

The key challenge in compounding the polymer composites is to get uniform filler dispersions and to avoid filler-filler agglomerations. Other than that, it is good to note that PP macromolecules do not have polar groups which is needed to interact with fillers in creating better bonding with the fillers. To overcome this issue, many researchers have conducted extensive studies on the addition of coupling agents.[8–11] Coupling agent are purposely added to improve the compatibility between filler and matrix which is projected to improve the interfacial adhesion characteristic of the polymeric resins. Generally, the choice of modification agent is made by considering some basic principle of its influence on both filler and matrix properties, such as increasing compatibility between filler and polymer matrix, dispersive properties of a filler, thermooxydation stability of the polymer, etc.[12] Among the highly used compatibilizer in polyolefin is maleic anhydride-*graft*-

TABLE I
Formulations for Various Kaolin Content

	0 (wt %)	5 (wt %)	10 (wt %)	20 (wt %)	30 (wt %)
PP (SM 240)	100	90	85	75	65
Kaolin	0	5	10	20	30
PPgMA	0	5	5	5	5

polypropylene (PPgMA). Several previous researches have proven that PPgMA is able to perform as an effective compatibilizer even in small amount.[3,13]

Commonly, extruder is used in the industry to transform the melted polymer into required end product. The greatest strength of screw extruders results from the intense shearing environment created within the flow channels of the screws. Extruders are able to continuously process highly viscous materials, such as polymer melts without the need for solvent, resulting in significant reductions in raw materials and equipment cost.[14] The inclusion of filler, however, makes the processing of polymers becomes more difficult due to changes in the rheological behavior of the filled polymer. Most filled polymers are incorporated with industrial fillers, such as glass fibres, carbon black, calcium carbonate, mica, and talc. Some of these fillers have complex structures, which may modify a clear interpretation of polymer flow characteristics and its rheological responses especially when extrusion process is used.

The above mentioned fact is attributed to strong dependence of polymer composites rheological behavior on a large number of parameters, such as filler volume fraction, shape, and size of the filler particle, filler–filler and filler-matrix interactions.[3,15,16] Moreover, many have also studied the effect of filler loading on the flow ability of the composites using a wide range of rheological instruments, temperatures, particle orientations, and types of coupling agent incorporation.[2,17] This article presents and evaluates flow behavior of PP-kaolin composites with the addition of PPgMA as a coupling agent which were conducted using a single-screw extruder. The melt elasticity phenomenon which are in the forms of extrudate swell and flow instability were also investigated to identify the influences of kaolin and PPgMa on PP matrix.

EXPERIMENTS

Materials

Polypropylene (PP) copolymer grade Pro-Fax SM240 with melt index of 25 g/10 min (ASTM D1238) supplied by Titan PP Polymer Malaysia was used as the matrix. Kaolin was provided by Finn Chemicals

with the density of 2.59 g/cm³ and mean particle diameter of 3.0 μm. Maleic PPgMA containing 1 wt % of MA was supplied by the Exxon Mobil Chemical.[2] Table I shows compound formulations used in this work.

Sample preparation

The compounding was carried out using heated two-roll mill at 185°C. Prior to the compounding procedure, kaolin filler was dried for 12 h in an oven at 80°C. The compounded material, of ±2 mm thickness, was then cut manually and fed into the Melt Flow Indexer (MFI) and single-screw extruder for melt flow and rheological properites characterization, respectively.

APPARATUS AND METHODOLOGY

Filler content determination

Because of fillers loss during compounding which is resulted from the open nature of the process, a polymer burn-off or ashing procedure was performed to check the final filler content in the composites once the process has been completed. The ashing test was performed following ASTM D5630. The samples were randomly collected and burnt off in a furnace with the temperature of 600°C for 4 h. The remaining residue was then weighed, and the corresponding weight fraction of the filler (W_f) are calculated using eq. (1),

$$W_f = \frac{W_\alpha - W_o}{W_c - W_o}, \qquad (1)$$

where W_α are the residue (i.e., filler) weight after ashing test and W_c and W_o are the weight of the composites and initial weight of the crucible, respectively. The exact kaolin content for the composites after being burnt are presented in Table II. The filler were cooled and conditioned at room temperature prior to weighing. From Table II it can be observed that the amount of filler loss during the compounding process was relatively minimum and controllable. Also, another fact that has to be taken into account was the contribution bound moisture dehydration during the ashing procedure. Nevertheless, small variation of the obtained filler content (∼

TABLE II
Kaolin Actual Content for Various Formulations

Sample (wt %)	Intended W_f	Measured W_f
5	0.0500	0.0488
10	0.1000	0.0938
20	0.2000	0.1930
30	0.3000	0.2940

within 6% reduction) with respect to initial filler loading proved that the aforementioned factor is not significantly affecting the overall filler content results.

MFI test

The materials MFI analysis using a Dynisco melt flow indexer model D4004HV which is in accordance with ASTM D1238-90b with some modifications were implemented on the experimental procedure. A load of 2.16 kg and test temperatures ranging from 190 to 230°C were used for data collection. The diameter and length of the die were 2.095 and 8.000 mm, respectively. The MFI is defined as the extrudate weight (W) in grams per 10 min. In this study, the cut time is measured in second, t, therefore the flow rate value needs to be converted into gram per 10 min using the following equations

$$MFI = 600W/t \qquad (2)$$

and

$$W = Al\rho_m, \qquad (3)$$

where A is the cross-sectional area of the piston (cm^2), l is the distance traveled by the piston (cm) and ρ_m is in g cm^{-3}. It can be seen from eq. (2) that the melt density (ρ_m) can be determined directly from the MFI using eq. (3).

