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Effects of temperature on nanocomposite extrudate swell

Kejian Wang*, He Jianyun

College of Mechanical and Electrical Engineering, Beijing University of Chemical and Technology,
Beijing 100029, (CHINA)

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ABSTRACT

Such processing variables as temperature and superposition of electromagnetic field can vary the molecular dynamics as reflected by the change in relaxation time. These material intrinsic properties were correlated with the extrudate swell ratio by one quantitative model, which was used to predict the variation in die swell due to temperature for phenolphthalein poly (ether ether ketone), organobentonite-filled polypropylene nanocomposite and the variation in die swell due to superposed magnetic field for polystyrene melt. The good agreement of calculated values with experimental data illustrated this idea fitful for polymer melts and their composites. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Extrudate swell;
Quantitative model;
Polymer;
Nanocomposite;
Temperature.

INTRODUCTION

When molten polymer flows through a die, molecular chains become oriented, uncoiled and disentangled due to the applied shear and tension. As melt leaves the die, molecular chains tend to recover in the flow direction and grow in the normal direction, leading to die swell. Die swell, also called extrudate swell or the Barus effect, is an important phenomenon determining the shape/size and quality of the extrudate products. Importantly, the extrudate swell can be used to assess the elasticity of the polymer upon melt extrusion. It is a topic in non-Newtonian fluid mechanics and polymer rheology^[1-10]. To make quantitatively reliable prediction of the extrudate swell behavior based on bulk flow properties has been a formidable challenge.

Up to now, elastic recovery or effect of residence time on the applied stresses is usually regarded to be

the mechanism and affect the degree of swelling of the extrudate. The common technique used to study rheological properties of polymer melts is capillary rheometry. Elastic recovery is affected by many factors, such as the flow properties of polymer^[11,12], applied shear rate/stress, temperature, L/D ratio, and the presence of fillers^[13-16].

In quantifying the extrudate swell, work has been conducted either on the extrusion in long capillary^[17] or in short capillary^[18]. The discrepancy lies in whether the entry effect from reservoir to capillary tube can be neglected. It is believed that the strong sheared chains can fully relax in long capillary while the forced state remains to affect the subsequent extrusion out of exit in short capillary. In the former case, the most pertinent theory of extrudate swell of the polymeric melts would be that of Tanner and that of Song^[20-22]. Tanner^[17] established his theory from the K-BKZ consti-

tutive equation and the free recovery from Poiseuille flow assuming the capillary is indefinite. Recently, Song^[22] developed one swell model from the O-W-F constitutive equation and the multiple transient-network model as well as the double relaxation dynamics of reentanglement-disentanglement transition (RE-DT) and recoil-uncoil transition (RC-UCT) in the Poiseuille flow with the different length-diameter ratio. The swell was thought to evolve in three stages (instantaneous swelling, delayed swelling and ultimate extrudate swelling). A new set of swell equations as the functions of molecular parameters, operational parameters and grow time under the steady and dynamic state were developed. The Song's model successfully described the die swell through long capillary of linear polyethylene (HDPE) and linear polybutadiene (PBD) with the different molecular weights at different processing variables^[22]. However, the model was established on the assumption that the chain elongation incurred at entry is fully relaxed. This is only true for extrusion in adequately long capillary. For short capillary, the entry effect exhibits prominently. Liang^[23] obtained some empirical correlations of swell ratio with material characteristics and operational parameters. The present authors developed one unified swell ratio equation by generalizing the previous achievements to apply to polymer extrusion in both long and short capillary^[24]. It was also noticed that the quantitative theory can be used for particle filled composites when the adopted viscosity is common for both polymer melt and polymeric composites. More importantly, the composite die swell ratio can be written as the polymeric matrix swell ratio multiplied by one concentration shift factor^[24], which is in turn the function of the filler shape, size, dispersion, concentration, surface state and stress or shear rate of flow field^[24]. The double correlations were successful in describing the extrudate swell behavior of several kinds of composites.

As fore-mentioned, the processing parameters in flow field are very important. The present study is aimed to explore the effects of temperature and superposition of magnetic field on the die swell of pure polymer and composite. The following work first briefly provide the relative equations in section II. Section III tests the theory using the published data of extrudate swell.

