

This is the peer reviewed version of the following article: Liang, J. Z., Chen, C. Y., Zhou, T. Y., Zou, S. Y., Huang, W. F., Tsui, C. P., Tang, C. Y., & Mišković-Stanković, V. (2017). Melt extrudate swell behavior of multi-walled carbon nanotubes filled-polypropylene composites. *Polymer Composites*, 38(11), 2433–2439, which has been published in final form at <https://doi.org/10.1002/pc.23829>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley's version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited.

Melt Extrudate Swell Behavior of Multi-walled Carbon Nanotubes Filled-Polypropylene Composites

J.Z. Liang^{ab*}, C.Y. Chen^a, S.Y. Zou^a, W.F. Huang^b, C.P. Tsui^{b*}, C.Y. Tang^b,
S.D. Zhang^a, Vesna Mišković-Stanković^c

^a Research Division of Green Function Materials and Equipment

School of Mechanical and Automotive Engineering

South China University of Technology, Guangzhou 510640, P.R. China

^b Department of Industrial and Systems Engineering, The Hong Kong Polytechnic

University, Kowloon, Hung Hom, Hong Kong, P.R. China

^c *Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11 000*

Belgrade, Serbia

ABSTRACT

The extrudate swell behavior of polypropylene (PP) composite melts filled with multi-walled carbon nanotubes (MWCNTs) was studied using with a capillary rheometer in a temperature range from 190 to 230°C and at various apparent shear rates varying from 50 to 800s⁻¹. It was found that the values of the extrudate swell ratio of the composites increased nonlinearly with increasing apparent shear rates, while the values of the extrudate swell ratio decreased almost linearly with increasing temperature. The values of the melt extrudate swell ratio increased approximately linearly with increasing shear stress, while decreased approximately nonlinearly with an increase of the MWCNT weight fraction. In addition, the extrudate swell mechanisms were discussed with observation of the fracture surface of the extrudate using scanning electronic microscopy. This study provides a basis for further

development of MWCNTs reinforced polymer composites with desirable mechanical and thermal properties.

Key words: polymer-matrix composites; rheological properties; extrusion; resin flow.

*Corresponding authors. E-mail address: scutjzl@sohu.com (J.Z. Liang); mfgary@polyu.edu.hk (Gary C.P. Tsui).

Rheological properties reflect the processing and use performances of polymeric materials. Melt extrusion is one of the major processing ways of polymers. Extrudate swell is an important parameter for characterizing the melt viscoelasticity of polymers during extrusion flow, and often required for the design of an extruder and a runner system of an injection mould tool [1]. Polypropylene (PP) is a type of widely used semi-crystalline thermoplastics owing to its low cost, good performance and processing properties. However, their mechanical properties and thermal stability are not enough to be used as engineering plastics. Therefore, PP is usually modified through blending with other resins or filling with inorganic fillers. It is meaningful for studying the extrudate swell behavior of PP composite melts from the perspectives of polymer processing and rheology. The effects of inorganic fillers, such as calcium carbonate [2], kaolin [3], $\text{Al}(\text{OH})_3/\text{Mg}(\text{OH})_2$ [4], diatomite [5], hollow glass bead [6], microencapsulated red phosphorus [7], and organobentonite [8], on the extrudate swell behavior of PP composite melts have been investigated,.

Carbon nanotube (CNT) is a new type of carbon filler, in the form of a cylinder

with both ends sealed through crimping a graphene layer as a tube [9, 10]. In addition to the special seamless nanometer tube structure, CNTs not only possess some properties of general nanometer materials, but also have excellent mechanical properties (Young's modulus up to 1TPa, and tensile strength up to 100GPa) [11] due to its high specific surface area and length to diameter ratio (length to diameter ratio can be up to 1000) [12], as well as outstanding electrical and thermal conductive properties [13]. The properties of polymeric materials can be improved or some new properties can be acquired when they are filled with CNTs [14-19]. CNTs can be divided into two categories: single wall carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). Owing to the lower cost of MWNTs, the applications of the MWNTs are more extensive than those of the SWNTs.

Recently, Liang and his colleagues [20] studied the melt flow behavior of PP/MWCNTs composites, and found that melt shear flow followed the power law relationship and the dependence of the melt shear viscosity on temperature obeyed the Arrhenius equation. However, there have been few studies on the extrudate swell behavior of polymer/GNPs composites. The objectives for the present study were to investigate the influence of filler content and processing conditions on the melt extrudate swell behavior of the PP/MWCNTs composites.

2 Experimental

2.1 Raw materials

The polypropylene with trademark CJS-700 serving as the matrix material was

supplied by the Guangzhou Petrochemical Works in Guangdong province (Guangzhou, China), and its density in a solid state and melt flow rate were 910 kg/m³ and 10 g/10min (230 °C, 2.16 kg), respectively.

The multi-walled nanotube (MWCNT) marked TNIM2 was selected as the filler to identify the influence of its content on the melt flow behavior of the composite systems. The MWCNT was supplied by the Chengdu Organic Chemical Co., Ltd. of the Chinese Academy of Sciences (Chengdu, China), and prepared by means of chemical vapor deposition method. The main properties include external diameter about 8-15 nm and length 30–50 μm, carbon content >90% and density 2.1 g/cm³.

2.2 Composite preparation

The PP was mixed with MWNTs in a high speed compounding machine with a model of GH-10 supplied by the Beijing Plastics Machinery (Beijing, China), and then the PP/MWCNT blends were melt-blended in a twin-screw extruder (Model SHJ-26) supplied by the Nanjing Chengmeng Machinery Ltd. Co. (Nanjing, China) at a screw speed of 100 rev/min and in a temperature range from 190 ~ 210 °C, for preparation of the PP/MWCNT composite systems. The weight fractions of the MWCNT were 1, 2, 3, 4 and 5 wt.% and the screw diameter was 26 mm, while the length to diameter ratio of the screw was 40. The granules of the fabricated composites were dried at 80 °C for five hours before testing.