Rheological test

The rheological test of the prepared sample was performed using a Brabender single-screw extruder KE 19/25 D. The test was conducted using a fabricated circular die with L/D ratio of 22/3. The processing temperatures were set differently at 190°C for the first zone, and 200°C for the second and third zone where the materials will be conveyed and sheared extensively, while the die was set at 210°C. The volumetric flow rates (Q) were calculated from the weight of the extrudate (W_{ext}) cut in grams for 15 sec and dividing it with the melt density (ρ_m) obtained from the MFI. This mathematical treatment would yield the volumetric flow rate, which is required to determine the apparent shear rate ($\dot{\gamma}_{app}$) parameter. Whereas, the solid composites density at room temperature (23°C) was measured using the gas pycnometer.

$$Q = \frac{W_{ext}}{\rho_m} \qquad (4)$$

While, the apparent shear stress (τ_{app}) was calculated from the known geometry of the die, i.e.,

length (L) and radius (R) of the circular die, together with the pressure generated at the die during the extrusion. These are expressed in eqs. (5) and (6).

$$\tau_{app} = \frac{RP}{2L} \text{ (apparent shear stress),} \qquad (5)$$

$$\dot{\gamma}_{app} = \frac{4Q}{\pi R^3} \text{ (apparent shear rate).} \qquad (6)$$

From the above expressions, the apparent shear viscosity can be calculated using the shear stress-shear rate relationship and this is shown in eq. (7).

$$\eta_{app} = \frac{\tau_{app}}{\dot{\gamma}_{app}}. \qquad (7)$$

The flow (i.e., Bagley and Rabinowitsch) corrections were not carried out since the aim of the study was not to determine true rheological values, but only to identify general trends for comparative study. The extrudate swelling phenomenon was indicated by the swelling ratio, B. For this measurement, the extrudates were cut carefully at $\sim$ 3-cm long strand after emerging from the die and straightaway quenched in water. The quenched extrudate diameter was determined using a high resolution digital camera equipped with Image-J software. The ratio of extrudate diameter to the MFI swell ratio was calculated using the following equation.

$$B = \frac{D_e}{D_d}, \qquad (8)$$

where D_e and D_d are the diameters of the extrudate and the die, respectively. The quench extrudate surface texture was also examined using the same image analysis facility mentioned previously.

RESULTS AND DISCUSSION

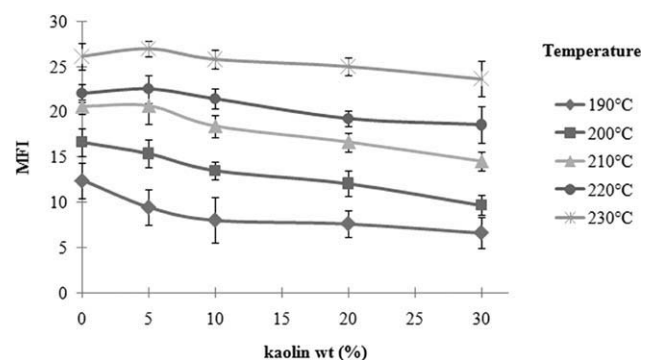Figure 1 illustrates the MFI values of polypropylene-kaolin (PP-kaolin) composites for various

Figure 1 MFI values of PP-kaolin at different temperature.

composition of kaolin at different temperatures. The plotted graph obviously shows that the MFI values were significantly affected by temperature. The MFI readings increased with increasing temperature suggesting that the polymer melt flow is very dependent upon the mobility of the molecular chains, and forces or entanglements which hold the molecules together. Increasing the temperature will result in increasing the chain mobility and flexibility and therefore, increase the flow ability of the material.

Measurements at 200°C and below showed that the MFI values decreased gradually as the amount of kaolin increased, however the trend started to change once the test temperature was increased (210°C and beyond). Generally, composites with higher amount of filler loading will provide greater filler–filler interaction that would be able to obstruct plastic melt flow which is the major cause for the reduction in the MFI values. Because of this facts, most researcher[17,18] claimed that when higher amount of filler is incorporated, lower MFI value is obtained. In this particular study, the results show good agreement with this statement as far as the results obtained below 200°C are concerned.

On the other hand, it is noted that above 200°C, the MFI value increased slightly with the addition of kaolin loading but showed an opposite trend when more than 5 wt % of kaolin loading was added in the system. This behavior is strongly connected by the effect of flake-like shape of kaolin particles which is able to slide in the polymer melt at high temperature. This claim was supported by the MFI slope plotted in between 0 to 5 wt % of kaolin at different temperatures (above 200°C) which clearly shows an increment, suggesting that increasing the temperature would promote higher tendency for the kaolin particles to slide against each other during the application of shear forces. Above 200°C, there is enough activation energy to generate ample free vol-
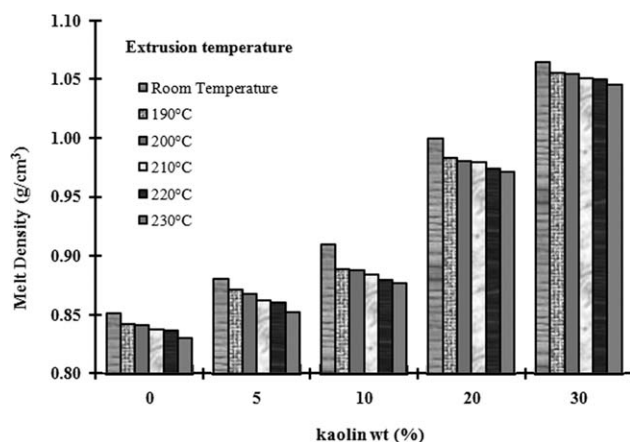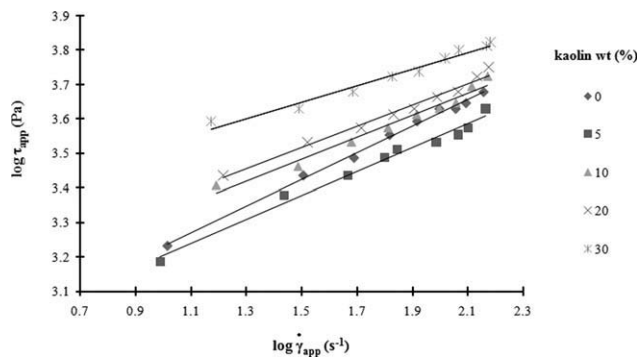

