CHAPTER V

OBSERVATION SHEAR, ELONATIONAL BEHAVIOR AND EXTRUDATE SWELL OF NANOMETRE CALCIUM CARBONATE FILLED POLYPROPYLENE ON CAPILLARY RHEOMETER.

ABSTRACT

The polypropylene-nano size $CaCO_3$ composites are observed the rheological properties on shear flow, elonagational flow and the extrudate swell phenomenon in various filler loading, ranging from 5 to 25 wt% during capillary extrusion process. In order to the data correction, neat iPP and composites exhibited shear thinning pseudoplastic behavior as real shear stress were a function of real shear rate. The $CaCO_3$ nanaparticles with treated the surface by stearic acid exhibited the hydrophobic shows the reduction of the rate of changing real shear stress on real shear rate with increasing amount of fillers as compared on non treatment surface composites. The flow curve occurred the plateau curve that meanwhile a critical shear stress on about 1100 s^{-1} of shear rate. All results show the real viscosity is decreased non linear manner with increasing the real shear rate. The uncoated nano composites exhibited difference values at the same real of rate in order of 0 to 25 wt% of filler. But, in case of coated nano composites present more equal. The percentage of extrudate swell at a given real shear influenced with increasing shear rate in non linear manner. Without surface coating was found to reduce of swell values with increasing amount of filler. The slope of linear regression draw to the data obtained for uncoated nano composites of given amount was found to decrease with increasing filler loading. As the same time, stearic acid coated nano composites exhibited slope value not difference as much. And increasing L/D ratios tend to differences a linear regression on lower L/D ratio. Due to an increasing the L/D ratios, it also increased the residence time of the composites in the die. Which affect to the already-good dispersion of nano particles on PP matrix. Finally, the elongational flow behavior reveals that the nano composites exhibit a typical extensional thinning phenomenon in a uniaxial extension. The nano composites increased the tensile stress following adjustment of the rate. They would destruct the entanglement of molecular chains and reorientation result in decreasing the elongational viscosity. As the same time, the viscosity was found increased with increasing amount of nano fillers.

Key-words: polymer nanocomposites; capillary rheometer; polymer rheology; extrudate swell; $CaCO_3$ nanoparticles; shear flow; elonagtional flow.

5.1 INTRODUCTION

Rheology is flow and deformation behavior of the materials as polymer melts. The manner in which polymer melts are important not only for control a quality of the products but its also useful to setting the machine operations [1-4]. The polymer melt flows consisted of shear flow and elongational or extensional flow and occurred instantaneous on the melts movement. To study rheology, the capillary rheometer is widely accepted on the accurate and precision [5]. The capillary rheometer is essentially a ram extruder whereby a piston driven down a high precision, heated, bore or barrel. Inside the barrel is the molten polymer, and under the action of the driven piston, the melt is expressed through a die of known geometry [6]. Generally, the dependence shear flow on shear stress, shear rate, and shear viscosity are examined for making the data corrections as Rabinowitsch's and Bagley's corrections [3,7,8]. The elongational flow is examined in the Cogswell's convergence flow model that it widely accepted and developed by Cogswell [9-12].

In various mineral fillers for the polymer, $CaCO_3$ has been most utilized materials, due to its availability and low cost [13-15]. The distribution of the fillers with in the polymer matrix is interesting that it related to the quality and properties of the product. Its can be improved by the surface treatment with dispersant [16-18].

Lazzeri et al. [17] reported the rheoloical and mechanical behavior of $CaCO_3$/HDPE nanocomposites on the effect of surface interaction. They influenced the surface treatment of the particle, with and with out stearic acid. It was found that the addition of 10 vol% $CaCO_3$ to HDPE cause rise the young's modulus and yield stress and also accompanied by a sharp drop in impact strength. The addition of strearic acid has the effect of slightly decreasing both young's modulus and yield stress as compared to uncoated composite. On the rheology, the addition of $CaCO_3$ (with and with out surfactant) cause to rise the viscosity respect to pure HDPE, and stearic acid added causes to decrease the viscosity. It can be expected that raising stearic acid content cause to a drop in the level of inter action between particles reducing the amount and the average size of agglomerates and improves the distribution of the particle in the matrix. So the decreasing in viscosity may be due to a reduction of immobilized polymer fraction because of the lower interfacial tension between the solid particle and surrounding liquid phase when a surfactant layer is present. Quing [18] studied the crystallization and impact energy of polypropylene/ $CaCO_3$ nanocomposites with nonionic modifier as polyoxyethylene nonyphenol (PN). The results showed the filling of small amount of PN (0.75-2.25 wt%) during the melt extrusion greatly improved the dispersion of $CaCO_3$ particles. Xiao L. X. et al. [14] investigated the rheological properties of PVC/ $CaCO_3$ nanocomposites prepared by in-situ polymerization on 0 to 7.5 wt% of nana $CaCO_3$. The nanocomposites showed shear thinning behavior and power law behaviors. The ball bearing effect of spherical nanoparticles decreased the apparent viscosity of the melts and the viscosity sensivity on show rate of PVC/ $CaCO_3$ nanocomposites is higher than that pristine PVC. L. Jiang et al. [19] compared the nano-sized and micron-sized of $CaCO_3$ on ABS matrix. The SEM examinations revealed that nano-sized particles/agglomerates were distributed in much smaller size in the composites than micron-sized. The layer interfacial area between the nanocomposites induced shear yielding in the alignment are believed to be the main reasons of the mechanical properties improvement. J. Z. Liang [20] researched melt rheology of ABS filled $CaCO_3$ nanocomposites during capillary extrusion in various volume fractions on 0-50 vol%. The results showed the shear flow did not strictly obey the power law under test conditions and the elongational viscosity calculated by Cogswell's theory was increased while entrance pressure drop and tensile stress decreased with addition of the filler volume fraction.

Research report recently, the author [21] investigated the melt rheology and extrudate swell of $CaCO_3$ nanoparticles filled isotactic polypropylene on the shear deformation in which occurring on capillary rheometer. All of results suggested that the apparent shear stress of both neat PP and composites increased non linear manner with increasing apparent shear rate and the stearic acid coated on nano$CaCO_3$ did not affect the apparent shear viscosity as much. The percentage of extrudate swell was found increased non linear manner with increasing the apparent shear rate while linear function on wall shear stress. The slope values of shear stress and swell was found decreased in case of uncoated nanoparticles greater than stearic acid coated.

