CHAPTER IV

MELT RHEOLOGY AND EXTRUDATE SWELL OF CALCIUM CARBONATE NANOPARTICLE-FILLED ISOTACTIC POLYPROPYLENE

ABSTRACT

Melt rheology and extrudate swell of isotactic polypropylene (iPP) filled uncoated and stearic acid-coated $CaCO_3$ nanoparticles in various amounts of filler (i.e. from 5 to 25 wt.%) during capillary melt-extrusion were investigated. The wall shear stress for both neat iPP and iPP compounds increased in a non-linear manner with increasing apparent shear rate. The apparent shear viscosity for all of the samples investigated was found to decrease in a non-linear manner with increasing apparent shear rate. Addition of uncoated $CaCO_3$ nanoparticles was responsible for increasing the apparent shear viscosity of the compounds, while stearic acid-coated ones did not affect the apparent shear viscosity of the iPP matrix as much. The percentage of extrudate swell was found to increase with increasing apparent shear rate in a non-linear manner, while it was found to increase linearly with increasing wall shear stress. Lastly, the percentage of extrudate swell was found to be a decreasing function of the filler loading.

Key-words: isotactic polypropylene; calcium carbonate; melt extrusion; extrudate swell

4.1 INTRODUCTION

Nowadays, inorganic fillers play an important role in plastics industry. The purposes of their use do not only confine to the cost reduction, but to improve mechanical performance like rigidity, dimensional stability, toughness, and transparency [1,2] as well. The level of such improvement depends significantly upon type, size and shape, content, and surface treatment of the fillers [3-5]. The latter determines the interaction between the polymer matrix and the fillers at the interface. Among the various mineral fillers, calcium carbonate ($CaCO_3$) has been the most utilized material, due partly to its availability and low cost [6].

Not only the presence but also the distribution of the fillers affects a great deal the viscoelasticity of the polymer matrix. The distribution of the filler within the polymer matrix can be improved by surface treatment with a dispersant, e.g. stearic acid, which helps reduce the viscosity of the matrix and, to some extent, prevent the fillers from forming a network [1,7,8]. An understanding of the rheological characteristics of filled polymer systems is beneficial to the design of a polymer processing equipment, with the ability for predicting the energy requirement, optimizing the processing conditions, and correlating with the structural development [9].

In polymer processing, the properties of the end products are dependent on not only the materials used, but also the design of the processing equipment, such as the geometry of the screw and die [10-12]. Die or extrudate swell is an important phenomenon determining the size and quality of the extrudate products. Importantly, the extrudate swell can be used to assess the elasticity of the polymer upon melt extrusion. The mechanism and degree of swelling of the extrudate are usually explained in terms of elastic recovery or effect of residence time on the applied stresses [12-14]. During a converging flow through a die, polymer molecules tend to uncoil. The entanglements will, to some extent, prevent the molecules from slipping past one another, thus preventing total relaxation of the molecules. At the die exit, recoiling of the molecules occurs to some extent, causing the extrudate to swell [9]. The most common technique used to study rheological properties of polymer melts is capillary rheometry [10,15].

Thio et al. [1] investigated the toughening of isotactic polypropylene (iPP) filled with CaCO₃ particles of varying average diameters (i.e. 0.07, 0.7, and 3.5 μm). In slow tension, addition of fillers increased the modulus and decreased the yield stress, irrespective of the filler type used. The strain at break was found to increase with initial incorporation of filler, but it was found to decrease at higher loadings. Chan et al. [4] studied crystallization and mechanical properties of iPP filled with CaCO₃ particles having the average diameter of ca. 44 nm. They found that CaCO₃ nanoparticles were an effective nucleating agent for iPP. The modulus was found to increase by ca. 85%, while the impact strength was found to improve by ca. 300%, from that of neat iPP. The effect of addition of talcum and CaCO₃ particles on mechanical and rheological properties of iPP was reported by da Silva et al. [2]. They found that marked improvement in the modulus, tensile stress at break, and yield stress was observed for talcum-filled iPP. Addition of the fillers enhanced the impact strength, but, with increasing filler content, the impact strength was found to decrease.

Though not totally relevant, Supaphol et al. [16] investigated the effects of CaCO₃ of varying particle size (i.e. 1.9, 2.8, and 10.5 μm), content (i.e. 0 to 40 wt.%), and type of surface modification (i.e. uncoated, stearic acid-coated, and paraffin-coated) on crystallization and melting behavior, mechanical properties, and processability of CaCO₃-filled syndiotactic polypropylene (sPP). It was found that CaCO₃ was a good nucleating agent for sPP. The nucleating efficiency of CaCO₃ for sPP depended strongly on its purity, type of surface treatment, and average particle size. Tensile strength was found to decrease, while Young's modulus was found to increase, with increasing CaCO₃ content. Both types of surface treatment on CaCO₃ particles helped improve particle distribution, hence impact resistance. Steady-state shear viscosity of CaCO₃-filled sPP was found to increase with increasing CaCO₃ content and decreasing particle size.

The present contribution focuses on investigating melt rheology and extrudate swell of isotactic polypropylene (iPP) compounded with CaCO₃ particles having the mean particle size of ca. 40 nm. The effects of content (i.e. 5, 10, 15, 20,

and 25 wt.%) and surface modification (i.e. neat and stearic acid-coated) of the filler on such properties were thoroughly investigated using a capillary rheometer.