2.3 Instrument and methodology

The rheological properties of the PP/MWCNT binary composite melts were measured using the capillary rheometer (Model Rheologic 5000) supplied by the Ceast Co. Ltd (Italy). The melt extrudate swell behavior tests were carried out in a temperature range of 180 ~ 230°C and apparent shear rates varying from 100 to 4000 s⁻¹. The diameter and the length to diameter ratio (L/D) of the capillary die were 1 mm and 40, respectively; the die entry angle was 180°. It is generally believed that the effect of the entrance pressure losses on extrusion flow behavior of polymer melts is insignificant when ratio of length to diameter of die is greater than 30 [21]. Thus, the shear stress at the channel wall (τ_w) may be expressed as follows:

$$\tau_w = \frac{\Delta P D}{4L} \quad (1)$$

And the apparent shear rate can be given by

$$\gamma_a = \frac{32Q}{\pi D^3} \quad (2)$$

Where, ΔP is the total pressure drop, and Q is the volume flow rate.

The extrudate with a length of 2 cm was taken as specimens when the shear rate was stable, and the specimen diameter (D_e) was then measured for three times after the extrudate was placed in a dry environment for one month, and the average value of the specimen diameter was recorded. Thus, the extrudate swell ratio is given by:

$$B = \frac{D_e}{D} \quad (3)$$

3 Results and Discussion

3.1 Dependence of extrudate swell ratio on apparent shear rate

Figure 1 presents the dependence of the melt extrudate swell ratio of the composites on apparent shear rates at 200 °C. It is found that, when the apparent shear rate is constant, the value of the melt extrudate swell ratio decreases with increasing the MWCNT weight fraction; while the values of the melt extrudate swell ratio increase nonlinearly with increasing apparent shear rates. Figure 2 illustrates the dependence of the melt extrudate swell ratio of the composite with 1 wt.% MWCNT on apparent shear rates at different temperatures. Similarly, the values of the melt extrudate swell ratio increase nonlinearly with increasing apparent shear rates; while the value of the melt extrudate swell ratio decreases with a rise in temperature. During die extrusion flow of polymer melts, the residence time of the melts in the channel decreases with increasing flow rate at a given temperature. The stress relaxation will not be completed if the residence time is smaller than the relaxation time of molecular chains polymer melts. For this case, the elastic recovery of deformation produced in the flow will increase correspondingly, resulting in an increase of the melt extrudate swell. In general, shear rate increases with an increase of flow rate during die extrusion of polymer melts. Therefore, the melt extrudate swell ratios of the PP/GNPs composite increase with increasing shear rates. Moreover, the molecular chains will be extended and oriented along the flow direction at a higher apparent shear rate level. For this case, the elastic energy stored in the melt can somewhat be decreased, leading to a reduction of the increase rate of the melt extrudate swell ratio.

3.2 Dependence of extrudate swell ratio on shear stress

Figure 3 displays the dependence of the melt extrudate swell ratio of the composite with 3 wt.% of MWCNTs on shear stress at different temperatures. It can be observed that the values of the melt extrudate swell ratio of the composite increase

roughly linearly with an increase of the shear stress, and the values of the melt extrudate swell ratio are close to each other at different temperatures. This is because, during die extrusion flow of polymer melts, the molecular chains will be extended and the molecular chains will be oriented along the flow direction under the effect of flow field, and the elastic strain energy stored will increase in this case. Thus, the shear deformation increases correspondingly with increasing shear stress when temperature is constant. As a result, the values of the melt extrudate swell ratio of the composite increase with increasing shear stress.

Figure 4 shows the dependence of the melt extrudate swell ratio of the composites on shear stress at 220 °C. Similarly, the values of the melt extrudate swell ratio of the composites decrease with increasing the MWCNT weight fraction; while the values of the melt extrudate swell ratio of the composite increase roughly linearly with an increase of shear stress, and the relationship between them can be described by following equation:

$$B = \lambda_0 + \lambda \tau_w \quad (4)$$

Where λ_0 and λ are the parameters related to polymer melt viscoelasticity. The values of λ_0 and λ of the composite melts under experimental conditions can be determined using a linear regression method. Table 1 lists the values of λ_0 and λ of the PP/MWCNTs composite melts at 220°C. It can be found that the absolute values of λ_0 decrease while the values of λ increase slightly with a rise in temperature. Moreover, the value of linear correlation coefficient (R) is higher than 0.96.

Table1 Values of λ_0 and λ of composite systems at 220°C

Materials	λ_0	λ	R
PP	1.09499	0.00349	0.96512

PP/MWCNTs (1wt.%)	1.06357	0.00314	0.98669
PP/MWCNTs (2wt.%)	1.04148	0.00295	0.97766
PP/MWCNTs (3wt.%)	0.98567	0.00317	0.98752
PP/MWCNTs (4wt.%)	0.9626	0.00286	0.97553
PP/MWCNTs (5wt.%)	0.95314	0.00252	0.98087

3.3 Dependence of extrudate swell ratio on temperature

Figure 5 presents the dependence of the melt extrudate swell ratio of the composites on temperature at an apparent shear rate of 100s^{-1} for two different MWCNT weight fractions of 1 and 3%. It can be found that the values of the melt extrudate swell ratio decrease almost linearly with a rise in temperature, and the relationship between them can be expressed by following equation:

$$B = \alpha_0 + \alpha T \quad (5)$$

Where α_0 and α are the parameters related to polymer melt viscoelasticity. Among them, α reflects the sensitivity of the melt extrudate swell to temperature. The values of α_0 and α of the composite melts under experimental conditions can also be determined using the linear regression method. Table 2 lists the values of α_0 and α of the PP/MWCNTs composite melts at the apparent shear rate of 100 s^{-1} . It can be seen that the absolute value of α increases with increasing MWCNT weight fraction, implying that the sensitivity of the melt extrudate swell of the composites to temperature is enhanced with increasing MWCNT weight fraction under the given experimental conditions. Moreover, the correlation coefficient is greater than 0.99.