In this paper deals the rheological properties following previous work as shear and elongational deformation and extrudate swell of their composites. The real shear stress, real shear rate, and real shear viscosity were carried out. The extrudate swell was examined. And lastly, the elongational rheology was calculated on the Cogswell's theory.

5.2 EXPERIMENTAL DETAILS

Materials and compounding

The base polymer, isotactic polypropylene (Moplen CH-42 HEXP), are supplied by HMC polymer Co, Ltd (Rayong Thailand). Certain properties provide by the manufacturer are density = 0.9 gcm^3, MFR = 12(2.16 kg at 230°C), notched izod impact strength= 100 Jm^{-1}, flexural modulus = 1200 MPa, tensile strength at yield = 24 MPa, and elongation at yield = 5%. $CaCO_3$ nanoparticles, both stearic coated and uncoated was supplied by Nano materials technology Pte. Ltd. (Singapore). The certain properties occurred on a previous work [22,23].

The compounding was first dried in an oven at 90°C for 24 hour and then dry mixed with PP pellets in a tumber mixer for 10 min then fed into a COLLIN ZK25 self wiping co-rotating twinscrew extruder operating at a screw speed 55 rpm and the die temperature at 190°C. Later, a Plantrol 075D pelletizer was used to pelletize the extrudate.

Rheological measurements and extrudate swell measurement

The rheological properties were measured on a capillary rheometer (CEAST Rhologic 5000 twin bore capillary rheometer). The inner diameter and the length of the bore were 15 and 300 mm respectively. Two capillary die on 2mm diameter and 10, 30 mm long were used (L/D = 5 and 15). The temperature of 190 °C was chosen for study. The equipment used a computer for data acquisition and handling. Extrudate swell was measured with laser scan analytical device (KEYENCE VG LASER). The data correction employed Rabinowitsch and bagley corrections for real shear stress, real shear rate, and shear viscosity values. The Cogswell theory used for calculated the elongational behavior.

5.3 RESULTS AND DISCUSSION

Dependence of real shear stress on real rate for neat PP and the composites from 5 to 25 wt% both uncoated and stearic acid coated $CaCO_3$ nanoparticles are illustrated in Fig. 5.1 In the whole rang were analyzed, all of sample exhibited an increase in the real shear stress value in non linear manner with increasing real shear rate while characteristic of shear thinning behavior of materials. With added amount of filler as the same rate, tend to influenced shear stress and maximum on 25 wt%. The flow curve occurred the plateau curve that meanwhile a critical shear stress about 1100 s^{-1} of shear rate. In various amounts of filler (0-25 wt%), it was it was found that not difference as much. According to Fig. 5.1a and 1b, the real shear stress on the same rate, the range of different values in various amount of filler (0-25 wt%) on the uncoated $CaCO_3$ (Fig. 5.1a) was greater than the stearic acid coated $CaCO_3$ nano particles. This result suggested that the coated surface of CaCO3 nano particles have more effect on the shear rheology and greatest support by previous work [21]. As increasing the L/D ratio of the capillary (Fig. 5.2a and 5.2b), it was found the same trend of short die series previously. According Fig 5.2a, the uncoated nano composites, the stress value show noticeable difference at the same rate in order of neat PP to 25 wt% of nano fillers.Fig. 5.3a and 5.3b show the shear viscosity as a function of the rate of shear in various amounts of filler. Both of the results show the real viscosity is decreased non linear manner with increasing the real shear rate. Evidently, as compare both results, the uncoated nano composites exhibited difference values at the same real of rate in order of 0 to 25 wt% of filler. But, in case of coated nano composites present more equal. These result is confirm that the surface coated on nano fillers have more effective for the shear rheology and related the dispersion and distribution of the nano fillers [18,21].

There is more literature presented about the relationship of extrudate swell, shear rate as well as wall shear stress [24]. The percentage of extrudate swell at a given real shear rate was shows on Fig. 5.4. The extrudate swell influenced with increasing shear rate in non linear manner. Without surface coating (see Fig. 5.4a), it was found to reduce of swell values with increasing amount of filler and more evidence on the previous work [25]. In addition, as the same rate, the different between both nano fillers (see Fig. 5.4a and 5.4b) was apparently, coated nano composites have more effective than another one as increasing amounts of filler to maximum value meanwhile the movement of polymer molecules chains are strongly and easily. Fig. 5.5 shows dependence of percentage of extrudate swell on the wall shear stress in various amount of fillers and L/D ratios of capillary geometry. It is obvious from these plots that the swelling exhibited a linear relationship with the wall shear stress as same as the author [21]. An increasing wall shear stress, the shear deformation energy stored in the molecules also increased leading to a corresponding increase in the swelling extrudate. At lower L/D ratio (L/D=5, see Fig. 5.5a and 5.5b) both uncoated and coated nano particles presented similarly behavior on previous work [21]. The slope of linear regression draw to the data obtained for uncoated nano composites of given amount was found to decrease with increasing filler loading. As the same time, stearic acid coated nano composites exhibited slope value not difference as much. This suggested that high wall shear stress may cause some agglomerates of fillers to break a part and can be limit the mobility of PP molecular chains. On the other hand, and increasing L/D ratios (L/D=15, see Fig. 5.5c and 5.5d) tend to differences a linear regression on lower L/D ratio. Due to an increasing the L/D ratios, it also increased the residence time of the composites in the die. Which affect to the already-good dispersion of nano particles on PP matrix.

The elongational flow behavior was demonstrated by Cogswell's method. Fig. 5.6 reveals that the nano composites exhibit a typical extensional thinning phenomenon in a uniaxial extension. The elongational viscosity was found to decrease non linear manner with increasing elongational rate. According to the flow mechanism of molecular chains though elonational flow, the tensile stress would either destruct the entanglement of macro molecular chains and result in decreasing the elongational viscosity. Or it would increased the orientation of macro molecular chains so as to increase the elongational viscosity [9]. For the nano composites as PP filled $CaCO_3$ nano particles, increasing the tensile stress following adjustment of the rate (see Fig. 5.7a and 5.7b) would destruct the entanglement of molecular chains and reorientation result in decreasing the elongational viscosity. As the same time, the viscosity was found increased with increasing amount of nano filler (ie. 0-25 wt%). Due to the nano filler would block the molecular chains movements and orientation as well as stretching force direction. Both the nano particle types exhibited similarly behavior. The 25wt% composites, the maximum values are either obtained. The elongational behavior is very interesting on the melt spinning processing. It is easier to produce the draw resonance when decreasing the viscosity. More over, it can be reduce the activation energy of the elongational flow.