4.2 EXPERIMENTAL DETAILS

Materials

A commercial grade of impact copolymer resin of iPP (Moplen CS-42 HEXP) used in this study was supplied by HMC Polymers Co., Ltd. (Rayong, Thailand). Certain properties of the resin, provided by the manufacturer, are as follows [17]: MFR (2.16 kg at 230°C) = 12 $g \cdot (10 \text{ min})^{-1}$, density = 0.9 $g \cdot cm^{-3}$, tensile strength at yield = 24 MPa, elongation at yield = 5%, flexural modulus = 1200 MPa, and notched Izod impact strength at 23°C = 100 $J \cdot m^{-1}$. Two grades of $CaCO_3$ nanoparticles were NPCC-111 and NPCC-201. Certain characteristics of these two grades are similar [18]: density $\approx$ 2.5 $g \cdot cm^{-3}$, average (primary) particle size = 40 nm, BET surface area = 40 $m^2 \cdot g^{-1}$, purity (unmodified basis) $\geq$ 97%, and particle shape = cubic. The main difference between the two grades was that the surface of NPCC-201 grade was partially modified with stearic acid to facilitate particle dispersion and distribution within the matrix, while that of NPCC-111 grade was uncoated $CaCO_3$ nanoparticles.

Compounding

$CaCO_3$ nanoparticles were first dried in an oven at 90°C for 24 hours and then pre-mixed with iPP pellets in a tumble mixer for 15 minutes in various compositional ratios (i.e. 5, 10, 15, 20, and 25 wt.%). The pre-mixed compounds were then fed into a Collin ZK25 self-wiping, co-rotating twin-screw extruder operating at a screw speed of 55 rpm and a temperature profile of 190 (die), 190 (zone 4), 180 (zone 3), 170 (zone 2), 160 (zone 1), and 70°C (feed zone). The extrudate was cooled in water and cut into pellet form by a Planetrol 075D2 pelletizer.

Rheological and extrudate swell measurements

A CEAST Rheologic 5000 twin-bore capillary rheometer was used to measure shear viscosity and extrudate swell of the iPP/CaCO3 nanoparticle compounds. The inner diameter and the length of the barrel used were 9.95 and 250 mm, respectively, while the inner diameter and the length of the die were 2 and 15 mm (i.e. L/D ratio = 7.5), respectively. The testing temperature was calibrated at 190 ± 0.5°C. The hold-on time and hold-on pressure for stages 1, 2, and 3 were 200 seconds and 10, 20, 30 Pa, respectively. An automatic data collection system was used to collect and analyze the test results. The extrudate swell was measured using the attached KEYENCE VG laser analytical device, which comprises a laser light source and a light sensor.

4.3 RESULTS AND DISCUSSION

Dependence of wall shear stress on apparent shear rate for neat iPP and iPP filled with 5 and 25 wt.% of both uncoated and stearic acid-coated CaCO3 nanoparticles is illustrated in Figure 4.1. Apparently within the apparent shear rate range investigated (i.e. ca. 50 to 360 s^{-1}), both neat iPP and iPP compounds exhibited an increase in the wall shear stress value with increasing apparent shear rate, but the rate of change was found to decrease with increasing apparent shear rate. This is a typical characteristic of a polymeric material exhibiting a shear thinning behavior. Other iPP/CaCO3 nanoparticle compounds also exhibited a similar behavior.

According to Figure 4.1a, the wall shear stress values at a given apparent shear rate for neat iPP and iPP filled with 5 wt.% CaCO3 nanoparticles (both uncoated and stearic acid-coated) were not much different from one another. With increasing filler content, the difference between the wall shear stress values of iPP filled with uncoated CaCO3 nanoparticles and neat iPP at a given apparent shear rate gradually increased, with the value iPP filled with uncoated CaCO3 nanoparticles being greater than that of neat iPP and the maximum of the difference between the stress values being observed at the filler content of 25 wt.% (within the filler content range investigated) (see Figure 4.1b). Contrarily, the wall shear stress value of iPP filled with stearic-acid coated CaCO3 nanoparticles was not much different from that

of neat iPP when the filler content was less than 20 wt.%. Only iPP filled with 25 wt.% stearic-acid coated $CaCO_3$ nanoparticles showed a noticeable difference in the wall shear stress values (see Figure 4.1).

Table 4.1 summarizes the wall shear stress values of neat iPP and iPP filled with both uncoated and stearic acid-coated with $CaCO_3$ nanoparticles in various amounts, ranging from 5 to 25 wt.%, at two apparent shear rates of 63.8 and 328.3 s^{-1}, respectively. Obviously, the difference between the wall shear stress values of iPP filled with uncoated $CaCO_3$ nanoparticles and neat iPP increased from ca. 1% at the filler loading of 5 wt.% to 45% at the filler loading of 25 wt.% for the apparent shear rate of 63.8 s^{-1} and from ca. 5% at the filler loading of 5 wt.% to 37% at the filler loading of 25 wt.% for the apparent shear rate of 328.3 s^{-1}. Interestingly, the difference between the wall shear stress values at higher shear rates was lower than those at lower shear rates, possibly due to the shear thinning behavior of the materials. Evidently from Table 4.1, the difference between the wall shear stress values of iPP filled with stearic acid-coated $CaCO_3$ nanoparticles and neat iPP at both apparent shear rates was not much different, excepted for those at the filler content of 25 wt.%.

