

Effect of Filler Treatments on Rheological Behavior of Calcium Carbonate and Talc-Filled Polypropylene Hybrid Composites

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ABSTRACT: Commercial stearic acid treated calcium carbonate (CaCO_3) was used to make a comparative study on rheological behavior of the CaCO_3 and talc-filled polypropylene (PP) hybrid composites with nontreated filler. Apparent shear viscosity and extrudate swell were investigated with variation of filler ratio and temperature with 30% by weight total of filler was used in PP composite. The Shimadzu capillary rheometer was used to evaluate shear viscosity and shear rate of the composite. It was found that the shear viscosities decrease with increasing shear rate. The apparent shear viscosity of the composite containing the stearic acid treated is slightly lower than untreated filler. Shear thickening behavior at higher shear rate has also shown by

15/15 treated composites at higher temperature about 220°C and investigation by SEM has proved that filler being densely packed at that condition. Treated composites also exhibit lower swelling ratio value than untreated composite, and swelling ratio also decreases linearly with increasing temperature and the die length–diameter ratio. It is believed that dispersion of filler play an important role not only on shear viscosity but also on swelling ratio of PP composite. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5421–5426, 2006

Key words: polypropylene; calcium carbonate; talc; shear viscosity; rheology; swelling ratio

INTRODUCTION

Mineral fillers play an important role as particle reinforcing agents in thermoplastics industry, especially talc and calcium carbonate (CaCO_3). Development of rigid polypropylene (PP) composites highly filled with CaCO_3 provides a great commercial significance because of increased performance of polymeric material, cost, and improved properties of materials. The degree of improvement not only depends on the judicious choice of filler origin, particle size, and shape, and the fraction of filler, but also on the filler surface treatment that promote interaction between the polymer matrix and filler.¹

However, the incorporation of filler in large amounts of resin introduces processing difficulty, whereby the addition of such particulates causes significant increases in the viscosity of thermoplastics. Thus, to obtain the best end properties of the composite product and to optimize processing conditions, understanding of the rheology of filled melt systems are very important.

Hydrophilic feature of mineral fillers usually promote difficulty to combine with most polymeric materials that are usually hydrophobic. Modification of filler not only contributes to reinforcement but is also very useful in increasing the interaction of particles to impart rheological properties, prevent sedimentation, aid dispersion, or prevent agglomeration. Previous study reported that agglomeration of filler will affect the processing, give poor appearance, and demonstrate inferior properties.²

Several methods were used to surface-treat the CaCO_3 particles to improve the fluidity and dispersion of the filler particles in PP composites. Surface treatment of CaCO_3 will reduce the inter particle interaction, enhances the polymer filler compatibility, and results in less increase in shear viscosity. Chapman and Lee³ reported that certain additives of surface treatment cause significant reduction in viscosity and yield stress of polymer compounds, which results from wetting and dispersion of filler.^{3–7} Pronounced effect of treatment will be obtained by decreasing the filler size.⁸

A low molecular weight of organic compound is the most used technique to change the particle–particle and polymer–particle interaction.^{6,9–11} For CaCO_3 , stearic acid is often used as it manifested better mechanical properties by improving dispersion of filler.^{8,11–13} Surface coating with fatty acid derivatives

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result in decreasing surface free energy of the filler and will result in reducing particle–particle interaction. Previous studies of the rheological properties of mixed particle compounds have been conducted by Kwang Jea et al. in polystyrene matrix and stated that the shear viscosity of the hybrid filler is generally higher than the CaCO_3 compounds, but lower than the talc compounds.¹⁴

In the present work, the effects of filler surface modification, filler ratio, and temperature on the rheological properties of hybrid composites have been studied. The sample extrudate swell has also been investigated at different temperatures and capillary dies length-to-diameter (L/D) ratios.

MATERIALS

Polypropylene (PP) copolymer grade Pro-Fax SM240 with melt index of 25 g/10 min supplied by Titan PP Polymer Malaysia.

Filler talc grade was supplied by Chung Chemicals Sdn. Bhd. and CaCO_3 grade OMYACARB 3-SA (untreated) and OMYACARB 3-TSA (stearic acid treated) were supplied by Malaysian Calcium Corp. Sdn. Bhd. Malaysia. Table I summarizes material specification for each filler used in this study.

Other additives used in the compound ingredient are antioxidant (Irganox 1010) and ultraviolet stabilizer (Tinuvin 770 DF), both from CIBA.