5.4 CONCLUSIONS

The rheological properties on shear flow, elonagational flow and the extrudate swell phenomenon in various filler loading, ranging from 5 to 25 wt% of the composites during capillary extrusion process. Neat iPP and composites exhibited shear thinning pseudoplastic behavior as real shear stress were a function of real shear rate. The $CaCO_3$ nanaparticles with treated the surface by stearic acid exhibited the hydrophobic shows the reduction of the rate of changing real shear stress on real shear rate with increasing amount of fillers as compared on non treatment surface composites. The flow curve occurred the plateau curve that meanwhile a critical shear stress on about 1100 s^{-1} of shear rate. Both of the results show the real viscosity is decreased non linear manner with increasing the real shear rate. In addition, the uncoated nano composites exhibited difference values at the same real of rate in order of 0 to 25 wt% of filler. But, in case of coated nano composites present more equal. The percentage of extrudate swell at a given real shear influenced with increasing shear rate in non linear manner. Without surface coating was found to reduce of swell values with increasing amount of filler. The slope of linear regression draw to the data obtained for uncoated nano composites of given amount was found to decrease with increasing filler loading. As the same time, stearic acid coated nano composites exhibited slope value not difference as much. And increasing L/D ratios tend to differences a linear regression on lower L/D ratio. Due to an increasing the L/D ratios, it also increased the residence time of the composites in the die. Which affect to the already-good dispersion of nano particles on PP matrix, the elongational flow behavior reveals that the nano composites exhibit a typical extensional thinning phenomenon. The nano composites increased the tensile stress following adjustment of the rate. They would destruct the entanglement of molecular chains and reorientation result in decreasing the elongational viscosity. As the same time, the viscosity was found increased with increasing amount of nano fillers.

5.5 ACKNOWLEDGMENTS

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5.6 REFERENCES

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

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

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

[4] C. Lei, D. Chen, R. Huang, G. Li, Y. Lu, Journal of Applied Polymer Science 85 (2002) 2793.

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

[6] D. J. Fleming, Polymer Testing 25(2004)*.

[7] F. N. Cogswell, Polymer Melt Rheology, wood head publishing, London, 1994.

[8] J. C. Huang, K. S. Leong, Journal of Applied Polymer Science 84 (2002) 1269.

[9] K. Chen, J. Shen, X. Tang, Journal of Applied Polymer Science 97 (2005) 705.

[10] F. N. Cogswell, Transactions of the society of rheology 16:3 (1972) 383.

[11] J. L. white, H. Tanaka, Journal of Applied Polymer Science 26 (1981) 579.

[12] J. C. Huang, Z. Tao, Journal of Applied Polymer Science 87 (2003) 1587.

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

[14] X. L. Xie, Q. X. Lui, R. K. Y. Li, X. P. Zhou, Q. X. Zhang, Z. Z. Yu, Y. W. Mai, Polymer 45 (2004) 6665.

[15] G. Wang, X. Y. Chen, R. Huang, L. Zhang, Journal of Materials Science Letters 21 (2002) 985.

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

[17] A. Lazzerri, S. M. Zebarjad, M. Pracella, K. Cavalier, R. Rosa, Polymer 46 (2005) 827.

[18] Q. X. Zhang, Z. Z. Yu, X. L. Xie, Y. M. Mai, Polymer 45 (2004) 5985.

[19] L. Jiang, Y.C. Lam, K. C. Tam, T. H. Chua, G.W. Sim, L.S. Ang, Polymer 46 (2005) 243.

[20] J.Z. Liang, Polymer International 51 (2002) 1473.

[21] R. Dangtungee, J. Yun, P. Supaphol, Polymer Testing 24 (2005) 2.

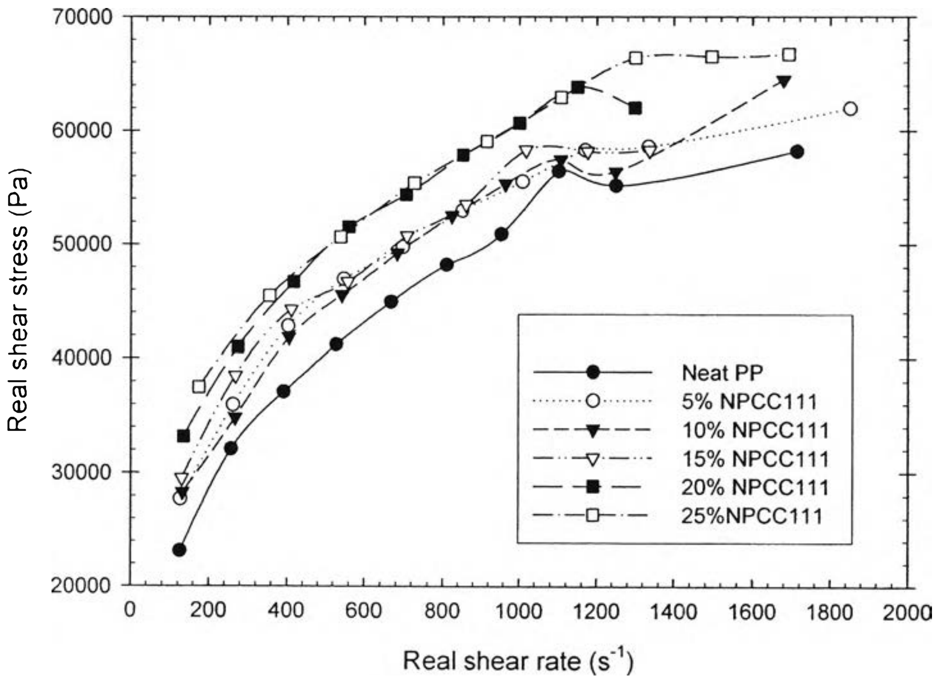
[22] Availablefromhttp://www.hmcpolymer.com/products/impact_/CS42_files/slide0019.html