Figure 4.2 shows dependence of apparent shear viscosity on apparent shear rate for neat iPP and iPP filled with 5 and 25 wt.% of both uncoated and stearic acid-coated $CaCO_3$ nanoparticles. Evidently within the apparent shear rate range examined (i.e. ca. 50 to 360 s^{-1}), both neat iPP and iPP compounds illustrated a decrease in the apparent shear viscosity with increasing apparent shear rate, but the rate of change was found to decrease with increasing apparent shear rate (in a similar manner to the wall shear stress values observed). The results obtained confirm the shear thinning behavior of these compounds. Other iPP/$CaCO_3$ nanoparticle compounds also exhibited a similar behavior.

According to Figure 4.2a, the apparent shear viscosity values at a given apparent shear rate for neat iPP and iPP filled with 5 wt.% $CaCO_3$ nanoparticles (both uncoated and stearic acid-coated) were not much different from one another. The difference between the apparent shear viscosity values of iPP filled with uncoated $CaCO_3$ nanoparticles and neat iPP at a given apparent shear rate was found to increase with increasing filler content, with the value of iPP filled with uncoated

$CaCO_3$ nanoparticles being the greater of the two and the maximum of the difference between the viscosity values being observed at the filler content of 25 wt.% (within the filler content range investigated) (see Figure 4.2b). On the other hand, the apparent shear viscosity value of iPP filled with stearic-acid coated $CaCO_3$ nanoparticles appeared to be quite similar to that of neat iPP (see Figure 4.2).

Table 4.2 summarizes the apparent shear viscosity values of neat iPP and iPP filled with both uncoated and stearic acid-coated with $CaCO_3$ nanoparticles in various amounts, ranging from 5 to 25 wt.%, at two apparent shear rates of 63.8 and 328.3 s^{-1}, respectively. Apparently, the difference between the apparent shear viscosity values of iPP filled with uncoated $CaCO_3$ nanoparticles and neat iPP increased from ca. 22% at the filler loading of 5 wt.% to 77% at the filler loading of 25 wt.% for the apparent shear rate of 63.8 s^{-1} and from ca. 5% at the filler loading of 5 wt.% to 40% at the filler loading of 25 wt.% for the apparent shear rate of 328.3 s^{-1}. In a similar to the wall shear stress values, the difference between the apparent shear viscosity values at higher shear rates was lower than those at lower shear rates.

In addition, the difference between the apparent shear viscosity values of iPP filled with stearic acid-coated $CaCO_3$ nanoparticles and neat iPP was found to increase from ca. 16% at the filler loading of 5 wt.% to 32% at the filler loading of 25 wt.% when the apparent shear rate was 63.8 s^{-1} and from ca. 4% at the filler loading of 5 wt.% to 7% at the filler loading of 25 wt.% when the apparent shear rate was 328.3 s^{-1}. Obviously, the difference between the apparent shear viscosity values at low apparent shear rates was greater than those at high apparent shear rates.

Figure 4.3 illustrates dependence of extrudate swell on apparent shear rate for neat iPP and iPP filled with uncoated and coated $CaCO_3$ nanoparticles at various filler loadings, ranging from 5 to 25 wt.%. The degree of extrudate swell was reported as the percentage of extrudate swell (i.e. $(D - D_0)/D_0 \times 100$, where D is the diameter of the extrudate and D_0 is the inner diameter of the die). Generally, the extrudate swell was found to increase with increasing apparent shear rate in a non-linear manner (i.e. the rate of change was a decreasing function of apparent shear rate). Apparently, addition of both uncoated and stearic acid-coated $CaCO_3$ nanoparticles reduced the severity of the extrudate swell and, with increasing $CaCO_3$

nanoparticle content, the severity of the extrudate swell was found to decrease. Liang [19] reported a similar observation on iPP/glass bead composites, in which he rationalized the observation as the limited mobility of the matrix molecular chains due to the presence of the filler particles. The limited mobility of the molecules caused the elastic recovery during die exit to be somewhat blocked.

Comparatively, for a given apparent shear rate and at the filler loadings of 5 and 10 wt.%, the extrudate swell for iPP filled with stearic acid-coated $CaCO_3$ nanoparticles was greater than that for iPP filled with uncoated $CaCO_3$ nanoparticles, while, at higher filler loadings (i.e. from 15 to 25 wt.%), the extrudate swell for iPP filled with uncoated $CaCO_3$ nanoparticles was greater than that for iPP filled with stearic acid-coated $CaCO_3$ nanoparticles. At filler contents of 5 and 10 wt.%, stearic acid-coated $CaCO_3$ nanoparticles may be dispersed and distributed much better in the iPP matrix than uncoated $CaCO_3$ nanoparticles. However, since strearic acid coating was not found to enhance the interfacial adhesion between $CaCO_3$ and the polymeric matrix [16], the presence of $CaCO_3$ nanoparticles within the iPP matrix may not be as effective in limiting the movement of the molecules during an elastic recovery upon leaving the die.