Sample preparation

Compounding was carried out with a Brabender Plastocorder at 185°C. Compounds were blended at a screw speed of 50 rpm and formulations of compound prepared is tabulated in Table II.

Rheological study

The shear viscosity of the compounds was measured in a series of three different ratios CaCO_3 : talc (30/0, 15/15, and 0/30). Rheological study was conducted using Shimadzu Rheometer Model CFT-500 (constant shear stress) in accordance with JIS K 6719-1977. Compounded samples about 1.5 g were cut into suitable size pellets, were loaded into the cylinder, and pre-

TABLE I
Materials Specification

Materials	Density (g/cm ³)	Hardness (Moh's scale)	Mean particle diameter (μm)
Talc (T)	2.79	1	6.3
Untreated CaCO_3 (UCC)	2.7	3	4.5
Treated CaCO_3 (TCC)	2.7	3	4.5

TABLE II
Formulations Comprising Single Filler and Hybrid Filler Composites

Sample	Composition (wt %)	
	PP/untreated CaCO_3 /talc	PP/treated CaCO_3 /talc
30/0	70/30/0	70/30/0
15/15	70/15/15	70/15/15
0/30	70/0/30	70/0/30

heated for 300 s. A circular die of L/D ratio 10 with a die diameter of 1 mm was used. The apparent shear viscosity (η) and apparent shear rate ($\dot{\gamma}$) are calculated from knowledge of the barrel diameter, length (L), and radius (R) of the capillary.

These are expressed as

$$\tau = \frac{RP}{2L} \quad (\text{shear stress}) \quad (1)$$

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \quad (\text{shear rate}) \quad (2)$$

where R is the die radius; P is the pressure difference; L is the die length; and Q is the flow rate.

The apparent shear viscosity is given by the relation

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (3)$$

η is the viscosity; τ is the shear stress; and $\dot{\gamma}$ is the shear rate.

No attempt to perform end-correction was made since the aim was not to determine absolute rheological values, but to detect general trends for comparative study.

Extrudate swell was indicated by swell ratio, B . The extrudates were cut carefully at 5 cm long strand from the capillary rheometer and the diameter was deter-

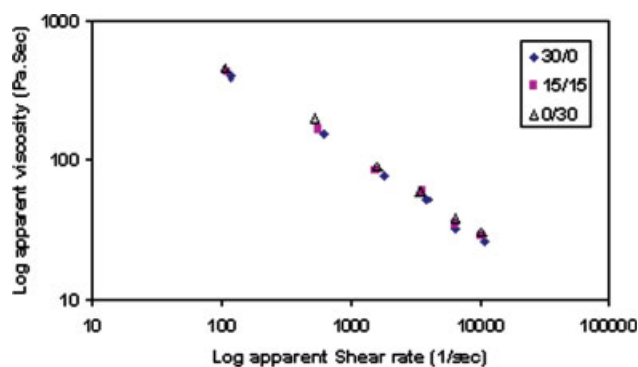


Figure 1 The apparent shear viscosity and apparent shear rate of PP composites untreated (CaCO_3 : talc) for different ratio under 180°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

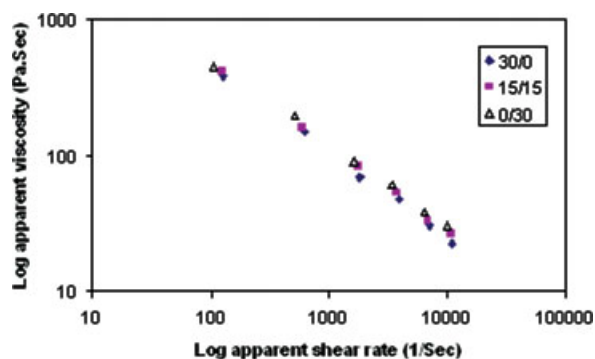


Figure 2 The apparent shear viscosity and apparent shear rate of PP composites treated (CaCO₃ : talc) for different ratio under 180°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mined using a micrometer. The ratio of extrudate diameter to the capillary diameter, swell ratio, was calculated using the following expression

$$\text{Swell ratio, } B = \frac{\text{Extrudate Diameter}(D_e)}{\text{Capillary Diameter}(D_c)} \quad (4)$$