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

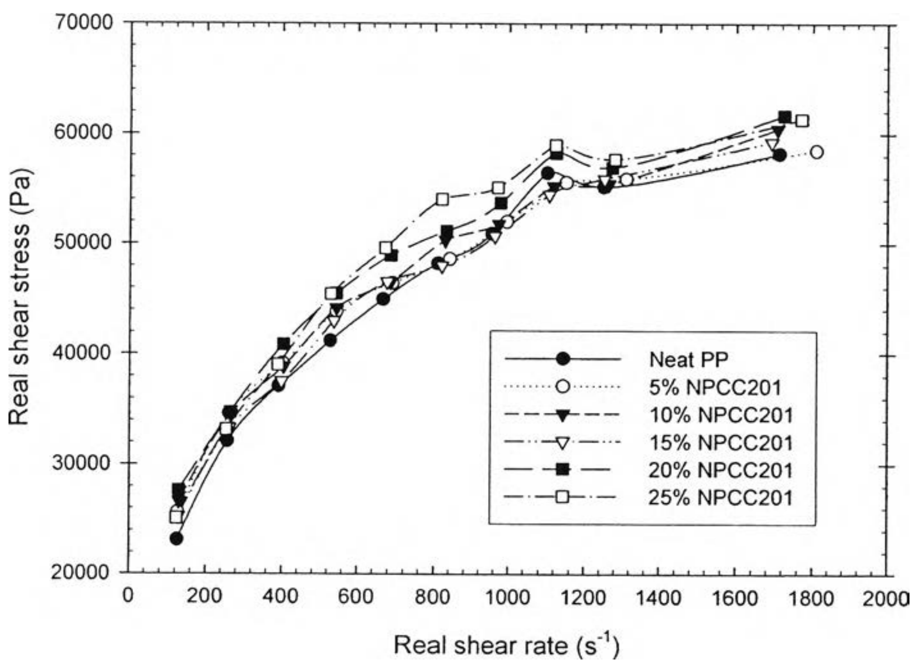
[24] J.Z. Liang, Polymer Testing 21 (2002) 927.

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

5.7 LIST OF FIGURE

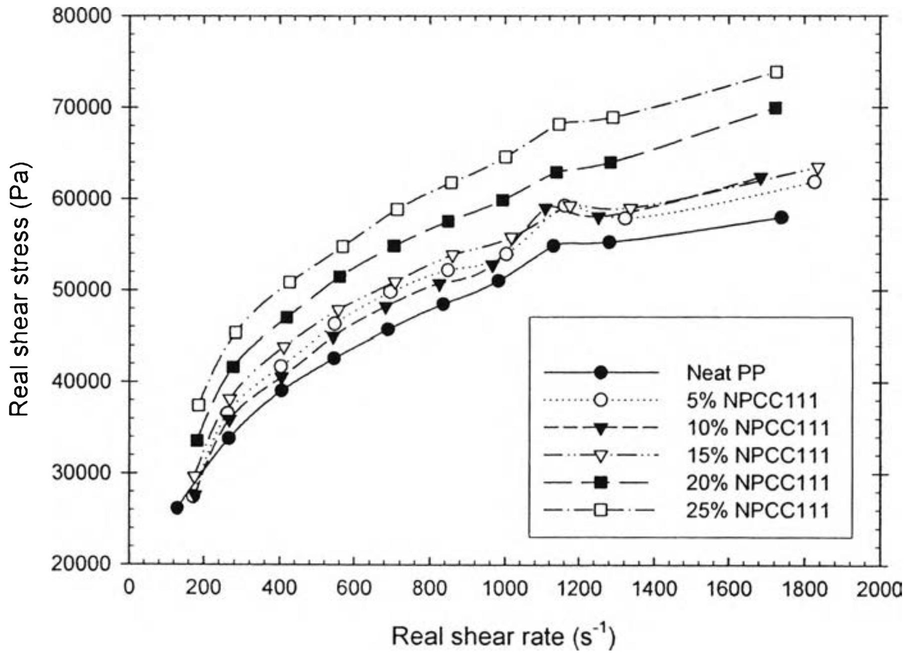

70000
60000
50000
40000
30000
20000
Real shear stress (Pa)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Real shear rate (s^{-1})
Neat PP
5% NPCC111
10% NPCC111
15% NPCC111
20% NPCC111
25%NPCC111

(a)

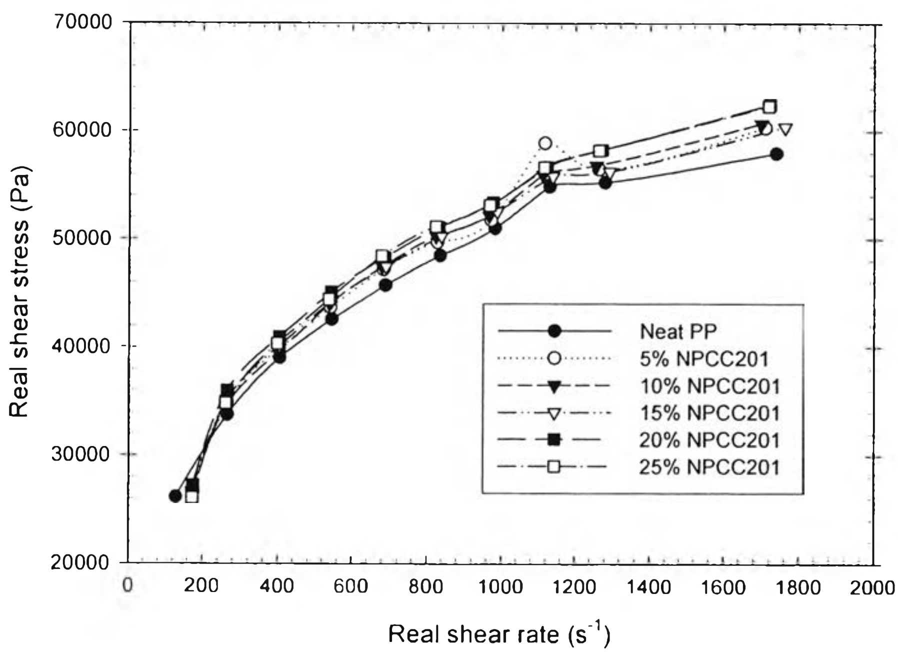

70000
60000
50000
40000
30000
20000
Real shear stress (Pa)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Real shear rate (s^{-1})
Neat PP
5% NPCC201
10% NPCC201
15% NPCC201
20% NPCC201
25% NPCC201

(b)