THEORETICAL MODEL

(1) The effect of temperature on constitutive parameters

In the steady shear flow, the shear viscosity can be described by eq. (1).

$$\eta(\dot{\gamma}) = \eta_0 / [1 + (\tau_0 \dot{\gamma})^a]^n \quad (1)$$

The coefficient of the first normal-stress difference ψ_1 in the steady shear flow is

$$\psi_1(\dot{\gamma}) = 2n\eta_0^{1+1/n} / (G_N^0)^{1/n} \left[1 + (\eta_0 \dot{\gamma} / G_N^0)^a \right]^{n+1} \quad (2)$$

From experimental data of η and $\psi_1(\dot{\gamma})$, the molecular parameters of η_0 , G_N^0 , n and a can be determined^[22]. However, flow conditions may affect their values. For instance, the dependence of shear viscosity on temperature T obeys the Arrhenius-Frenkel Eyring expression:

$$\eta(\dot{\gamma}, T) = \eta(\dot{\gamma}) \exp\left(\frac{\Delta E}{RT}\right) \quad (3)$$

Thus, η_0 and τ_0 varies with T in the similar way.

Muksinga et al.^[25] also found that the activation energy (ΔE) decreased gradually with increasing shear rate and increased with filler concentration above a certain level for the composites. Extrudate swell increases non-linearly with increasing shear rate. It increases linearly with increasing shear stress and/or decreasing temperature. The last phenomena will be further analyzed in the following.

(2) Extrudate swell theory

Details of the evolutions of the extrudate swell theory please refer to^[24]. Here presented the expressions useful in this paper.

$$B = \left(\frac{k_{IM}}{4} * (n * \tau_0^{(1/n)} \dot{\gamma} / (1 + (L/D)^a))^{(1-n)} + 5.098/4\right)^{f_w} \quad (7)$$

B depends on molecular parameters and the operational variables [L/D and $\dot{\gamma}$ or τ]. $(1 - \bar{w})$ is the fraction of the recoverable conformation on the entangled polymeric chain (or at entangled state) in the flow. f_w is one component showing the deviation of the prediction from Song's original model^[22]. k_{IM} is one composite coefficient effects of the entry from reservoir, capillary length and the medium out of the capillary.

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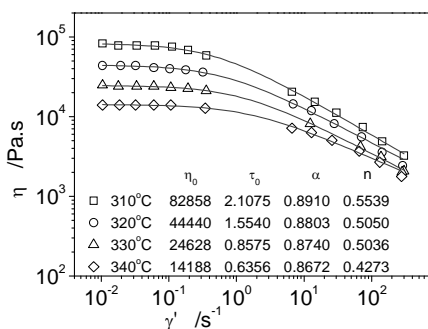


Figure 1 : Viscosity versus shear rate for PEK-C at (a)T=310C, (b)T=320°C, (c)T 330°C,(d)T=340°C

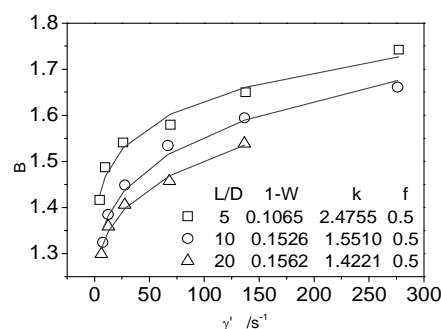


Figure 2 : Die swell ratio vs. shear rate for PEK-C calculated and measured for different L/D at T= 320°C

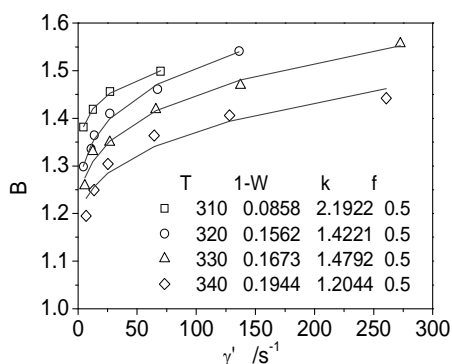


Figure 3 : Die swell ratio vs. shear rate for PEK-C at different temperatures at L/D = 20