RESULTS AND DISCUSSION

Mostly for compounds with higher loading of filler, the shear viscosity will increase since incorporation of fillers will obstruct plastic to flow. The apparent viscosity as a function of shear rate graphs of hybrid filler composites for untreated and treated compounds, respectively, at three ratios, are shown in Figures 1 and 2. Different symbols are used for different filler ratio. The shear viscosities decrease with increasing shear rate¹⁴ and many other researchers reported that shearing did not cause chain scission but rather a re-

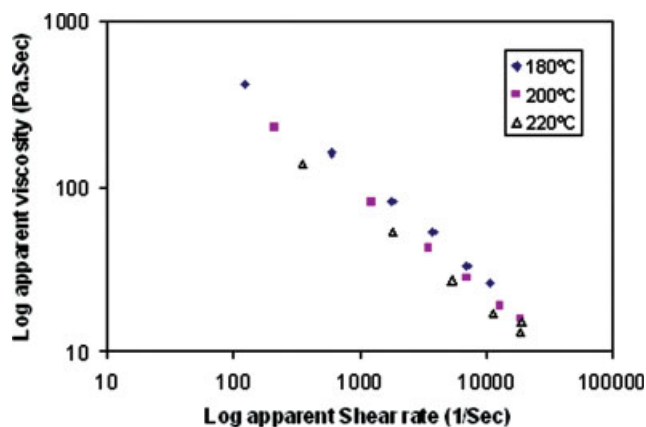
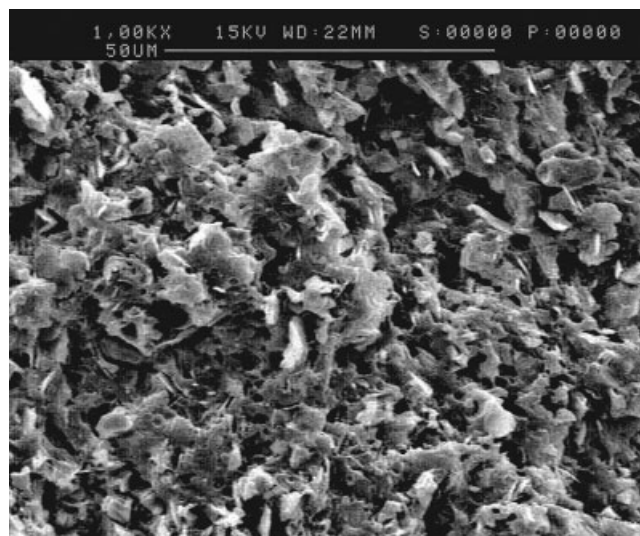
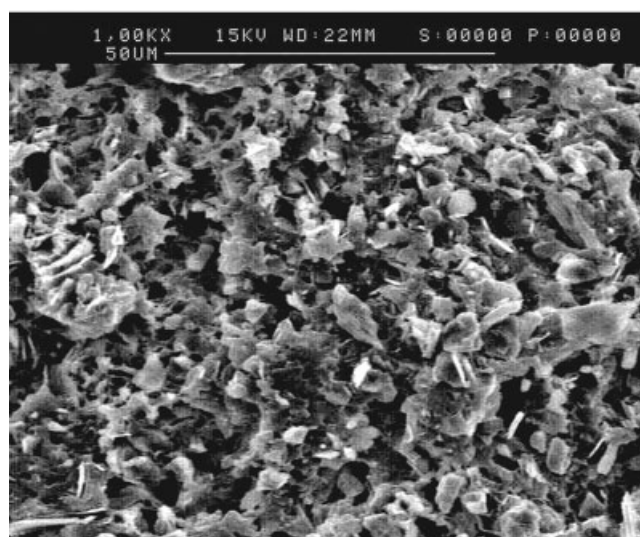


Figure 3 The apparent shear viscosity and apparent shear rate of PP composites treated for 15/15 (CaCO₃ : talc) under different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

versible process of disentanglement.¹⁵ It was found that the viscosity of the 0 : 30 (CaCO₃ : talc) provide a higher viscosity than the rest of the ratio. Talc particles are well known to have a disc shape, while CaCO₃ particles are roughly spherical.¹⁴ The disc shape of talc particles will promote sliding against each particle during the application of shear forces due to its platy shape, which allows a decrease in the plastic flow.¹⁶ In the previous study, talc with finest particle sizes are the most efficient specimens increasing onset of crystallization, and it was believed that crystallinity of talc in PP matrix also restricts the composite to flow.¹⁷ The overall of CaCO₃-filled PP is lower than the rest of the composites, which can signify that CaCO₃ has the ability to increase the plastic-



(a)



(b)

Figure 4 SEM micrograph of PP composites treated for 15/15 (CaCO₃ : talc) at 220°C: (a) low shear rate and (b) high shear rate.