Figure 3 Melt flow curve of PP-kaolin composites for various kaolin loading at 210°C.

ume and subsequently decrease the melt strength which promote better flow for the composites. Whereas below 200°C, insufficient free volume cause the filler to obstruct flow. As expected, composite with filler loading above 5 wt % displayed lower MFI value due to formation of stronger particle–particle interaction and eventually forming agglomerations which would hinder the matrix flow.[2]

As for solid density and melt density results which are presented in Figure 2, the melt densities measured at all test temperatures are obviously lower compared with the solid density that is measured at room temperature. Basically, the melt density seems to decrease with increasing temperature and it is also observed that, all values increased linearly with increasing amount of filler loading. This is due to the fact that above glass transition temperature, T_g, polymer density was reduced resulted from increasing amount of free volume.[16,19] Theoretically and experimentally, the density increases as the amount of filler increases and this was due to the contribution of kaolin density which is higher than that of polypropylene. Although the MFI value increased at 5 wt % of filler loading for temperatures exceeding 200°C, the composites melt density was not significantly affected by filler incorporation.

Construction of a flow curve is important in characterizing the processing properties of polymer melts under certain extrusion conditions. Figure 3 displays the apparent flow curve of PP-kaolin composites for various kaolin loadings at 210°C, obtained from the single-screw extruder. Evidently, the apparent wall shear stress (τ) increased with increasing value of the apparent shear rate ($\dot{\gamma}_{app}$).

Although the power law relation would not be able to predict the experimentally observation of a Newtonion plateau at very low and very high shear rates, it is widely used for non Newtonian fluids in many engineering applications to relate the dependence of shear stress upon the shear rate. Theoretically, the polymer melts supposedly exhibit a power law relationship where τ_w and $\dot{\gamma}_{app}$ are linear in a

Figure 2 Melt density of PP-kaolin composites at various temperature.

TABLE III
Power Law Index (n) for PP-Kaolin Composites

Wt (%)	PP-Kaolin
0	0.3880
5	0.3476
10	0.3192
20	0.3053
30	0.2400

double logarithm coordinate system.[20] In this work, when this mathematical model is used on the obtained experimental data, it is proven that the melt shear flow basically obeys the power law relationship in their flow behavior.

$$\tau_w = K\dot{\gamma}_{app}^{n}, \qquad (9)$$

where K is the consistency constant and n is the power law index. The n value of the power law relationship presented in eq. (9) can be obtained from the slope of the linear plot of log τ_w versus log $\dot{\gamma}_{app}$, and the results are indicated in Table III. Obviously all n values were less than one, indicating the pseudoplastic nature of the composites melts that is common in thermoplastic composites/blend systems. Moreover, the value of n decreased with kaolin loading indicating an increase in pseudoplasticity. Similar results were attained in i-PP/Kaolin composites,[18] thus providing support for the claim that kaolin is quite capable of introducing pseudoplastic behavior to the melt.

It can also be observed from Figure 3 that at the same temperature, the value of τ_w of the composites melt was higher with respect to the pure PP melts except for 5 wt % of kaolin. This means that the flow resistance was increased, resulting from the addition of kaolin fillers in the system, which also caused by the rise in pressure.[21] But in this study, an anomaly was discovered where at low kaolin content of 5 wt %, the composites exhibited lower shear stress compared to the pure PP. To support this finding, results reported by Maiti et al. were consulted where they stated that the shear stress initially decreased with an increase in filler volume fraction (φ_f) and with further increase in filler content the shear stress increased for i-PP/CaSiO$_3$ system.[11] This definitely has interrelation with the flaky shape of kaolin particles, where at low contents of 5 wt % kaolin, flow-favoring orientation of plate-like kaolin particles may contribute to the decrease of shear stress in PP composites containing kaolin fillers. Meanwhile, above 5 wt %, the filler-matrix interaction is gradually replaced by the filler–filler interaction due to the presence of reasonably large amount of filler in the system which hinder the composites flow.[5]

Figure 4 displays the relationship between apparent melt viscosity (η_{app}) with $\dot{\gamma}_{app}$ at a test temperature of 210°C. As shown in Figure 4, the shear viscosity decreases with increasing shear rate. Normally, shearing does not cause chain scission but rather a reversible process of disentanglement.[15] It can be seen that the apparent viscosity decreases rapidly with increasing shear rate for both filled and unfilled PP, which implies a shear thinning behavior of the materials.