Table 2 Values of α_0 and α of composite systems at shear rate of 100s^{-1}

Composites	α_0	α	R
1.0wt.%CNTs	1.4406	-0.0011	0.9949
3.0wt.%CNTs	1.5186	-0.0017	0.9939

Figure 6 illustrates dependence of the melt extrudate swell ratio of the composite with MWCNT weight fraction of 3% on temperature at different apparent shear rates. Similarly, the values of the melt extrudate swell ratio decrease approximately linearly with a rise in temperature. The values of α_0 and α of the PP/MWCNTs composite melts with the MWCNT weight fraction of 3% at different apparent shear rates are summarized in Table 3. It can be observed that the absolute values of α increase with increasing apparent shear rates, meaning that the sensitivity of the melt extrudate swell of the composites to temperature is enhanced with increasing apparent shear rates under the given experimental conditions. Moreover, the correlation coefficient is greater than 0.95.

Table 3 Values of α_0 and α of composites with 3 wt.% of MWCNTs at different shear rates

Apparent shear rates (s^{-1})	α_0	α	R
100	1.5186	-0.0017	0.99394
200	1.6299	-0.0020	0.97325
500	1.8292	-0.0026	0.9534
800	1.9862	-0.0032	0.98605

It is generally believed that, with a rise in temperature, the activity ability of macromolecular chains will be enhanced, and the stress relaxation process in the

extrusion die is shortened. Moreover, the elastic recovery of the deformation of polymer melt generated in the extrusion flow reduces correspondingly, leading to a reduction of the melt extrudate swell degree (i.e. the value of the extrudate swell ratio). In addition, the viscous dissipation of the macromolecular chains energy stored in the extrusion flow will increase with increasing temperature. As a result, the values of the melt extrudate swell ratio of the PP/MWCNTs composites decrease with increasing temperature under given conditions. Moreover, it can also be observed that the values of the melt extrudate swell ratio of the composites are roughly close to each other under different shear stresses. This indicates that the effect of temperature on the melt extrudate swell ratio is insignificant under action of the shear stress.

3.4 Relationship between melt extrudate swell ratio and MWCNT content

Figure 7 displays the relationship between the melt extrudate swell ratio and the MWCNT weight fraction of the PP composites under the apparent shear rate of 200 s^{-1} at two different temperatures of 200 and 220°C . It can be observed that the values of the melt extrudate swell ratio decrease almost linearly with increasing MWCNT weight fraction. When the MWCNT weight fraction is constant, the values of the melt extrudate swell ratio reduce with a rise of temperature. It is known that the relationship between the melt extrudate swell ratio and the MWCNT weight fraction of the composites can be expressed by following equation:

$$B = \beta_0 + \beta\phi_f \quad (5)$$

Where β_0 and β are the parameters related to polymer melt viscoelasticity. Among

them, β reflects the sensitivity of the melt extrudate swell to temperature. The values of β_0 and β of the composite melts under the experimental conditions can also be determined using the linear regression method. Table 4 lists the values of β_0 and β of the PP/MWCNTs composite melts at the apparent shear rate of 200 s^{-1} . It can be seen that the absolute value of β increases with increasing MWCNT weight fraction, meaning that the sensitivity of the melt extrudate swell of the composites to the MWCNT weight fraction is enhanced with increasing temperature under the given experimental conditions. Moreover, the correlation coefficient is greater than 0.96.

Table 4 Values of β_0 and β of composites at apparent shear rate of 200 s^{-1}

Temperature ($^{\circ}\text{C}$)	β_0	β	R
200	1.30048	-0.02466	0.98156
220	1.27805	-0.03029	0.96592

Figure 8 shows the correlation between the melt extrudate swell ratios and the MWCNT weight fraction of the PP composites at 220°C under different apparent shear rates. Similarly, the values of the melt extrudate swell ratio decrease approximately linearly with increasing MWCNT weight fraction. The values of the melt extrudate swell ratio increase with increasing apparent shear rates when the MWCNT weight fraction is fixed, while decrease almost linearly with increasing MWCNT weight fraction. The values of β_0 and β of the PP/MWCNTs composite melts at 220°C under different apparent shear rates are summarized in Table 5.

Table 5 Values of β_0 and β of composites at 220°C

Apparent shear rates (s^{-1})	β_0	β	R
50	1.1622	-0.0218	0.9394
100	1.2320	-0.0250	0.9323
200	1.2790	-0.0304	0.9620
500	1.3331	-0.0262	0.9426
800	1.3886	-0.0319	0.9935

It is generally believed that the activity of macromolecular chains of polymer composite systems is somewhat limited by the inclusions in the resin matrix. This is because that the MWCNTs can serve as the entanglement points between the macromolecular chains, and they will block the movement of the macromolecular chains, leading to a reduction of the elastic recovery of the shear and elongation deformation generated in the extrusion flow. Therefore, the elastic recovery of the elongation and shear deformation of polymer composite melts generated in the die extrusion flow is blocked by the filler particles in the matrix, resulting in a reduction of the melt extrudate swell ratio. Furthermore, the content of the resin in the composite systems decrease with increasing the filler content, and the viscoelastic properties are weakened correspondingly in this case. Thus, the values of the melt extrudate swell ratio of the PP/MWCNTs composites decrease with increasing MWCNT weight fraction.

3.5 Morphology

In general, the rheological behavior of polymer composite melts in the extrusion flow is dependent, to a great extent, upon the dispersion or distribution of the filler

particles in the resin matrix. In order to understand the dispersion or distribution of the MWCNTs in the PP matrix, the fracture surface of the extrudate of the composites was observed using scanning electronic microscopy (SEM). Figures 9 (a)-(d) are the SEM photographs of the extrudate fracture surfaces of the PP/MWCNTs composite systems for different MWCNT weight fractions of 1%, 2%, 3%, 4% and 5%. It can be observed that the dispersion and distribution of the MWCNTs in the PP matrix are roughly uniform. The values of the extrudate swell ratio vary relatively small for different MWCNT weight fractions. That is, there is no obvious fluctuation of the values of the extrudate swell ratio of the PP/MWCNTs composites under the experimental conditions (see Figures 7 and 8).