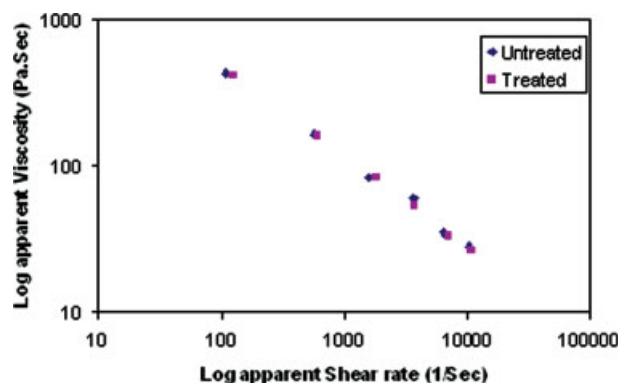


Figure 5 The comparison of apparent shear viscosity and apparent shear rate of PP composites treated and untreated for 15/15 (CaCO₃ : talc) under 180°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

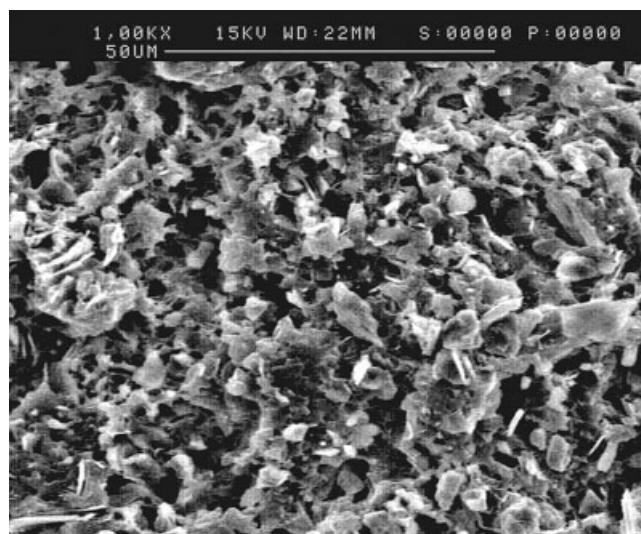
ity and processability of the polymer. The similar trend was also found for the treated filler, but the difference among the ratio is small for both the plots of treated and untreated, especially when a high shear rate was applied.

At higher shear rates, the data for the three of the ratios (0/30, 15/15, and 30/0) are close. Since at high shear rates, particle shape of fillers did not provide a significant effect on viscosity of the composite, because the composite structure is broken and the viscosity is dominated by the hydrodynamic interactions.¹⁸

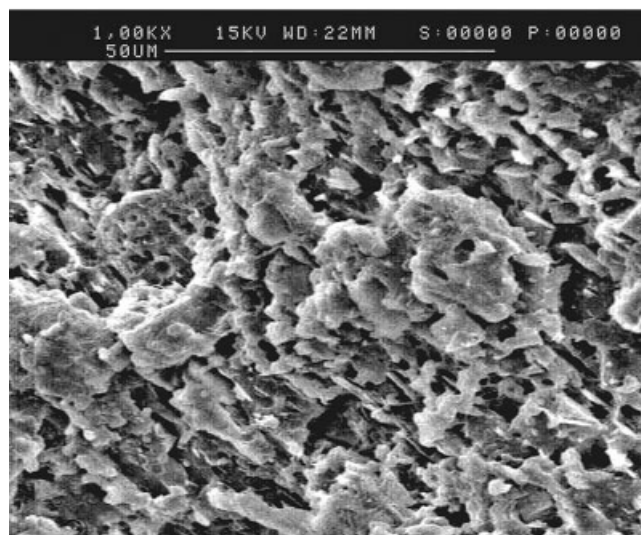
Figure 3 shows the effect of temperature on viscosity of hybrid composite at different shear stresses. Three different temperatures have been used (180, 200, and 220°C). Barnes et al.¹ claimed that as the temperature increases, the viscosity decreases rapidly and the viscous part becomes more evident than elastic part. It is found that the slope of the curves is different and become converged at high shear rate. In this case, the viscosity of the composite at 220°C is lower than the rest of the temperature. However, the viscosity of the composite increases at high shear rate, where it exhibits shears thickening behavior. Hoffman¹⁹ assumed that under the influence of hydrodynamic forces the dispersed particles arrange themselves in ordered layers, and the layered structure is maintained due to the presence of electrostatic or steric repulsion forces. This behavior will hinder the melt to flow and thus increase the viscosity. As shown in Figure 4(b), both of the filler particles in PP composite (70/15/15) at high shear rate have dispersed evenly and densely packed compared to the low shear rate [Fig. 4(a)].