It has also been discussed by Maiti et al. that the apparent viscosity of PP-kaolin composites system shows a similar trend with the iPP/CaSiO$_3$ composites, which initially decreased at low concentration of filler loading.[5] Nevertheless, the values of η_{app} were increased with further increase in kaolin loading. A decrease in viscosity indicated better molecular motions between polymer chain and filler, which might be due to plasticizing action induced by the geometry of kaolin particles. This means that at 5 wt % of kaolin content, the particle–particle network was ruptured by shear forces, disposing the flaky particles in a flow-favoring orientation causing η_{app} to decrease. Without doubt, the incorporation of kaolin in PP system is the main reason of the above mentioned behavior.

In PP-kaolin melt, it is strongly believed that the kaolin particles are able to slide among each other during the application of shear forces. The ease of melt flow depends upon the mobility of the molecular chains and the forces or entanglements holding the molecules together. Nonetheless, at a critical concentration level which is above 5 wt % of filler loading (only valid for this experimental work), the η_{app} is expected to increase with increasing amount of kaolin. The effective collisions between particles at high shear forces lead to densed packing of the particles as they are closer to each other. At this stage the filler–filler interaction is more dominant compared to filler-matrix interaction. Therefore, the polymer chain mobility are significantly affected by
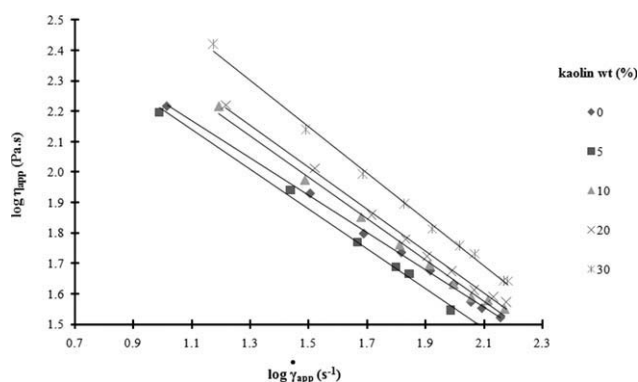

Figure 4 Viscosity curve of PP-kaolin composites for various kaolin loading at 210°C.
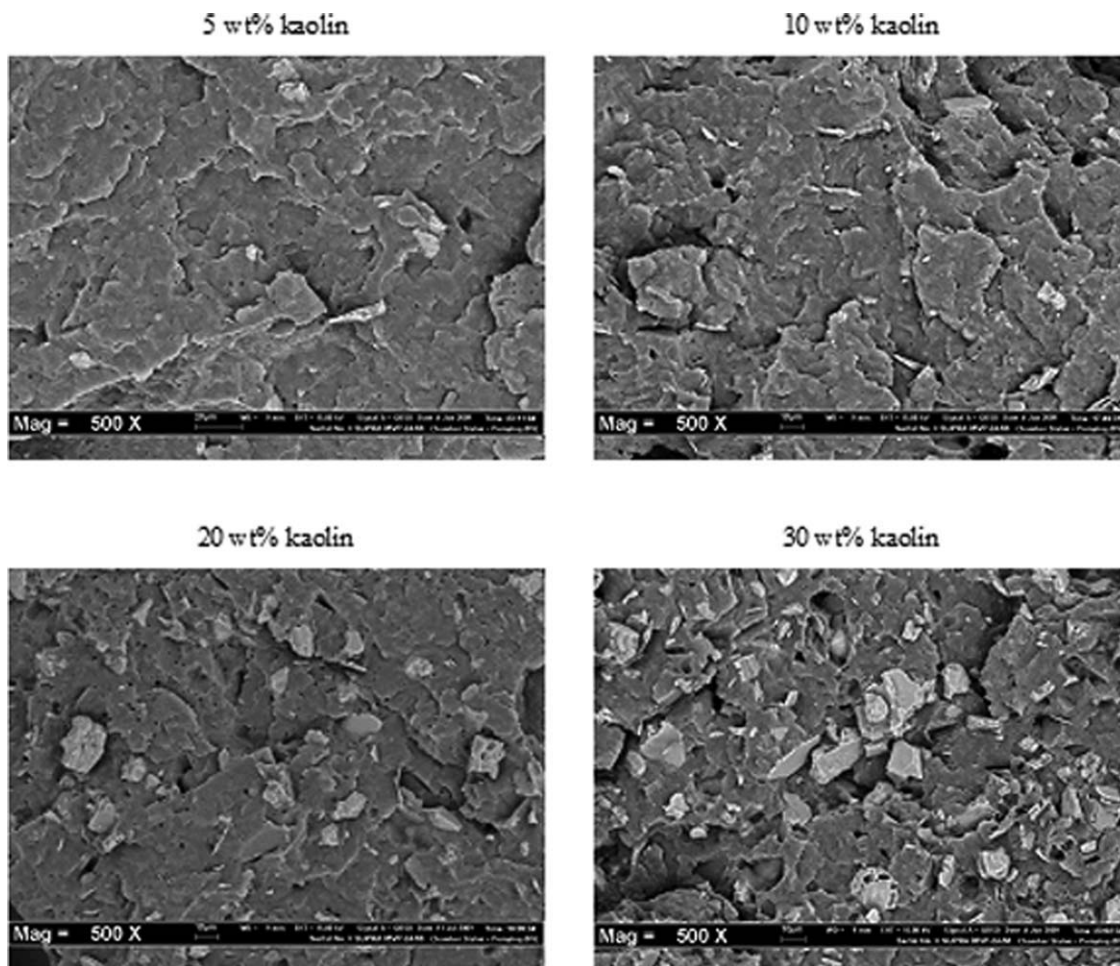
Figure 5 SEM micrograph of PP-kaolin composites for various kaolin loading at 210°C.

the overloading of kaolin particles in the system, which could easily perturb the normal flow and hinder the mobility of chain segments in melt flow, consequently increasing the value of η_{app}.[6,7]

The claims was proven by the SEM micrograph displayed in Figure 5 where at 30 wt % of kaolin loading, the filler was densely packed and show a sign of agglomeration compared to lower wt % of kaolin loading. Below 30 wt % of kaolin loading, the well dispersed kaolin was contributed by the incoporation of PPgMA. Otherwise at 30 wt % of kaolin loading, even the addition of PPgMA as a wetting agent was not able to prevent agglomeration. The scenario is due to particle–particle interaction is more pronounce when higher amount of filler loading was used in comparison to low amount of filler loading which would promote polymer–particle interaction.