At higher filler contents (i.e. from 15 to 25 wt.%), uncoated $CaCO_3$ nanoparticles within close proximity could interact to one another to form agglomerates much easier than stearic acid-coated ones, causing the number of secondary $CaCO_3$ particles in the matrix of iPP filled uncoated $CaCO_3$ nanoparticles to be less than that filled with stearic acid-coated $CaCO_3$ nanoparticles. The reduction in the number of secondary $CaCO_3$ particles caused the movement of the molecules to be less limited, thus iPP filled with uncoated $CaCO_3$ nanoparticles exhibited greater extrudate swelling than that filled with the uncoated ones. The offered explanation may be valid when the apparent shear rate is not too high.

Figure 4.4 shows dependence of extrudate swell as a function of wall shear stress for neat iPP and iPP filled with uncoated and stearic acid-coated $CaCO_3$ nanoparticles of various filler contents, ranging from 5 to 25 wt.%. It is obvious from these plots that the extrudate swell exhibited a linear relationship with the wall shear stress. Liang [19,20] also observed a linear relationship between the extrudate swell and the wall shear stress for glass bead-filled iPP, $CaCO_3$-filled natural rubber,

and carbon black-filled natural rubber. The linearity between the percentage of extrudate swell (B) and the wall shear stress (τ_w) can be approximated as

$$B = B_0 + B_1 \tau_w,\qquad\qquad(4.1)$$

where B_0 and B_1 are an arbitrary constant and a constant related to the melt elasticity (i.e. a slope), respectively.

During capillary extrusion, a part of the shear deformational energy was stored in the molecules in the form of an increase in the internal energy (i.e. through the change in the conformational states). Upon exiting the die, the molecules need to re-equilibrate their internal energy in the form of elastic recovery (which may accompany by a temperature change) through conformational rearrangements, hence the extrudate swelling results. With increasing wall shear stress, the shear deformational energy stored in the molecules also increases, leading to a corresponding increase in the swelling of an extrudate.

Careful consideration of Figure 4.4 reveals that iPP filled with both uncoated and stearic acid-coated $CaCO_3$ nanoparticles exhibited a decrease in the extrudate swelling with increasing filler loading. As stated previously, limited mobility of the matrix molecular chains due to the presence of the filler particles should be responsible for such an observation. One can see from Figure 4.4a that the slope of a linear regression drawn to the data obtained for iPP filled with uncoated $CaCO_3$ nanoparticles of a given amount was found to decrease with increasing filler loading (see Table 4.3). This suggests that high wall shear stress may cause some $CaCO_3$ agglomerates to break apart (i.e. better dispersion), resulting in a larger number of secondary $CaCO_3$ particles that can limit mobility of iPP molecules. On the other hand, the slope of a linear regression drown to the data obtained for iPP filled with stearic acid-coated $CaCO_3$ nanoparticles of a given amount slightly decreased with increasing filler content (see Table 4.3). The less dependence of the slope on the amount of filler added for iPP filled with stearic acid-coated $CaCO_3$ nanoparticles could be due to the already-good dispersion of the $CaCO_3$ nanoparticles and to the poor interfacial adhesion between iPP matrix and coated $CaCO_3$ surface.

4.4 CONCLUSIONS

In the present contribution, melt rheology and extrudate swell of isotactic polypropylene (iPP) compounded with uncoated and stearic acid-coated $CaCO_3$ nanoparticles in various filler loadings, ranging from 5 to 25 wt.%, during capillary melt-extrusion were investigated. The wall shear stress for both neat iPP and iPP compounds was found to increase in a non-linear manner with increasing apparent shear rate. With increasing filler content, the difference between the wall shear stress values of iPP filled with uncoated $CaCO_3$ nanoparticles and neat iPP was found to increase, with the maximum of the difference being observed at the filler content of 25 wt.%. On the contrary, only iPP filled with 25 wt.% stearic acid-coated $CaCO_3$ nanoparticles showed a noticeable difference in the wall shear stress values from that of neat iPP. The apparent shear viscosity for all of the samples investigated was found to decrease in a non-linear manner with increasing apparent shear rate, an indication of a shear-thinning material. Addition of uncoated $CaCO_3$ nanoparticles was found to increase the apparent shear viscosity of the compounds, while stearic acid-coated ones did not affect the apparent shear viscosity of the iPP matrix as much. The percentage of extrudate swell was found to increase with increasing apparent shear rate in a non-linear manner, while it was found to have a linear relationship with the wall shear stress. Lastly, the percentage of extrudate swell was found to be a decreasing function of the filler loading.

4.5 ACKNOWLEDGMENTS

4.6 REFERENCES

[1] Y.S. Thio, A.S. Argon, R.E. Cohen, M. Weinberg, Polymer 43 (2002) 3661.

[2] A.L.N. da Silva, M.C.G. Rocha, M.A.R. Moraes, C.A.R. Valente, F.M.B. Coutinho, Polymer Testing 21 (2002) 57.

[3] A. Tabtiang, R. Venables, European Polymer Journal 36 (2000) 137.