4. Conclusions

The influence of the multi-walled carbon nanotubes (MWCNTs) content on the melt extrudate swell behavior of polypropylene (PP) composites was significant in a temperature range of 190 ~ 230°C and at various apparent shear rates of 50 ~ 800s⁻¹. It was found that the values of the extrudate swell ratio of the composites increased nonlinearly with increasing apparent shear rates, while the values of the extrudate swell ratio decreased almost linearly with a rise in temperature. The values of the melt extrudate swell ratio increased approximately linearly with increasing shear stress, while decreased almost nonlinearly with an increase of the MWCNT weight fraction. Moreover, the dispersion and distribution of the MWCNTs in the PP matrix were roughly uniform from the observation of the cross section of their extrudate fracture

surfaces using scanning electronic microscopy

Acknowledgement

The authors would like to thank for the support from the Research Committee of The Hong Kong Polytechnic University (Project code: G-UC81 and RTE9).

References

- [1] Liang J.Z. Melt extrudate swell behavior of POM/EVA/HDPE/nano-CaCO₃ composites. *J. Polym. Eng.*, 2013, 33(1):19-26.
- [2] Dangtungee R., Yun J., Supaphol P. Melt rheology and extrudate swell of calcium carbonate nanoparticle-filled isotactic polypropylene, *Polym. Test.* 2005, 24: 2-11.
- [3] Ariffin A., Ariff Z.M., Jikans S. Evaluation on extrudate swell and melt fracture of polypropylene/kaolin composites at high shear Stress. *J Reinf Plast Compos*, 2011, 30 (7) : 609—619.
- [4] Liang J.Z., Yang J., Tang C.Y. Die-swell behavior of PP/Al(OH)₃/Mg(OH)₂ flame retardant composite Melts. *Polym. Test.*, 2010, 29 (5): 624-628. □
- [5] Liang J.Z. Effects of diatomite on extrudate swell behavior of polypropylene composite melts. *J. Appl. Polym. Sci.*, 2010, 118(1):385-389. □
- [6] Liang J.Z., Zhong M.Q. Melt extrudate swell behavior of polypropylene composites filled with hollow glass beads. *J. Polym. Eng.*, 2012, 32 (4-5): 259-263.
- [7] Liang J.Z., Feng J.Q., Tsui C.P., Tang C.Y. Extrudate swell behavior of polypropylene composites filled with microencapsulated red phosphorus. *J. Appl.*

- Polym. Sci., 2013, 129(6): 3497-3501.
- [8] Muksing N., Nithitanakul M., Grady B.P., et al. Melt rheology and extrudate swell of organobentonite-filled polypropylene nanocomposites[J]. Polymer Testing, 2008, 27(4): 470-479.
- [9] Meyyappan M. Carbon nanotubes: science and applications. CRC press, 2004.
- [10] Mittal G., Dhand V., Rhee K Y., et al. A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites. Journal of Industrial and Engineering Chemistry, 2015, 21: 11-25.
- [11] Skipa T., Lellinger D., Böhm W., et al. Influence of shear deformation on carbon nanotube networks in polycarbonate melts: Interplay between build-up and destruction of agglomerates. Polymer, 2010, 51(1): 201-210.
- [12] De Volder M.F.L., Tawfick S.H., Baughman R.H., et al. Carbon nanotubes: present and future commercial applications. Science, 2013, 339(6119): 535-539.
- [13] Bose S., Khare R.A., Moldenaers P. Assessing the strengths and weaknesses of various types of pre-treatments of carbon nanotubes on the properties of polymer/carbon nanotubes composites: A critical review. Polymer, 2010, 51(5): 975-993.
- [14] Spitalsky Z., Tasis D., Papagelis K., et al. Carbon nanotube–polymer composites: chemistry, processing, mechanical and electrical properties. Progress in polymer science, 2010, 35(3): 357-401.
- [15] Amr I T, Al-Amer A, Al-Harhi M, et al. Effect of acid treated carbon nanotubes on mechanical , rheological and thermal properties of polystyrene nanocomposites. Composites Part B: Engineering, 2011, 42(6): 1554-1561.

- [16] Wu D., Wu L., Zhang M., et al. Viscoelasticity and thermal stability of polylactide composites with various functionalized carbon nanotubes. *Polymer Degradation and Stability*, 2008, 93(8): 1577-1584.
- [17] Shieh Y.T., Liu G.L. Effects of carbon nanotubes on crystallization and melting behavior of poly (L - lactide) via DSC and TMDSC studies. *Journal of Polymer Science Part B: Polymer Physics*, 2007, 45(14): 1870-1881.
- [18] Quigley J.P., Herrington K., Baird D.G. Enhanced electrical properties of polycarbonate/carbon nanotube nanocomposites prepared by a supercritical carbon dioxide aided melt blending method. *Polymer*, 2014, 55(23): 6167-6175.
- [19] Mazov I.N., Ilinykh I.A., Kuznetsov V.L., et al. Thermal conductivity of polypropylene-based composites with multiwall carbon nanotubes with different diameter and morphology. *Journal of Alloys and Compounds*, 2014, 586: S440-S442.
- [20] Liang J.Z., Chen C.Y., Zou S.Y., Tsui C.P., Tang C.Y., Zhang S.D. Melt flow behavior of polypropylene composites filled with multi-walled carbon nanotubes during extrusion. *Polym. Test.*, 2015, 45: 41-46.
- [21] Liang J.Z. *Rheology in polymer materials processing*. Beijing: National Defense Industry Press, 2007.

Caption of figures

Fig. 1 Dependence of melt extrudate swell ratio on apparent shear rates at 200°C.

Fig. 2 Dependence of melt extrudate swell ratio on apparent shear rates under different temperatures (1wt.% MWCNTs).

Fig. 3 Dependence of melt extrudate swell ratio of on shear stress under different temperatures (3wt.% MWCNTs).

Fig. 4 Dependence of melt extrudate swell ratio on shear stress at 220°C.

Fig5 Dependence of melt extrudate swell ratio on temperature at apparent shear rate of 100s^{-1} .

Fig6 Dependence of melt extrudate swell ratio on temperature under different apparent shear rates (1wt.% MWCNTs).

Fig7 Relationship between melt extrudate swell ratio and MWCNT weight fraction under different temperatures and apparent shear rate of 200 s^{-1} .