The elasticity of polymer melt is a major concern in the processing of plastics and it is usually reflected by dimensional stability during and after processing procedure. Extrudate swell is often related to elastic recovery of the materials at the extrusion die inlet. An elastic melt will normally swell to a much greater diameter than the actual orifice when it is extruded from a die or flows from an exit of a tube. This swelling phenomenon can be affected by several factors which include load, temperature, shear stress, shear rate, L/D, and several others. Most composites with higher loading of filler
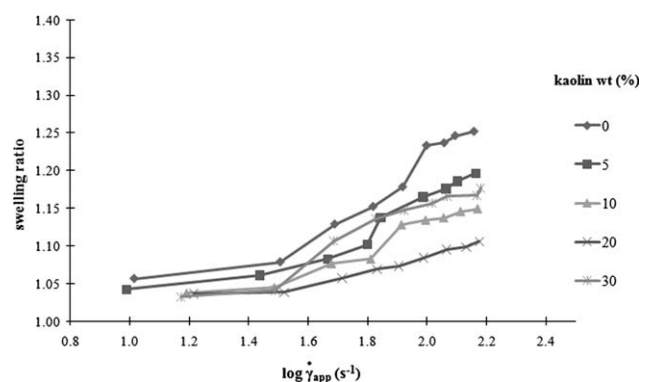

Figure 6 Swelling ratio vs. shear stress of PP-kaolin composites for various kaolin loading at 210°C.
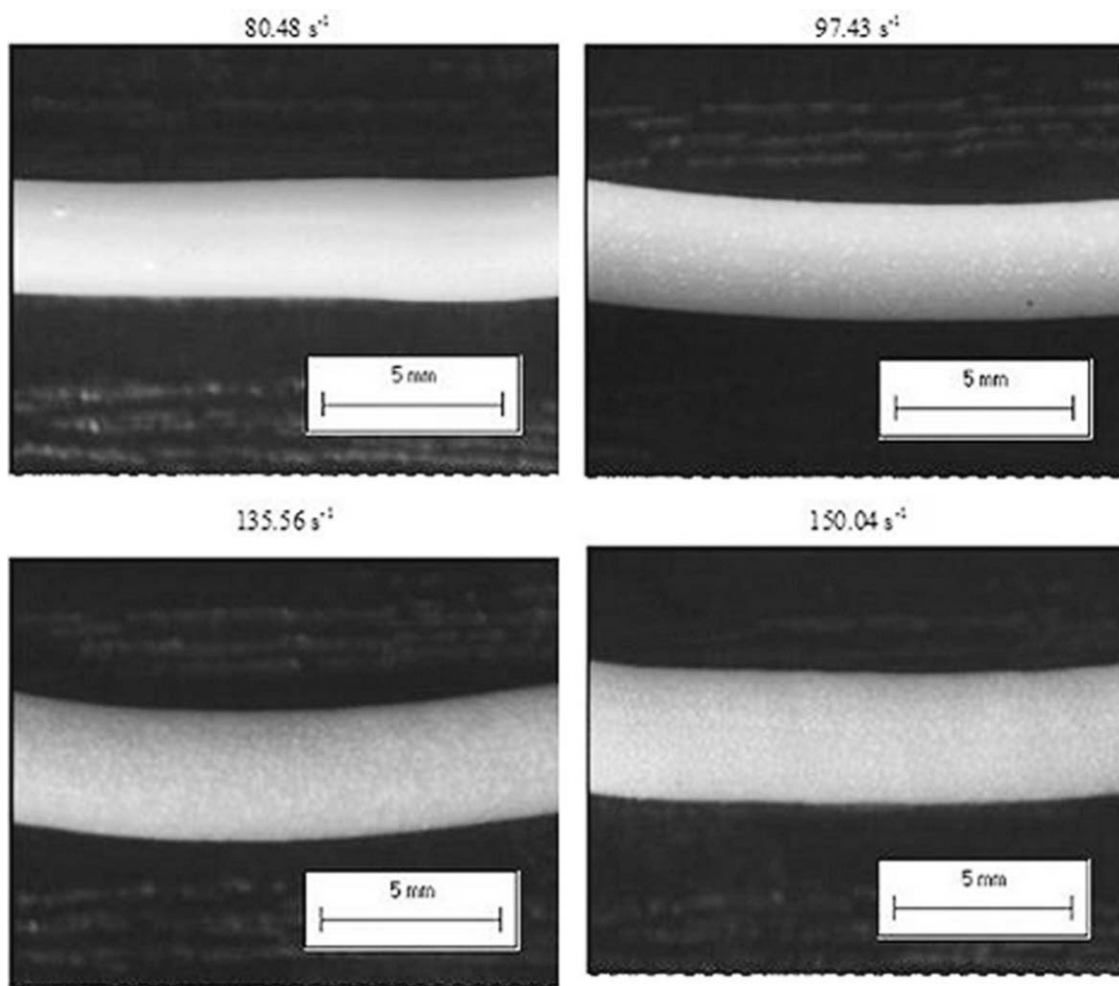
Figure 7 Extrudate surface texture for 20 wt % of kaolin at different $\dot{\gamma}_{app}$.