[4] C.M. Chan, J.S. Wu, J.X. Li, Y.K. Cheung, Polymer 43 (2002) 2981.

[5] J. Gonzalez, C. Albano, M. Ichazo, B. Diaz, European Polymer Journal 38 (2002) 2465.

[6] S. Miao, Applied Surface Science 220 (2003) 298.

[7] G. Nowaczyk, S. Glowinkowski, S. Jurga, Solid State Nuclear Magnetic Resonance 25 (2004) 194.

[8] B. Haworth, S. Jumpa, N.A. Miller, Polymer Testing 19 (2000) 459.

[9] P.R. Hornsby, Advances in Polymer Science 139 (1999) 155.

[10] N. Sombatsompop, R. Dangtungee, Journal of Materials Science Letters 20 (2001) 1405.

[11] N. Sombatsompop, R. Dangtungee, Journal of Applied Polymer Science 82 (2001) 2525.

[12] N. Sombatsompop, R. Dangtungee, Journal of Applied Polymer Science 86 (2002) 1762.

[13] S.V. Nair, Z. Oommen, S. Thomas, Materials Letters 57 (2002) 475.

[14] J.Z. Liang, Polymer Testing 21 (2002) 69.

[15] J.A. Bryson, Flow Properties of Polymer Melts, Van Nostrand Reinhold, New York, 1970.

[16] P. Supaphol, W. Harnsiri, J. Junkasem, Journal of Applied Polymer Science 92 (2004) 201.

[17] Availablefromhttp://www.hmcpolymer.com/products/impact_/CS42_files/slide 0019.html.

[18] Available from http://www.nanomt.com/products/npcc.asp.

[19] J.Z. Liang, Polymer Testing 21 (2002) 927.

[20] J.Z. Liang, Polymer Testing 23 (2004) 441.

4.7 CAPTION OF FIGURES

Figure 4.1   Wall shear stress as a function of apparent shear rate for neat iPP and iPP filled with (a) 5 and (b) 25 wt.% of both uncoated and stearic acid-coated $CaCO_3$ nanoparticles.

Figure 4.2   Apparent shear viscosity as a function of apparent shear rate for neat iPP and iPP filled with (a) 5 and (b) 25 wt.% of both uncoated and stearic acid-coated $CaCO_3$ nanoparticles.

Figure 4.3   Percentage of extrudate swell as a function of apparent shear rate for neat iPP and iPP filled with (a) 5, (b) 10, (c) 15, (d) 20, and (e) 25 wt.% of both uncoated and stearic acid-coated $CaCO_3$ nanoparticles.

Figure 4.4   Percentage of extrudate swell as a function of wall shear stress for neat and iPP filled with (a) uncoated and (b) stearic acid-coated $CaCO_3$ nanoparticles of various filler loadings, ranging from 5 to 25 wt.%.

Table 4.1 Wall shear stress (τ_w) at apparent shear rates of 63.8 and 328.3 s^{-1} for neat iPP and iPP filled with $CaCO_3$ nanoparticles in various amounts, ranging from 5 to 25 wt.%

Filler content (wt.%)	Apparent shear rate = 63.8 s^{-1}				Apparent shear rate = 328.3 s^{-1}			
	τ_w for iPP filled with uncoated $CaCO_3$ (Pa)	% Difference[1]	τ_w for iPP filled with stearic acid-coated $CaCO_3$ (Pa)	% Difference[1]	τ_w for iPP filled with uncoated $CaCO_3$ (Pa)	% Difference[1]	τ_w for iPP filled with stearic acid-coated $CaCO_3$ (Pa)	% Difference[1]
0 (neat iPP)	39140				67860			
5	39530	1.0	37980	-3.0	70940	4.6	69020	1.7
10	43810	11.9	38760	-1.0	73660	8.6	68630	1.2
15	45370	15.9	39140	0.0	77160	13.7	69020	1.7
20	49230	25.8	40310	3.0	83360	22.8	70180	3.4
25	56610	44.6	42640	8.9	92680	36.6	72880	7.4

[1] % Difference = percentage of difference of the τ_w value from that of neat iPP

Table 4.2 Apparent shear viscosity (η_a) at apparent shear rates of 63.8 and 328.3 s^{-1} for neat iPP and iPP filled with CaCO$_3$ nanoparticles in various amounts, ranging from 5 to 25 wt.%

Filler content (wt.%)	Apparent shear rate = 63.8 s^{-1}				Apparent shear rate = 328.3 s^{-1}			
	η_a for iPP filled with uncoated CaCO$_3$ (Pa·s)	% Difference[1]	η_a for iPP filled with stearic acid-coated CaCO$_3$ (Pa·s)	% Difference[1]	η_a for iPP filled with uncoated CaCO$_3$ (Pa·s)	% Difference[1]	η_a for iPP filled with stearic acid-coated CaCO$_3$ (Pa·s)	% Difference[1]
0 (neat iPP)	613.2				206.7			
5	748.0	22.0	714.2	16.5	216.1	4.6	215.3	4.2
10	832.8	35.8	714.2	16.5	224.3	8.6	209.0	1.2
15	866.9	41.4	739.8	20.7	235.0	13.7	210.2	1.7
20	943.7	53.9	748.3	22.0	253.9	22.8	213.7	3.4
25	1087.9	77.4	807.2	31.7	289.6	40.1	222.0	7.4