Fig8. Correlation between melt extrudate swell ratio and MWCNT weight fraction under different apparent shear rates and temperature of $220\text{ }^{\circ}\text{C}$.

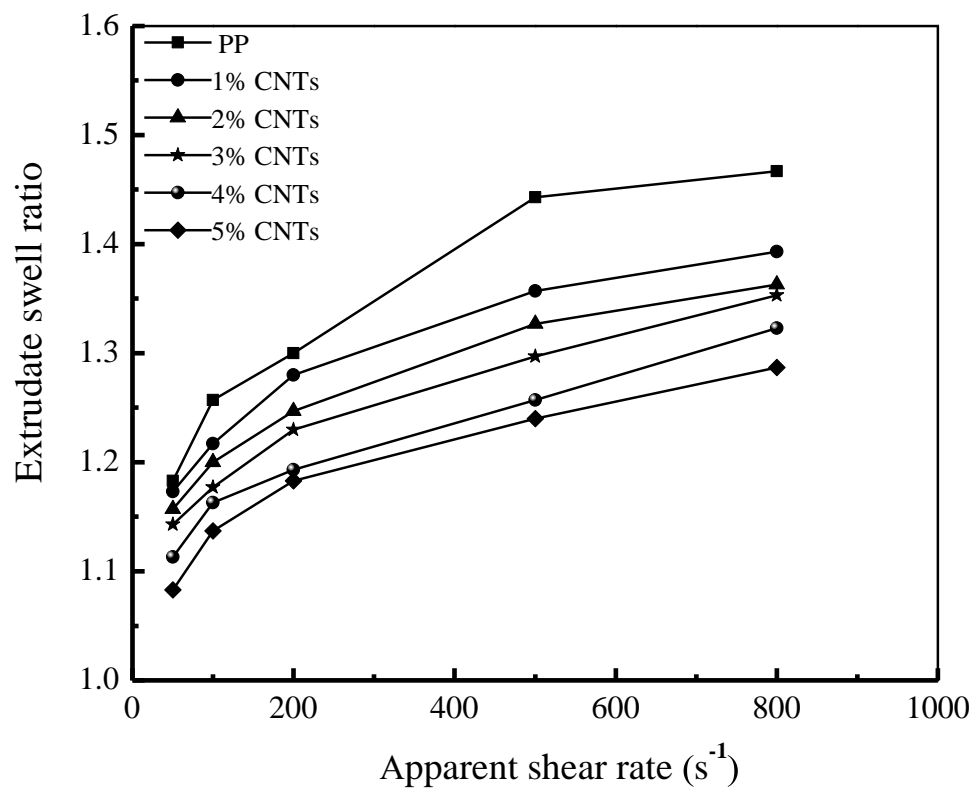