demonstrated that the melt elasticity of the composites weakens with increasing filler concentration.[17,20,22] Whereas, when test temperature is fixed, extrusion rate increases with the increase of shear stress at the channel wall, and the converging flow is correspondingly enhanced.[21,23]

Figure 6 illustrates a plotted graph of swelling ratio versus log $\dot{\gamma}_{app}$ for composites at various kaolin loading. Overall, the results indicated that swelling ratios of all compounded composites increase rapidly with increasing $\dot{\gamma}_{app}$ but then experience gradual increment at certain range of shear rate. This trend can be said to be adhering to common trend reported by previous researchers[7,13,21] that used other types of polymeric matrices and the results usually confine to kaolin loading of below 20 wt %. Generally, it is predicted that the swelling ratio would decrease with increasing amount of kaolin loading due to the melt looses its melt elasticity. While, at constant temperature during melt flow, the swelling ratio increase with increasing shear stress due to increase in stored elastic energy in the melt.

Consequently, the extrudate swell will increase when the extrudates emerge from the die, owing to the shape memory effect and the elastic recovery of the macromolecular chain.

This suggests that when higher $\dot{\gamma}_{app}$ is introduced to the system, it will enhance the flow rate making the resident time shorter for the melt to pass through the die. At this stage, the molten composites are still able to restore its elastic energy thus contributes to increasing value of the composites swelling ratio. Both pure PP and PP-kaolin composites up to 20 wt % of kaolin loading demonstrate that the swelling ratio increase gradually at high $\dot{\gamma}_{app}$ in the range of 10^2 s^{-1}. This is because the presence of high shear stress creates an elongational orientation of macromolecular chains trailing the flow direction hence more elastic deformation energy was generated leading to a deliberate increase in the swelling behavior. The discussed phenomena reveals that the trend of swelling ratio is strongly dependent on $\dot{\gamma}_{app}$. The result agrees with the work on PS and LLDPE melt reported by Sombatsompop and Charoen, and LDPE
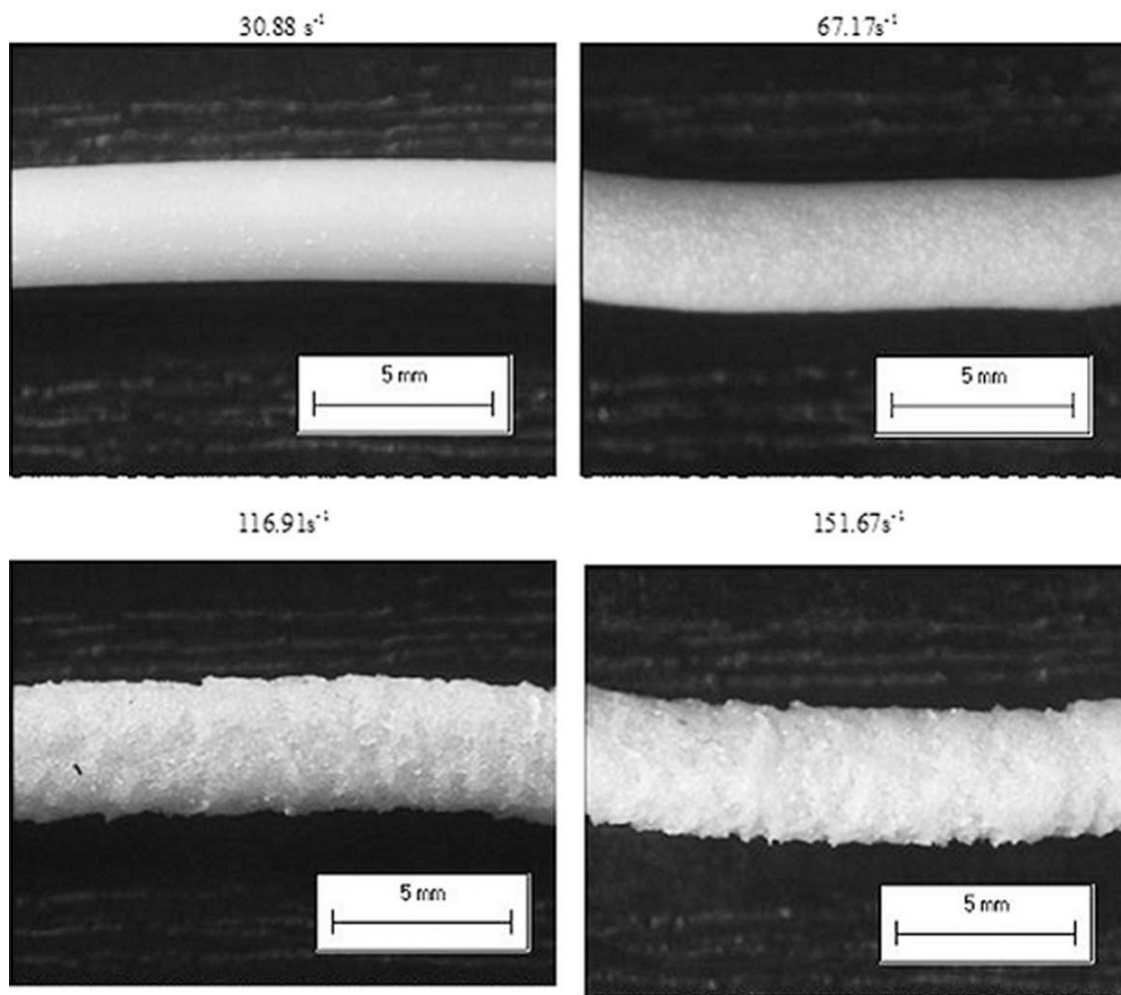
Figure 8 Extrudate surface texture for 30 wt % of kaolin at different $\dot{\gamma}_{app}$.

glass bead composites done by Li et al.[4,24] It is also observed that the compound with higher kaolin loading provided a significant improvement in swelling behavior except for 30 wt % of kaolin loading which will be discussed later. This fact is due to the ability of filler to hold the matrix and reduce the polymer chain mobility. The movements of the oriented and aligned polymer molecules were delayed and sustained thus decelerating the elastic recovery and reducing the extrudate swell of the composites.