Figure 5 shows the comparison of apparent shear viscosity of 15/15 CaCO₃ and talc for treated and untreated filler under 180°C. The curves show that the viscosity for both the composites decreases at higher

shear rate. A decreasing pattern in shear viscosity by surface treatment at filler has been reported by several researchers.^{4,5,7} Stearic acid treated CaCO₃ significantly decreases the magnitudes of the shear viscosity, which the filler–filler interaction substantially reduced with surface treatment. In this case, stearic acid treated CaCO₃ filler exhibit lower viscosity than the untreated one, but the difference is very small and tends to converge at high shear rate. Decrease in viscosity value indicates a better molecular motion between polymer chain and filler, which might be due to a plasticizing action induced by stearic acid. Filler treatment with stearic acid also reduces the particle–particle interaction and this will lead to a better dispersion of the particles in the host matrix polymer,



(a)



(b)

Figure 6 SEM micrograph of PP composites 15/15 (CaCO₃ : talc) at 180°C: (a) untreated and (b) treated.

thus promotes the fluidity of the composites and decrease in viscosity. The morphology of the composites for untreated and treated filler is shown in Figures 6(a,b). Treated CaCO₃ particles show an almost homogeneous dispersion and effective bind to the matrix, and untreated particles shows a much coarser structure.

Extrudate swell

Extrudate swell is often related to the elastic recovery of the material at the inlet of the die. When an elastic liquid is extruded from a die or flows from the exit of a tube, it usually swells to a much greater diameter than that of the orifice. Newtonian liquids can also show die swell, but only at low rates of flow, and as the flow rate increases the swelling decreases.⁸ For non-Newtonian liquid or elastic liquid, the swelling ratio increases with increasing flow rate. This swelling behavior is highly affected by a number of factors, such as temperature, load, L/D ratio, etc. In this study, effect of shear stress on extrudate swell of hybrid composite (15/15) under 180°C for both of the series treated and untreated have been investigated.

A plot of extrudate swell ratio against shear stress for treated and untreated CaCO₃ is shown in Figure 7. The swelling ratio increase with increasing shear stress. However, at 1.96×10^7 the swelling ratio of untreated filler started to decrease rapidly while the treated filler becomes more stable at 2.45×10^7 . This might be due to better filler dispersion at high shear stress. It also can be seen that untreated filler provides higher swelling ratio than treated filler. It is believed that a good dispersion of stearic acid treated CaCO₃ particle affected the swelling ratio, which the fillers can hold the matrix sufficiently and hinder the matrix from swelling.

Increase in temperature will cause a decrease of the swelling ratio due to decreasing melt strength with

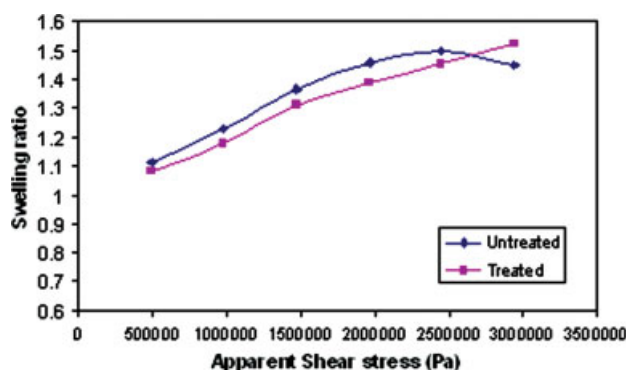


Figure 7 Swelling ratio vs. shear stress graph of PP composite treated and untreated for 15/15 (CaCO₃/talc) under 180°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