Figure 5.1

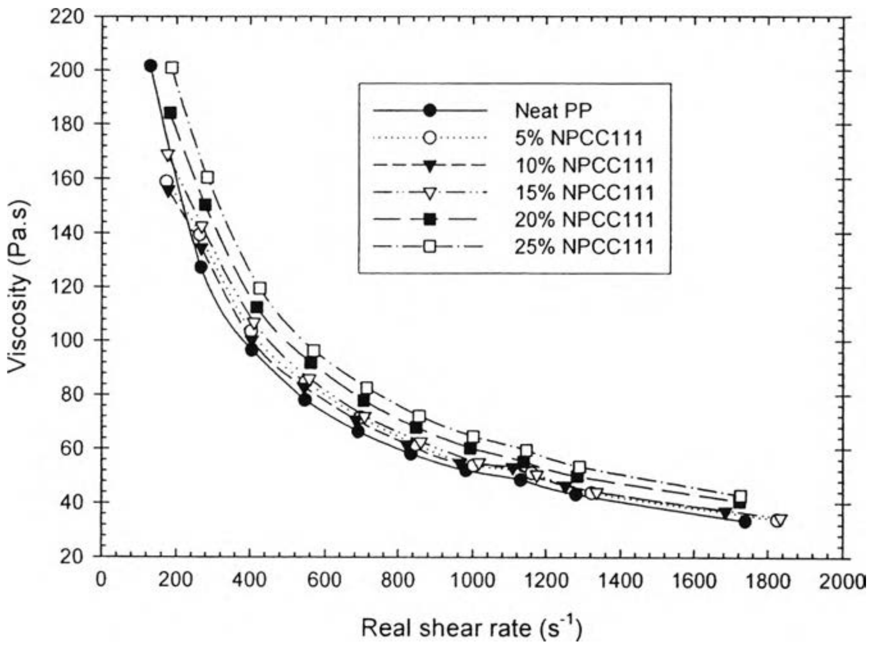

Real shear stress (Pa)
Real shear rate (s-1)
Neat PP
5% NPCC111
10% NPCC111
15% NPCC111
20% NPCC111
25% NPCC111

(a)

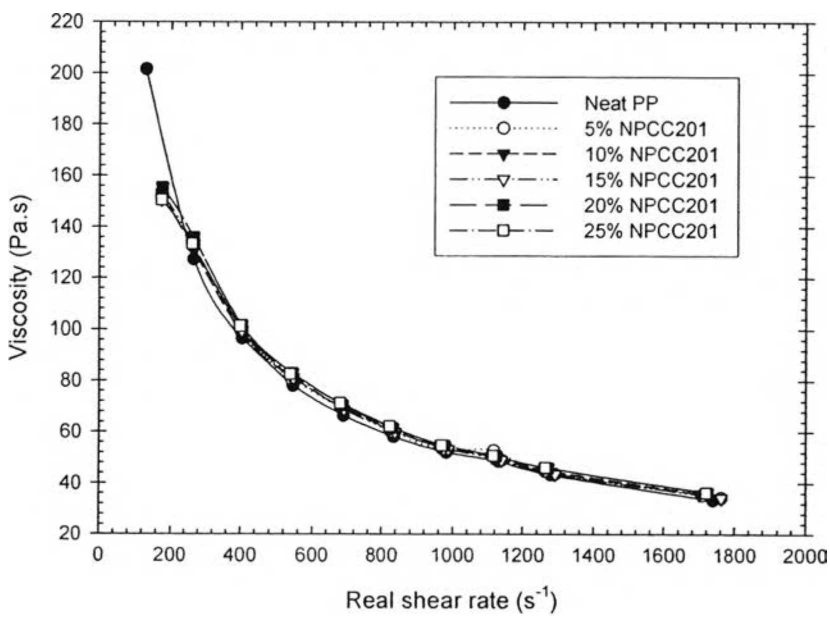

Real shear stress (Pa)
Real shear rate (s-1)
Neat PP
5% NPCC201
10% NPCC201
15% NPCC201
20% NPCC201
25% NPCC201

(b)

Figure 5.2

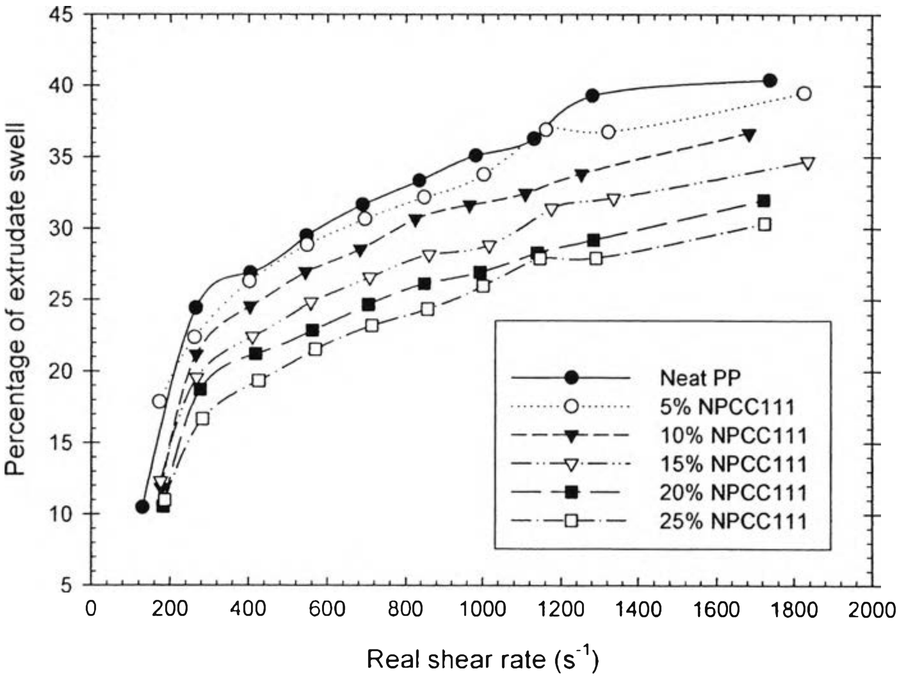

Viscosity (Pa.s)
Real shear rate (s-1)
Neat PP
5% NPCC111
10% NPCC111
15% NPCC111
20% NPCC111
25% NPCC111

(a)


Viscosity (Pa.s)
Real shear rate (s-1)
Neat PP
5% NPCC201
10% NPCC201
15% NPCC201
20% NPCC201
25% NPCC201