At 30 wt % of kaolin loading, the swell ratio rose incredibly as the $\dot{\gamma}_{app}$ increased. Based on other research findings, the swelling ratio is supposed to reduce as the amount of kaolin increased.[3,13,20] By further examining the extrudate texture, it is clear from Figures 7 and 8 that the peculiar high extrudate swell was assisted by formation of void in the center of extrudate which occurred at high $\dot{\gamma}_{app}$ but was not severe enough to be detected visually when the filler content is less than 20 wt %. The extrudate void structure became more pronounced at 30 wt %

of kaolin at mostly all shear rate range, the extrudate is hollow in the center and displaying a foam-like surface appearance.

This can be attributed to higher amount of filler loading which tend to promote cell nucleation and becoming the nucleation site for the claimed foaming occurence in the matrix. Generally, fillers are added to improve foamablity and crosslinking of polymer matrix. In addition, the presence of filler also promotes heterogeneous cell nucleation where they remain solid and thermally stable during the foaming process. Although the PP-kaolin composites are compounded without any addition of blowing agent, kaolin is still able to nucleate with enough force applied to overcome the existing surface energies barrier.[23] In this particular case, the formation of bubbles on the extrudate surface structure were only generated for composites with kaolin content of exceeding 20 wt % and this indicates that at such level of kaolin loading, there is sufficiant $\dot{\gamma}_{app}$ applied to the system to overcome the surface
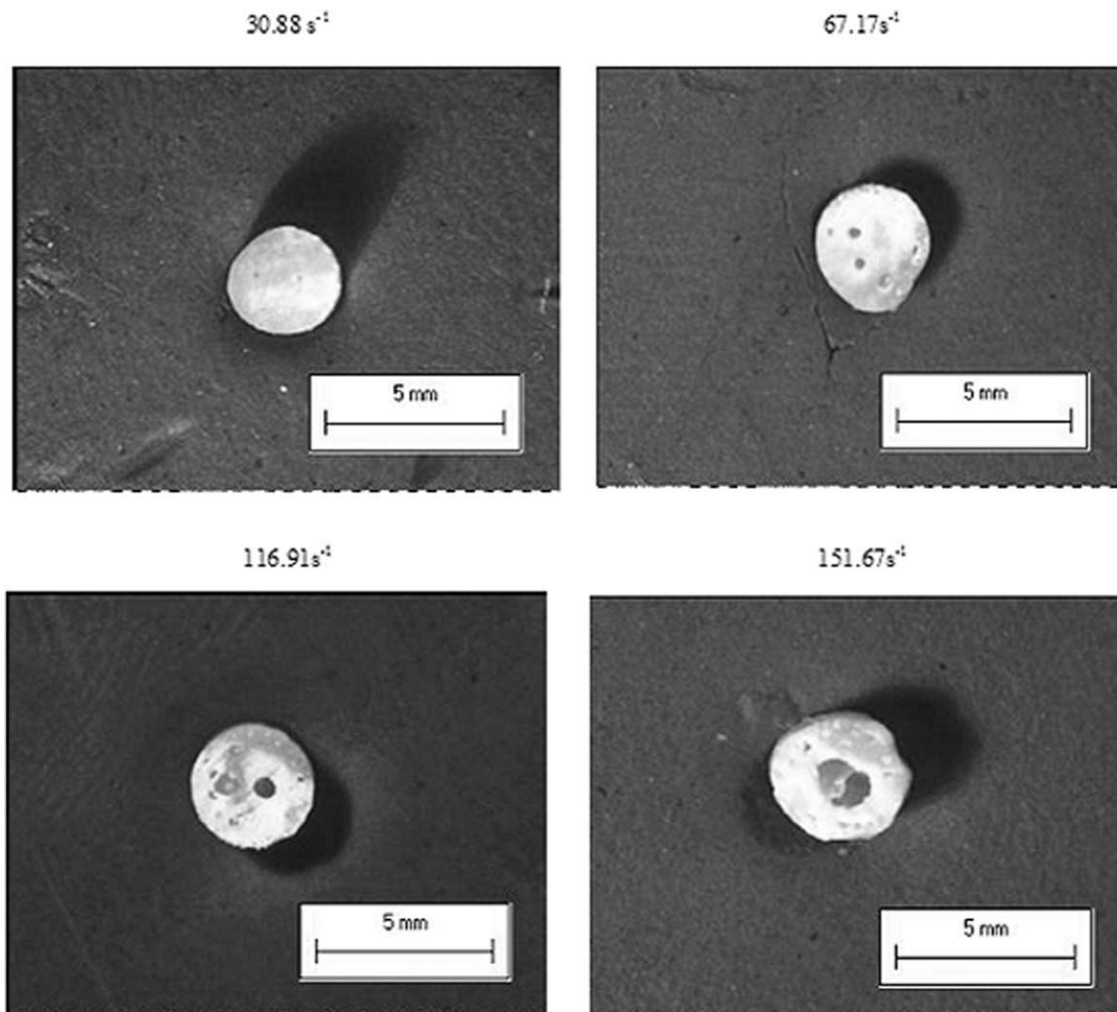
Figure 9 Extrudate cross-sectional area for 30 wt % of kaolin at different $\dot{\gamma}_{app}$.

energy barrier mentioned previously. Obviously, below the critical value of $\dot{\gamma}_{app}$ and kaolin content, a smooth extrudate surface texture can be observed.