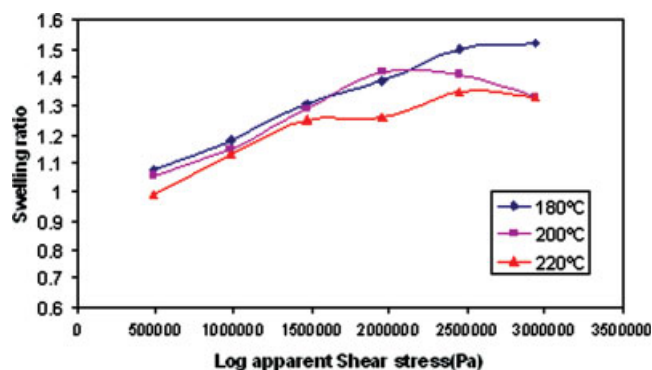


Figure 8 Swelling ratio vs. shear stress graph of PP composite treated for 15/15 (CaCO₃/talc) under different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increasing temperature.²⁰ It is shown in Figure 8 that when the temperature is increased, it tends to give situation where molecular chain motion of the composites are quickened and the relaxation process is shortened, thus the swelling ratio decreases. If relaxation of molecular chain is long, molecular chain structure will recoil and subsequently display evidence of extrudate swelling. Furthermore, at higher temperature, portion of viscous component of the melt is higher than that of elastic component, thus the ability of the melt to recover to its original structure is less, and consequently the expansion of extrudate samples are also less.²¹ At higher shear stress, 200–220°C swelling ratio tend to decrease, which might be due to better filler dispersion, thus able to hold the PP matrix from swell.

In Figure 9 decreasing of L/D ratio has caused an increase in the swelling ratio for 15 : 15 (CaCO₃ treated), which is known as the elastic memory effect that is related closely to the linearity of the molecular structure. It also depends upon the amount of elastic energy stored in the melt flow or the stress relaxation speed. In the reservoir, the polymer molecules are

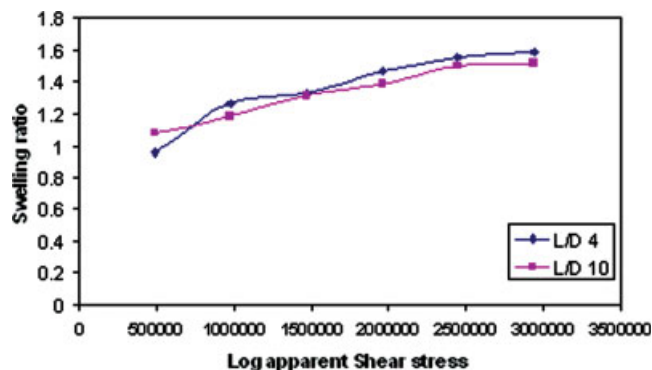


Figure 9 Swelling ratio vs. shear stress graph of PP composite treated for 15/15 (CaCO₃/talc) under 180°C for different L/D ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

coiled up in an almost random structure. In the die entry region there is considerable molecular (un-coiling) orientation and the oriented molecules then pass down the capillary. During flow down of capillary the shearing tends to maintain molecular orientation, although random Brownian movement of chain segments and disentanglement of chains leads to a net reduction in orientation. When the melt emerges from the die, the Brownian movement causing chain randomization (in effect, chain coiling or re-coiling) continues and because of the cessation of shearing action, molecular coiling is able to proceed, while the polymer remains in the molten state. This leads to side expansion or swelling of the extrudates.¹⁵ When the length of die is short, the molten polymer spends shorter period of time in the die, thus lead to an increased swelling ratio value.²²

CONCLUSIONS

The effects of the surface treatment of filler with stearic acid on the rheological properties of the PP hybrid composite highly filled with the CaCO₃ and talc particle were investigated in this study. It can be concluded that shear viscosities decrease with increasing shear rate. Surface treatment of CaCO₃ particles with stearic acid results in the obvious improvement in fluidity and dispersion of the composites. For hybrid composite, the shear viscosity decreases with increasing temperature. However, at higher temperature and shear rate, the viscosity shows some increment, which elucidates a shear thickening behavior. This trend has manifested by SEM micrograph of extrudate samples that dispersed particles that arrange themselves in ordered layers to provide a

packing of fillers and thus increase viscosity of composite. Surface treatment with stearic acid also promotes fluidity and dispersion of filler in matrix and consequently reduces the die swell of the composite which manifest that the filler is able to hold the matrix from swelling.

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