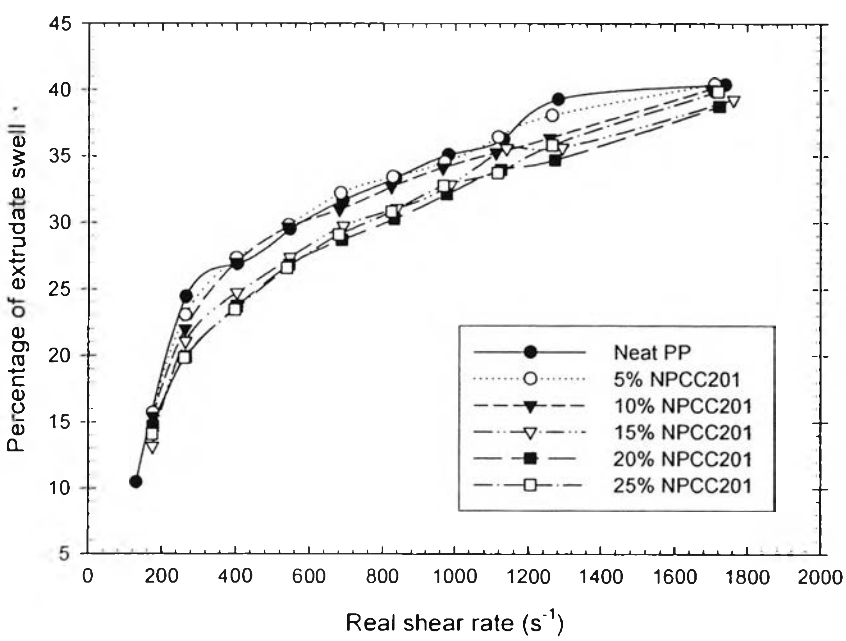
(b)

Figure 5.3



Percentage of extrudate swell
Real shear rate (s^{-1})
Neat PP
5% NPCC111
10% NPCC111
15% NPCC111
20% NPCC111
25% NPCC111

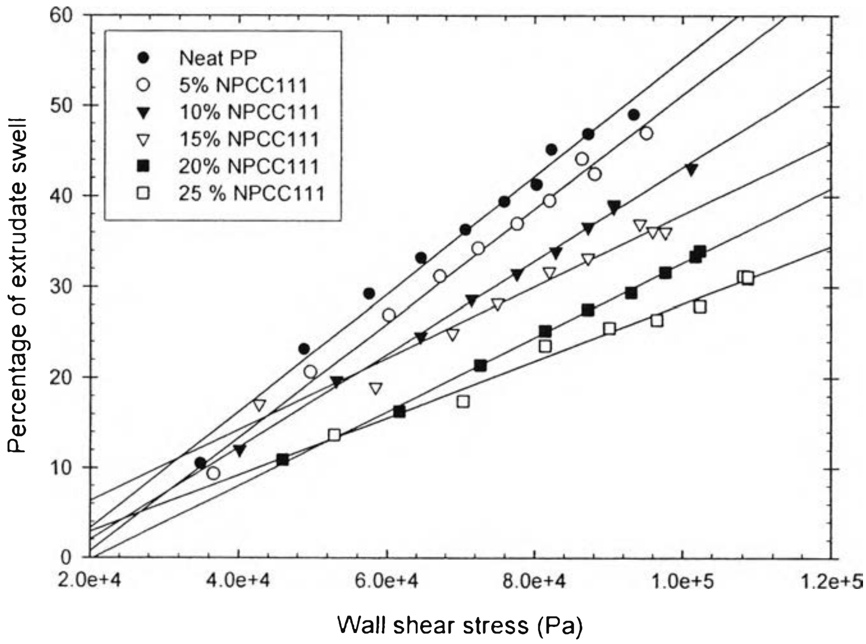
(a)



Percentage of extrudate swell
Real shear rate (s^{-1})
Neat PP
5% NPCC201
10% NPCC201
15% NPCC201
20% NPCC201
25% NPCC201

(b)

Figure 5.4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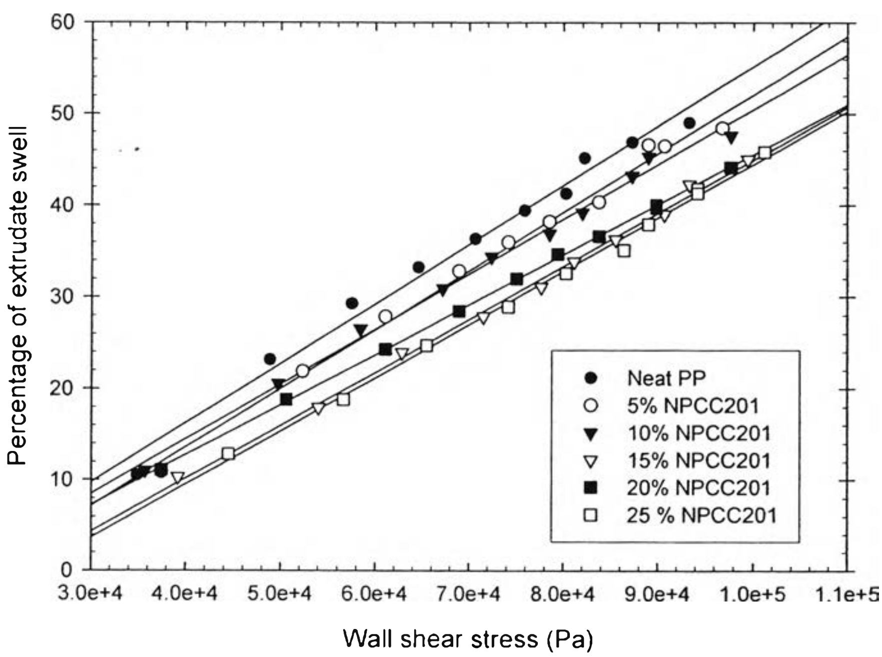
50
40
30
20
10
0
2.0e+4
4.0e+4
6.0e+4
8.0e+4
1.0e+5
1.2e+5
Percentage of extrudate swell
Wall shear stress (Pa)
Neat PP
5% NPCC111
10% NPCC111
15% NPCC111
20% NPCC111
25 % NPCC111