[1] % Difference = percentage of difference of the τ_w value from that of neat iPP

Table 4.3 Slope (B_1) obtained from a plot of the percentage of extrudate swell versus the wall shear stress for neat iPP and iPP filled with uncoated and stearic acid-coated $CaCO_3$ nanoparticles in various amounts, ranging from 5 to 25 wt.%

Filler content (wt.%)	Slope value (B_1) (Pa^{-1})	
	iPP filled with uncoated $CaCO_3$	iPP filled with stearic acid-coated $CaCO_3$
0 (neat iPP)	0.000670	
5	0.000597	0.000648
10	0.000534	0.000642
15	0.000520	0.000563
20	0.000459	0.000539
25	0.000356	0.000532
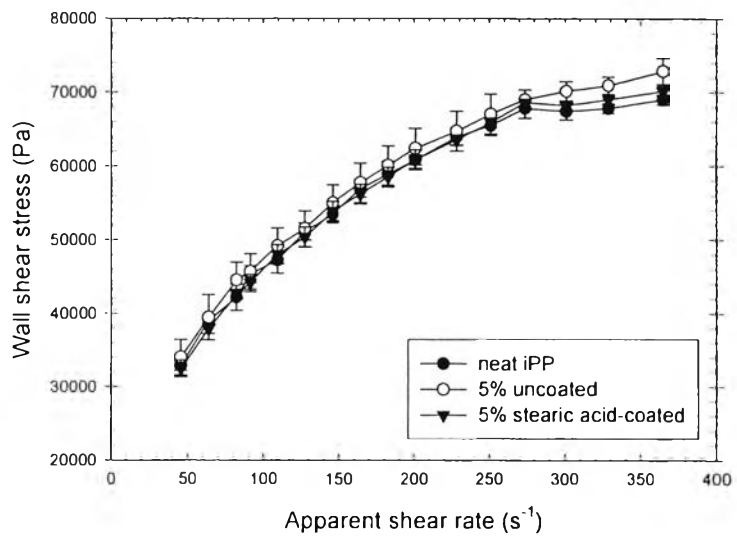
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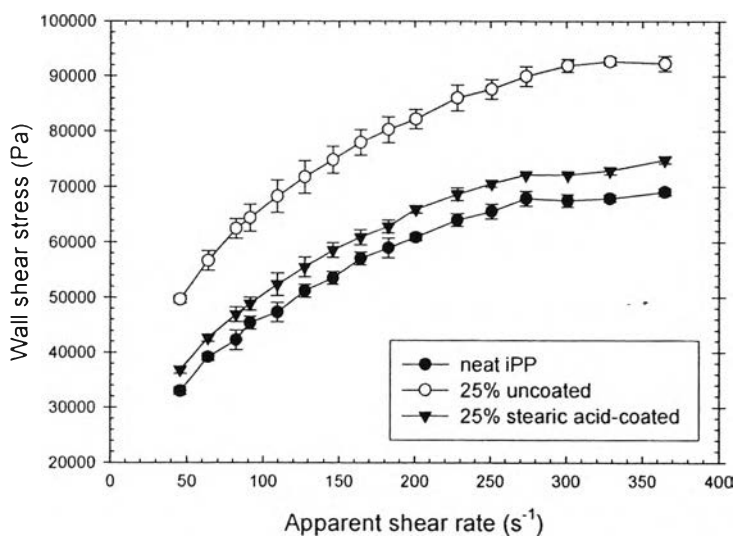
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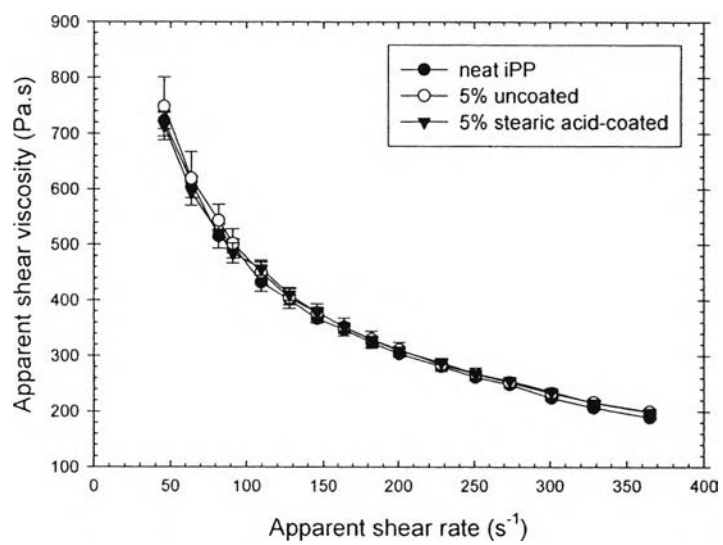
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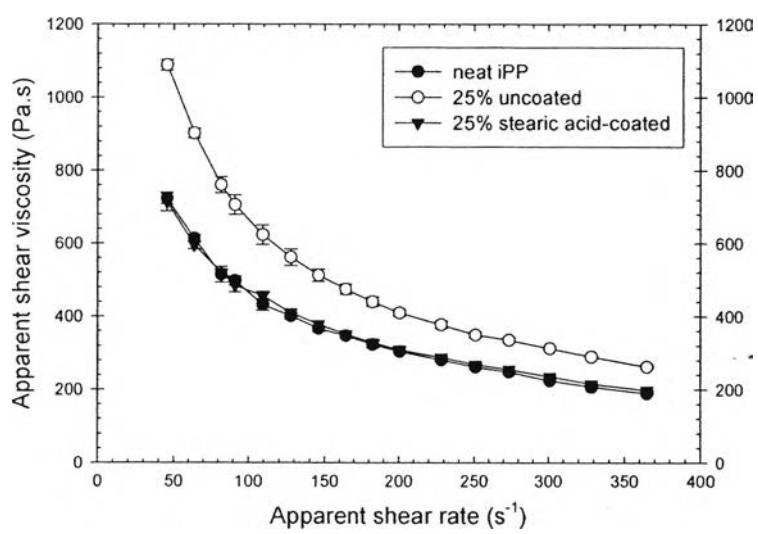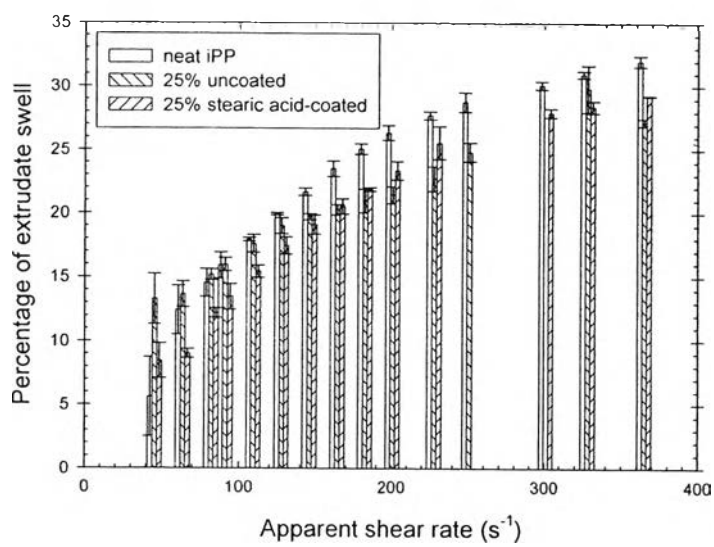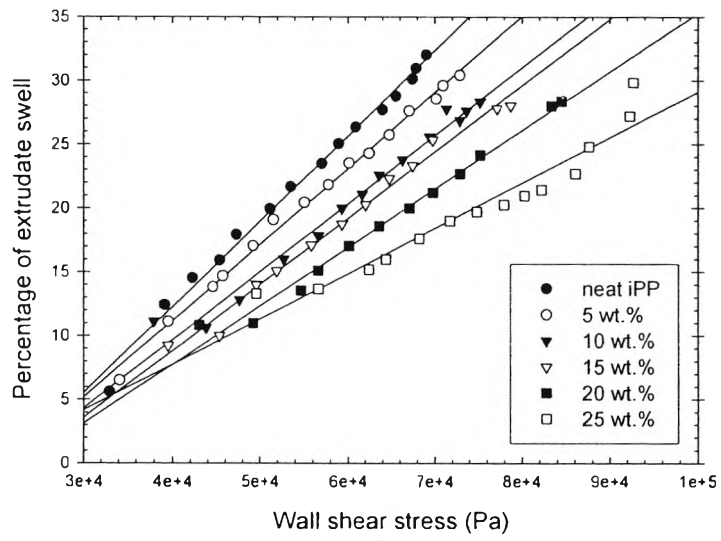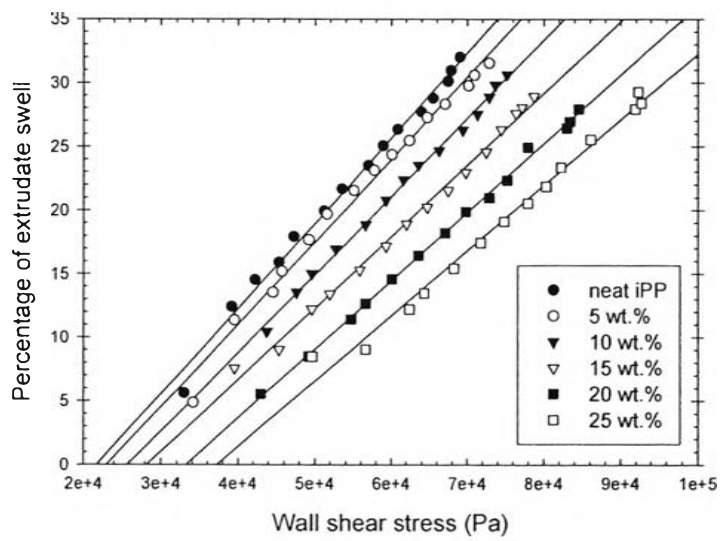