Fig. 1

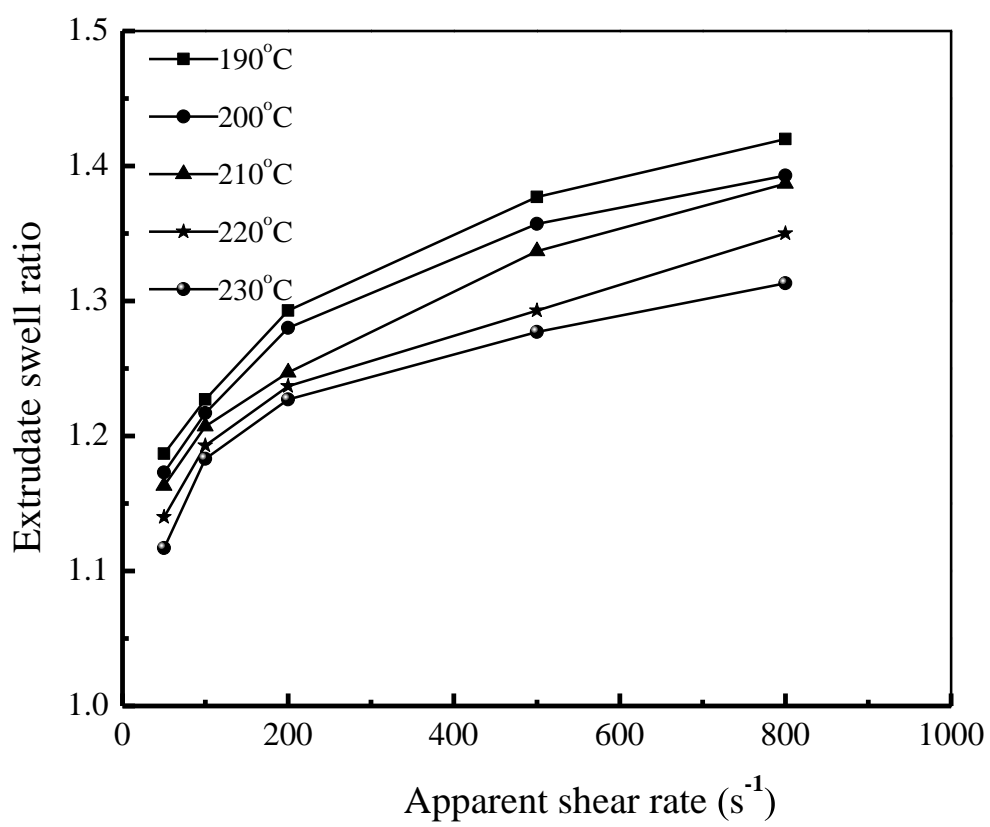


Fig. 2

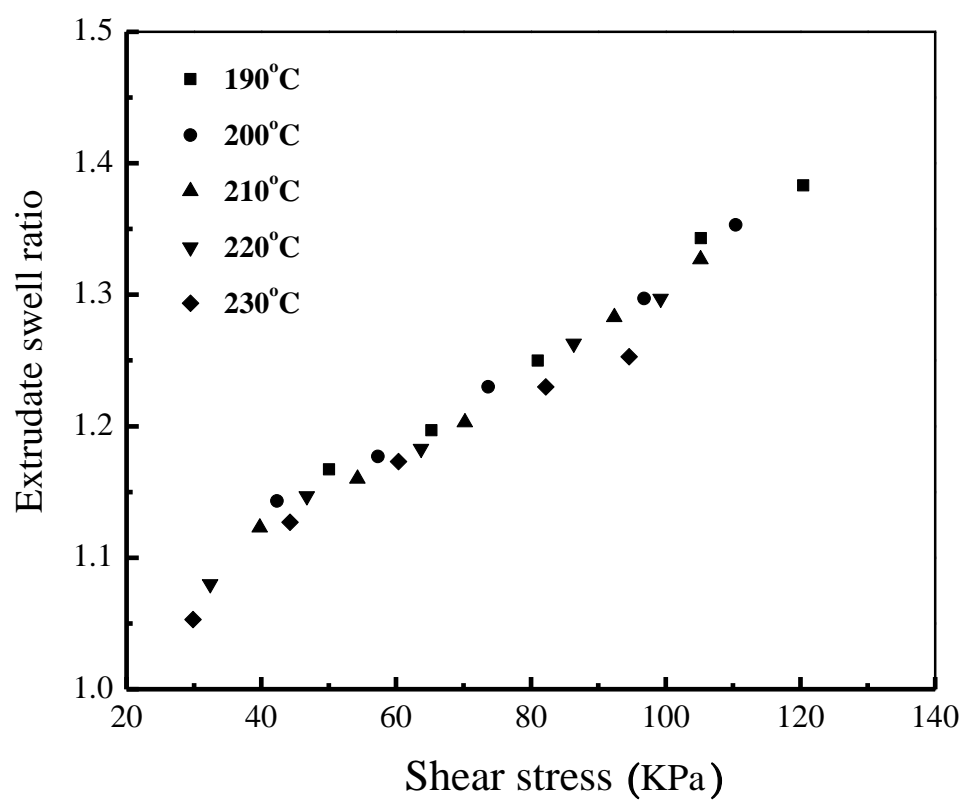


Fig. 3

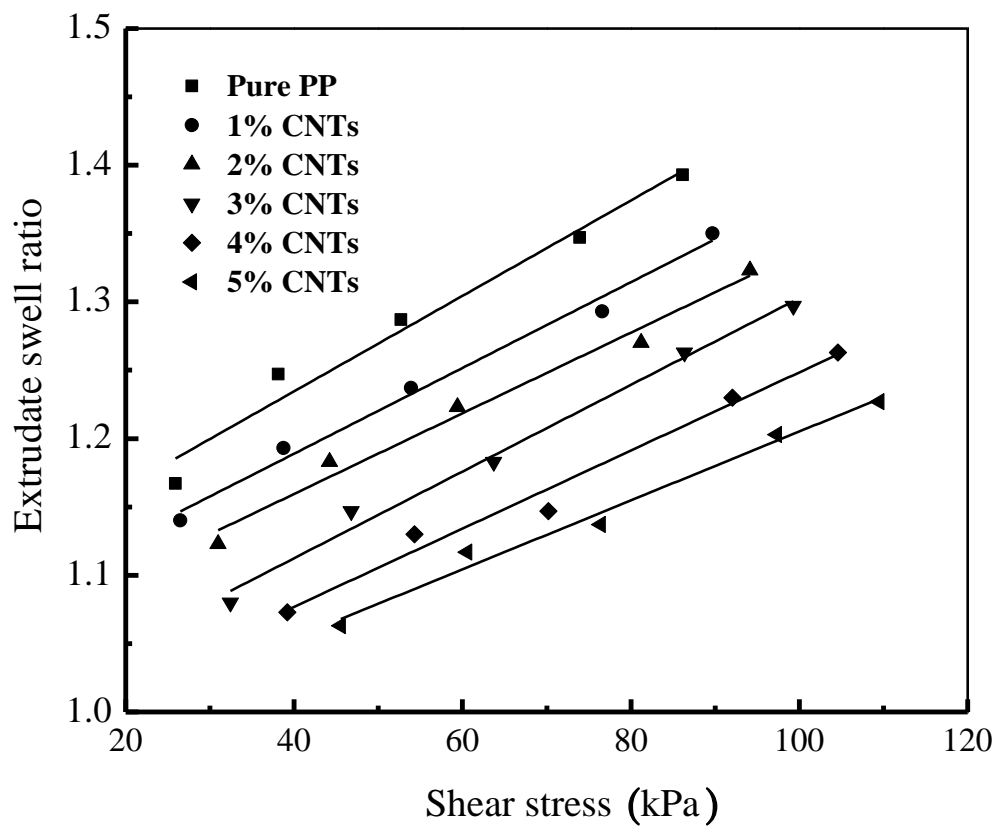


Fig. 4

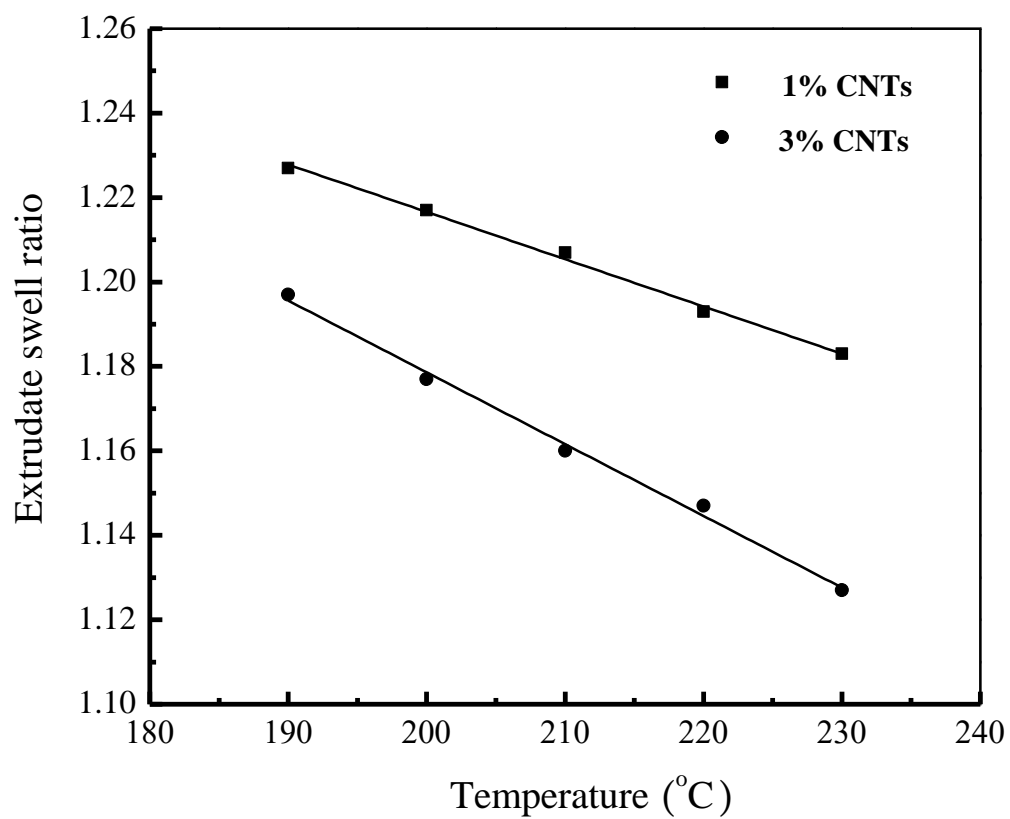