In spite of that when kaolin content exceeded 30 wt %, even at low $\dot{\gamma}_{app}$ the formations of blistered surface texture were quite severe. The reason is that, as more kaolin was incorporated inside the matrix, the activation energy barrier was reduced due to the particle–molecule interface which led to increasing number of nucleation sites and was able to increase the nucleation rate. Consequently, less force was required to overcome the activation energy barrier, resulting in the formation of more bubbles on the extrudate surface and subsequently turn to foam-like surface texture as the $\dot{\gamma}_{app}$ increased. Besides that, stick-slip phenomenon can also be observed at high $\dot{\gamma}_{app}$ and which are presented by visible periodic waviness of extrudate surface as shown in Figure 8. This is due to the ability of the extrudate to emerged out of the die even at a semisolid state resulted from high applied pressure exceeding the critical shear

stress limit. Above this critical shear stress, it is believed that the applied pressure would result in a stick-slip phenomenon at the die wall.

Meanwhile, it was also discovered that extrudates at 30 wt % of kaolin content tended to form void in the cross section of the extrudates and the void became larger as the $\dot{\gamma}_{app}$ increased. At high $\dot{\gamma}_{app}$, the viscosity of the melt will increase which subsequently cause significant reduction in the melt elastic component adhering to a common trend found in the effect of temperatures and filler loading towards viscosity. During the emergence of extrudate of the die exit, the melt suddenly goes from high pressure to atmospheric pressure and undergo a sudden quench in cool water that indicates a large temperature gradient. This type of process condition is favorable for residual stress formation which is one of the factors that can cause shrinkage in many polymer products and in this case, the extrudates.

The extensional flow along the melt will cause an orientation to the polymer chains. Solidification of

the polymer will freeze the surface in this orientation direction. In the meantime, the flow between the solid layer is affected by the temperature gradient resulting in unbalance cooling where the inner layer cools slowly with respect to the skin layer. During application of shear forces on the extruded composites, orientation of the polymer chains will occur while the presence of kaolin will restrict and hinder the polymer chains from relaxing. As mentioned previously, after exiting the die the composites will swell first then followed by cooling. The composites with high kaolin wt %, will have less chance of relaxation after swelling due to reduction of elastic component. Thus after quenching, the surface layer of the extrudates will solidify first while the inner layer is still in a molten stage. Soon after, as the inner melted layer cools down, it will be attracted to the cooled skin of the extrudate layer. Thus a void is created in the composites extrudate since the total composites volume reduces with time as the temperature gradient drops.[25–27] The existance of this void within extrudate can be observed in Figure 9.

Then, the void became more severe and it turned into a hollow feature as the $\dot{\gamma}_{app}$ increases. As the $\dot{\gamma}_{app}$ increases, the volumetric flow rates are also increased which resulted form fast quenching compared to extrudates produced at low $\dot{\gamma}_{app}$. As swelling takes place after exiting the die, faster quenching will eventually solidify the skin layer of the extrudate surface quicker hence enhancing the formation of voids within the extrudates as the composites total volume drop due to increasing value of composites melt density on the skin layer compared to the inner layer. This significant effect is connected to the peculiar swelling behavior of the composites at high $\dot{\gamma}_{app}$ as discussed earlier.[5,26]

CONCLUSION

From the results, several conclusions can be made as follows; when the MFI test temperature increases from 190 to 200°C, the MFI value of the composites also increases mainly due to the increasing amount of free volume. Nevertheless, addition of high loading of kaolin in the composites will significantly reduce the MFI value and this can be related to the presence of kaolin which hinders the plastic flow. Meanwhile, the melt density displays a linear increase when the kaolin amount increases and it reduces deliberately as the temperature rises up which also in close relation with the increasing value of free volume. However, for temperature above 200°C a different set of reading were obtained. At 5 wt % of kaolin loading, the MFI increases but exceeding that value a reverse trend of MFI was observed. The kaolin flake-like shape and tempera-

tures play a vital role in this occurrence and it was also supported by the generated melt flow curve. High processing temperature promotes better condition for the kaolin particles to slide against each other during the application of shear forces.

In addition, the composites obeys the power law relation and are capable of displaying pseudoplastic behavior. In spite of that, the swelling extrudate data proposed that the swelling ratio increases with increasing $\dot{\gamma}_{app}$, which suggests that at higher $\dot{\gamma}_{app}$, the molten composites are able to restore its elastic energy. As the kaolin wt % increases, the swelling phenomena reduces and this is contributed by the kaolin ability to hold the matrix which reduces polymer chain mobility and decelerate elastic recovery. Nevertheless, at 30 wt % of kaolin content, the swell ratio increases instead. This may only takes place provided that enough kaolin is present that could develop into more nucleation sites in the matrix which will eventually initiate bubble formation in the extruded composites. Meanwhile, severe shrinkage occurs at 30 wt % compared to extrudates with lower kaolin content and it becomes more pronounced at higher $\dot{\gamma}_{app}$. The factor is contributed by the combination of swelling and fast quenching phenomenon occurred in PP-kaolin composites with high kaolin loading.

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