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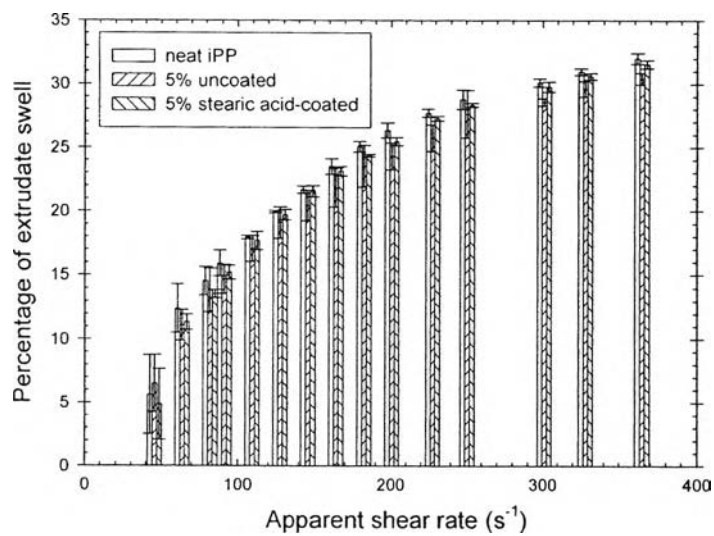
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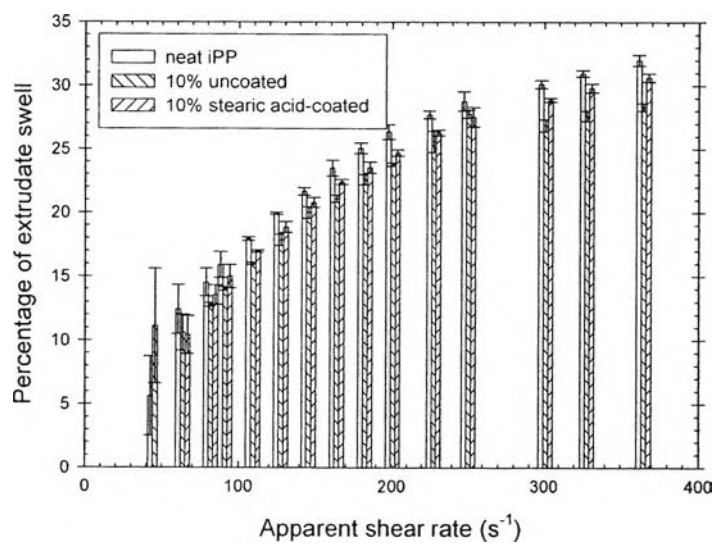
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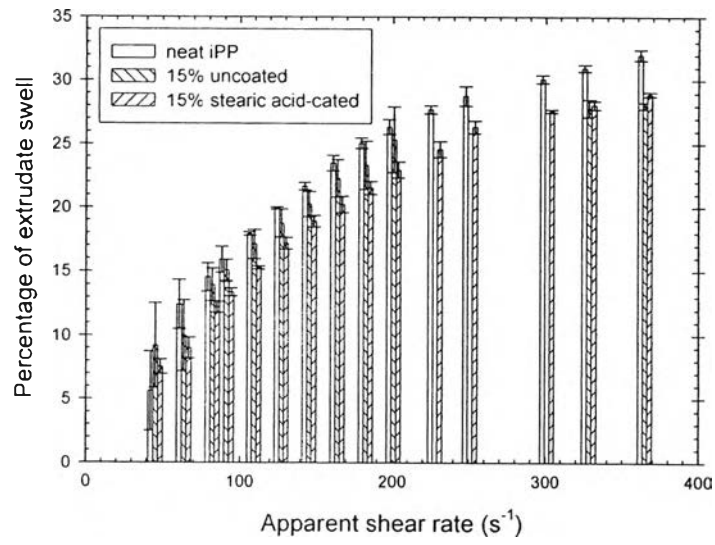
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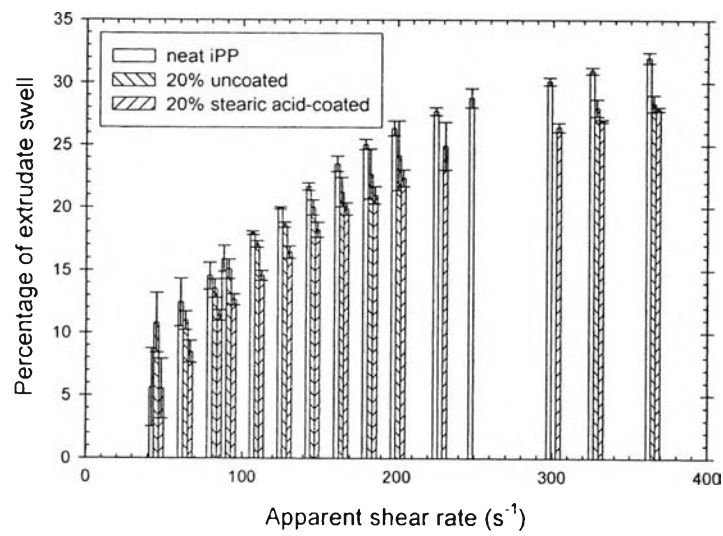
(d)

Figure 4.3 (cont.)

(e)

Figure 4.3 (cont.)

(a)

(b)

Figure 4.4