(a)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50
40
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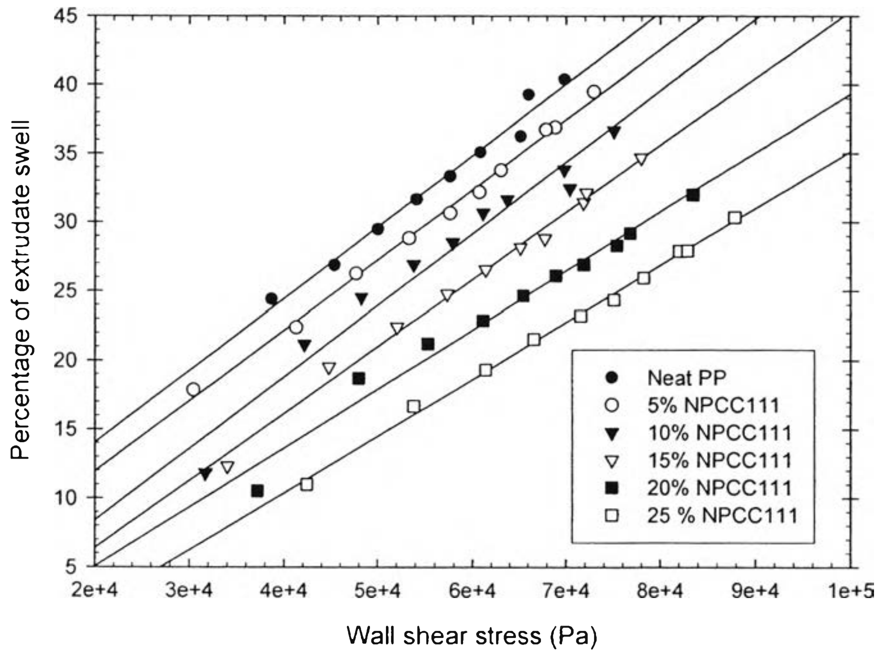
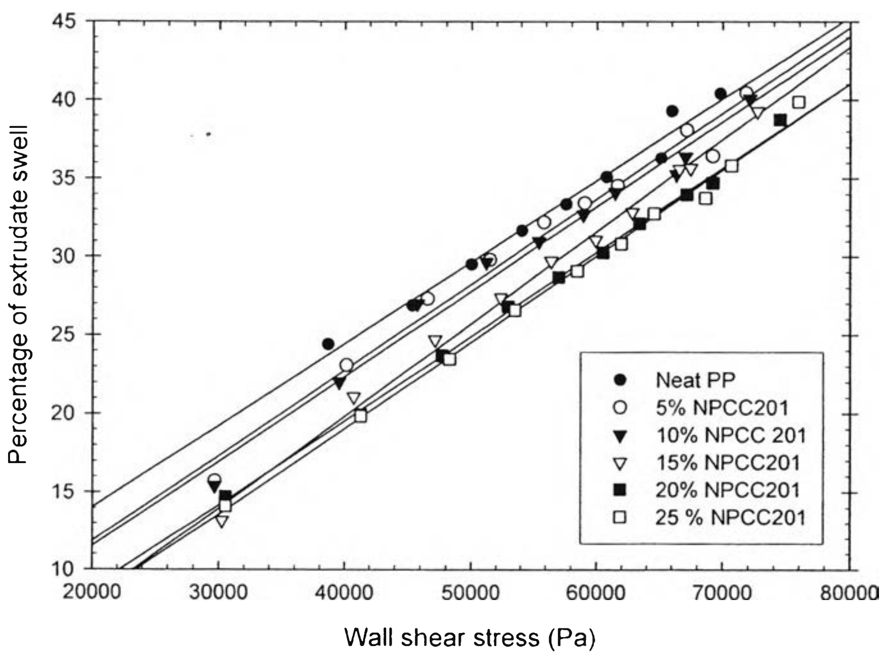
3.0e+4
4.0e+4
5.0e+4
6.0e+4
7.0e+4
8.0e+4
9.0e+4
1.0e+5
1.1e+5
Percentage of extrudate swell
Wall shear stress (Pa)
Neat PP
5% NPCC201
10% NPCC201
15% NPCC201
20% NPCC201
25 % NPCC201

(b)

Figure 5.5

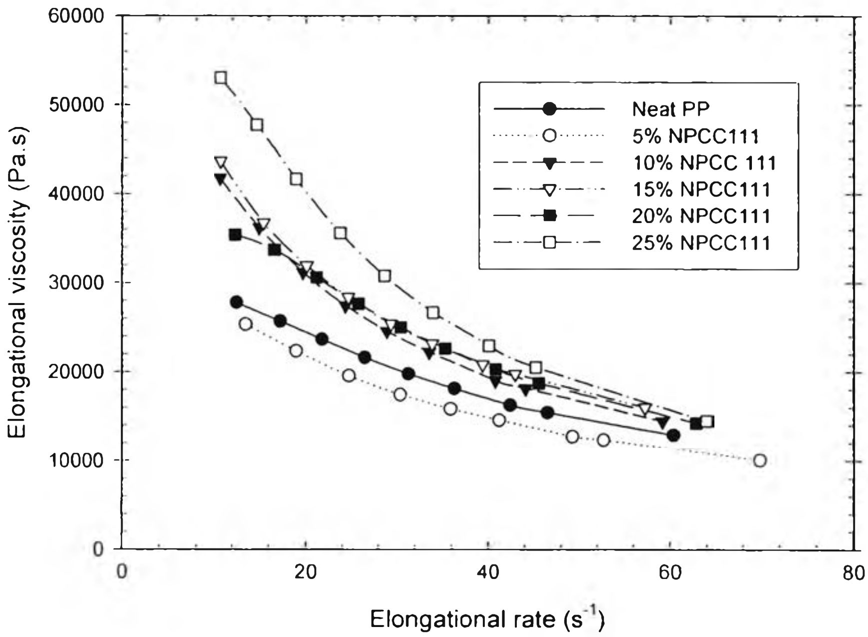


(c)