Fig. 5

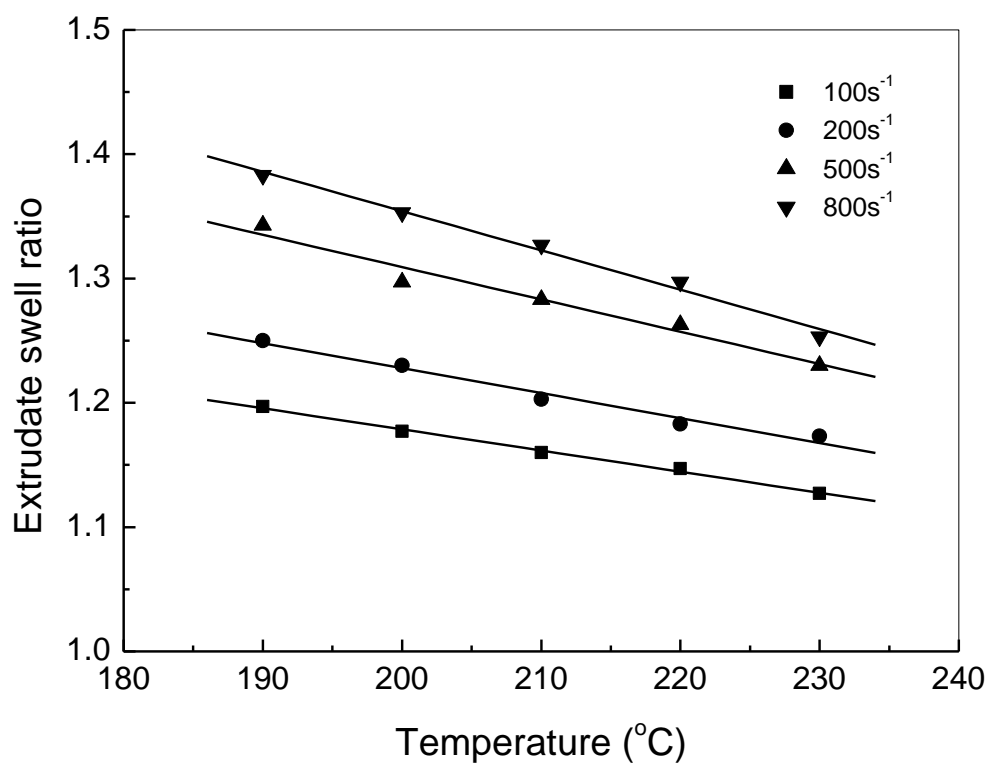


Fig. 6

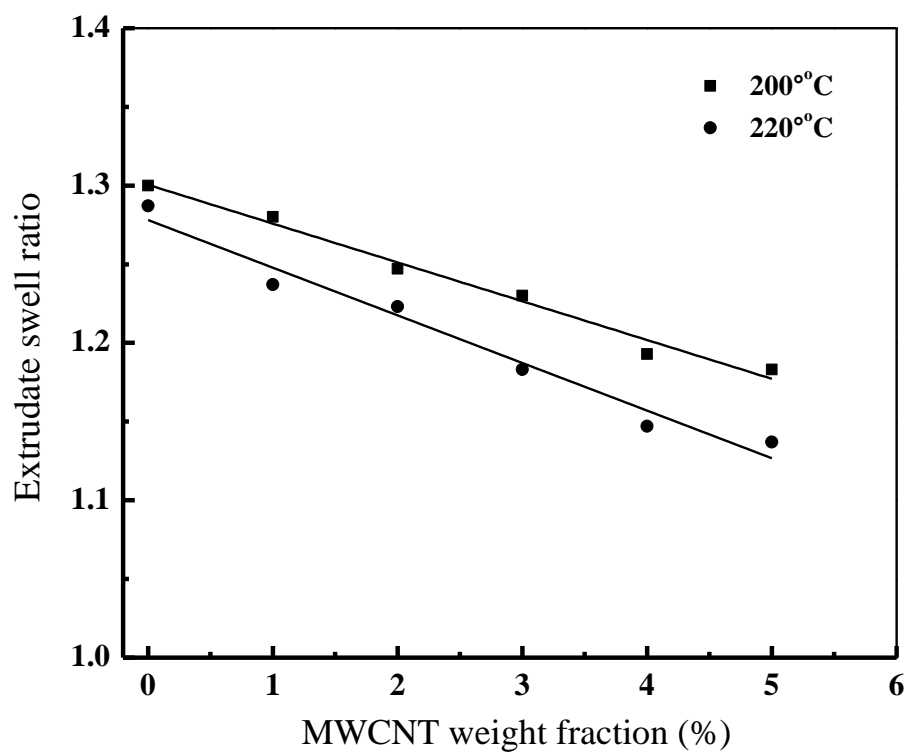


Fig. 7

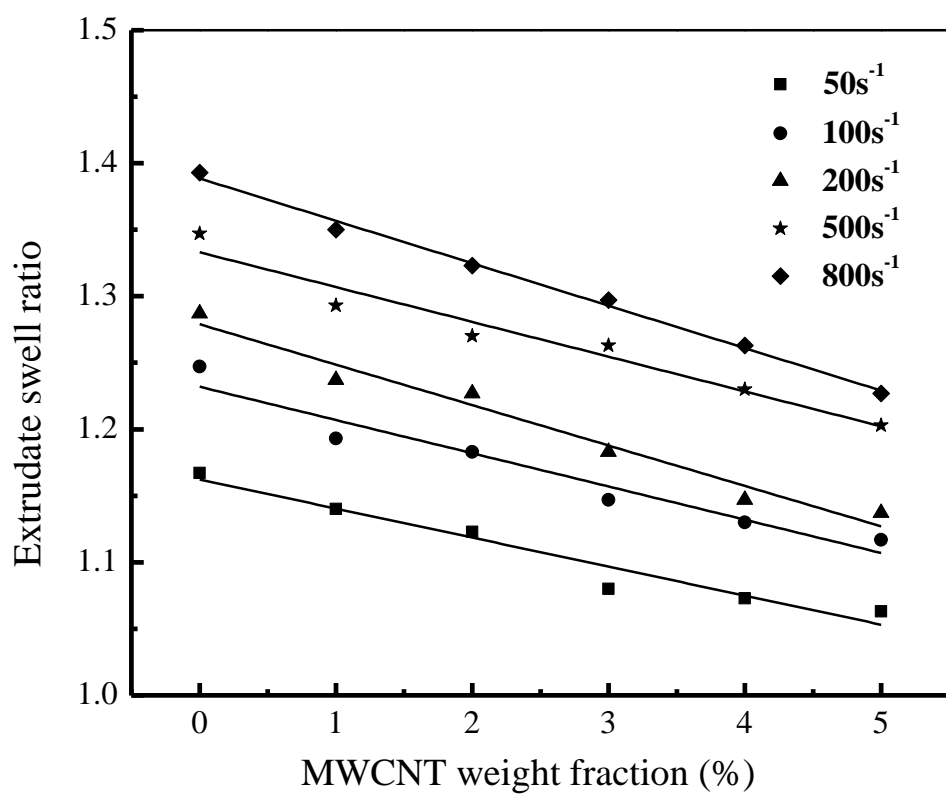


Fig. 8