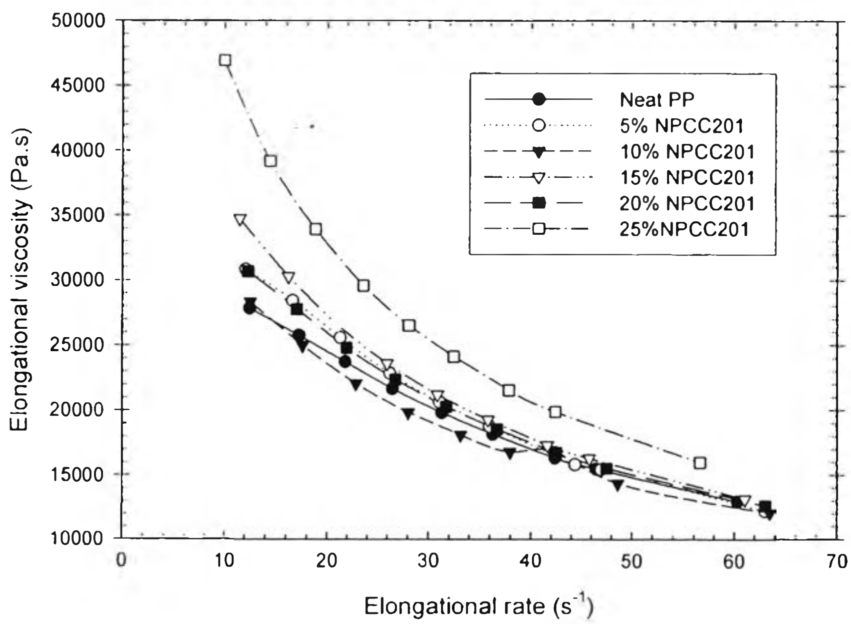
(d)

Figure 5.5 (cont.)



Elongational viscosity (Pa.s)
Elongational rate (s⁻¹)
Neat PP
5% NPCC111
10% NPCC 111
15% NPCC111
20% NPCC111
25% NPCC111

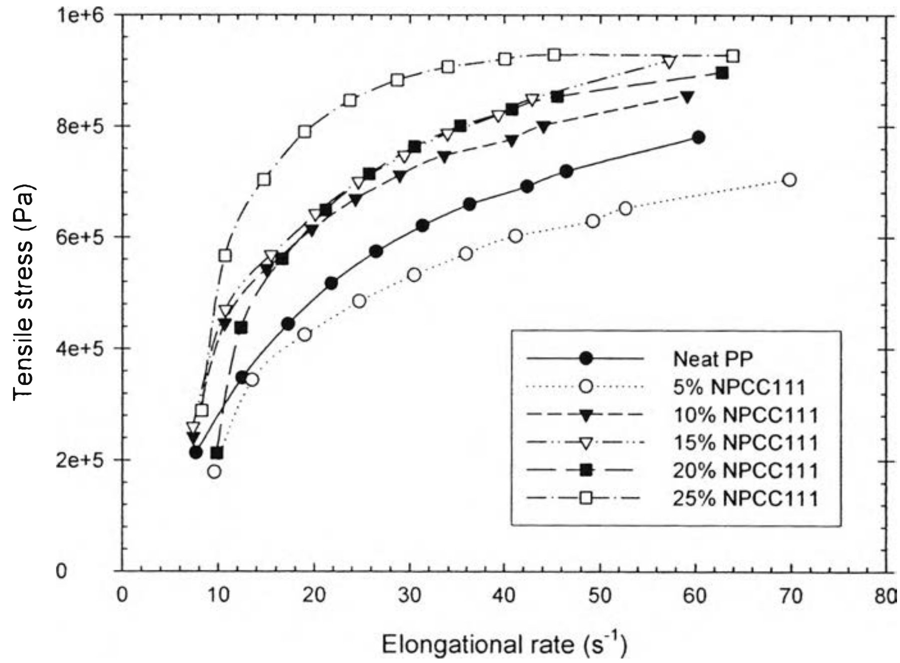
(a)



Elongational viscosity (Pa.s)
Elongational rate (s⁻¹)
Neat PP
5% NPCC201
10% NPCC201
15% NPCC201
20% NPCC201
25%NPCC201

(b)

Figure 5.6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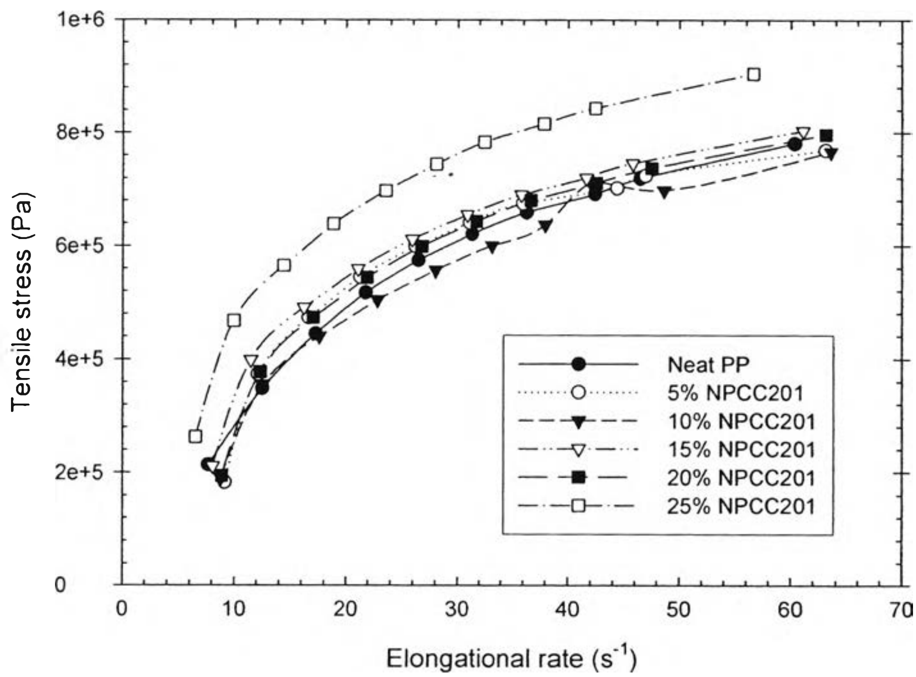
8e+5
6e+5
4e+5
2e+5
0
Tensile stress (Pa)
0
10
20
30
40
50
60
70
80
Elongational rate (s-1)
Neat PP
5% NPCC111
10% NPCC111
15% NPCC111
20% NPCC111
25% NPCC111

(a)


1e+6
8e+5
6e+5
4e+5
2e+5
0
Tensile stress (Pa)
0
10
20
30
40
50
60
70
Elongational rate (s-1)
Neat PP
5% NPCC201
10% NPCC201
15% NPCC201
20% NPCC201
25% NPCC201

(b)

Figure 5.7