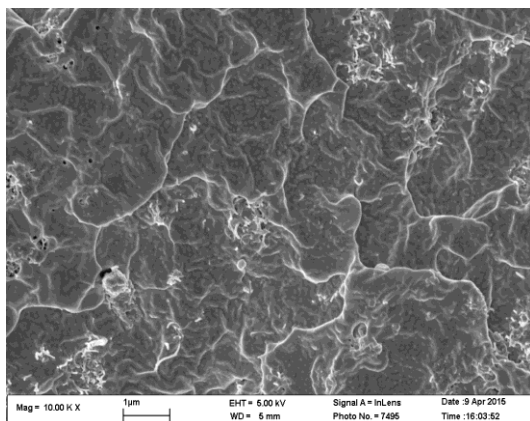
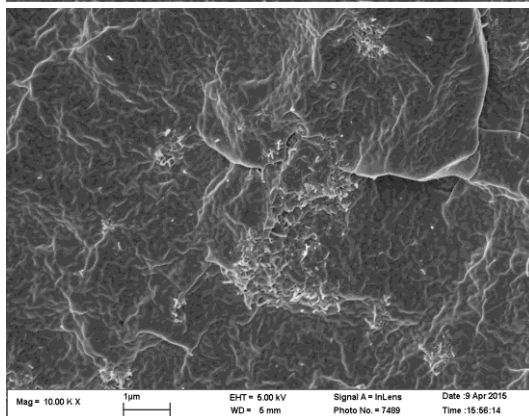
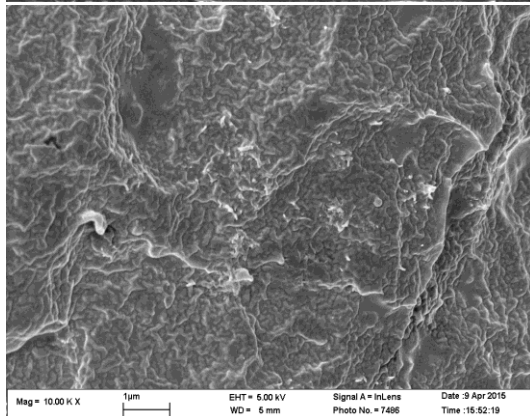
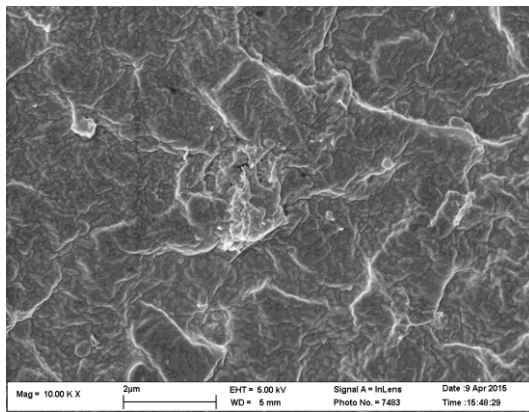
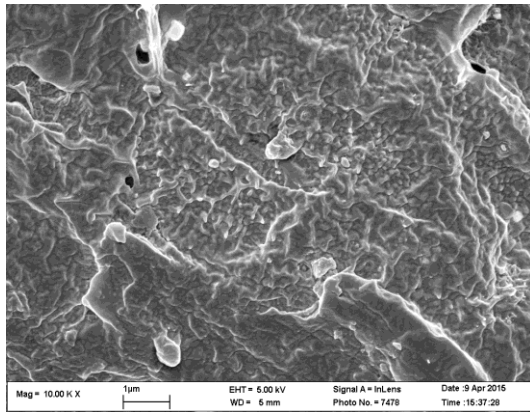


Fig. 9