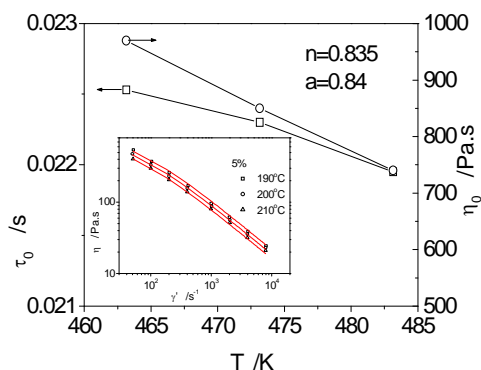


Figure 4 : The constitutive values for the 5wt% nanocomposites at different temperatures

VERIFICATION OF DIE SWELL THEORY USING THE EXPERIMENTAL DATA

Experimental

The first set of die swell experimental data was from Ref.^[26]. The polymer, phenolphthalein poly(ether ether ketone), briefly called PEK-C, was one amorphous engineering thermoplastics with $T_g=220^\circ\text{C}$. The PEK-C was from Xuzhou Engineering Plastics Co. in the form of powder with the reduced viscosity of 0.49dl/g in chloroform at 25°C . Melt rheology has been investigated at low shear rates by a rotational rheometer, Rheometrics RDSII, equipped with a cone-and-plate geometry ($D=25\text{mm}$ and cone angle 0.1rad). At the higher shear rates, a capillary rheometer, Ceast Rheoscope 1000 was used with flat dies of $D=1\text{mm}$ and length-to-diameter ratios from 5 to 20. In both experimental temperatures of 310, 320, 330 and 340°C were used. Die swell was investigated using the capillary rheometer, quenching the extrudates in air after they were extruded from the capillary and then measuring their diameters at a constant distance of 2cm from the

exit of the capillary at room temperature using a micrometer. The ratio of the extrudate diameter to the capillary diameter is defined as the die swell ratio.

The second set of experimental data is for organobentonite-filled polypropylene nanocomposite from Ref.^[25]. The used resin was polypropylene (Moplen HP550R, HMC Polymers Co. Ltd., Thailand) with MFI 22g/min. Polypropylene-grafted maleic anhydride (PP-g-MA, 1wt% MA grafted level) was used as the compatibilizer at the weight percent of 15%. Na-Bentonite (Mac-Gel, Grade SAC) was modified with hexadecyltrimethylammonium [$\text{C}_{16}\text{H}_{33}\text{N}+(\text{CH}_3)_3$] bromide salt as before being mixed into resin at different contents. Melt rheology and extrudate swell for the nanocomposites were carried out by using a CEAST Rheologic 500 twin bore capillary rheometer. The length-to-inner diameter (L/D) of the circular die was 20/1. Studies were done at three test temperatures of 190, 200, and 210°C and the apparent shear rate was varied from 50 to 8000s^{-1} .

The third experiment was on polystyrene melt from an electro-magnetized capillary die in an extrusion rheometer^[27]. The magnetic flux density was varied as 1.51,

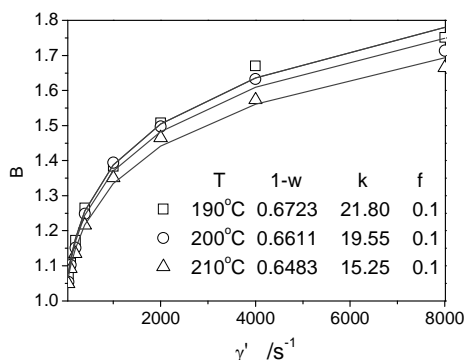


Figure 5 : Die swell ratio vs. shear rate for 5wt% nanocomposite at different temperatures

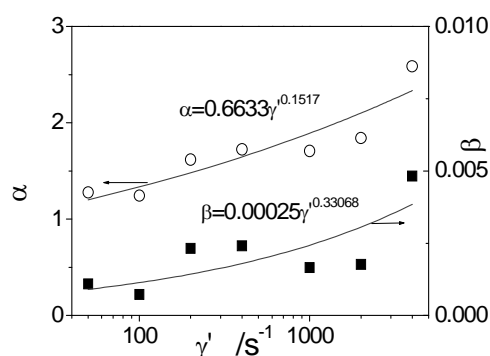


Figure 6 : The effects of shear rate on temperature coefficients for 5wt% nanocomposite

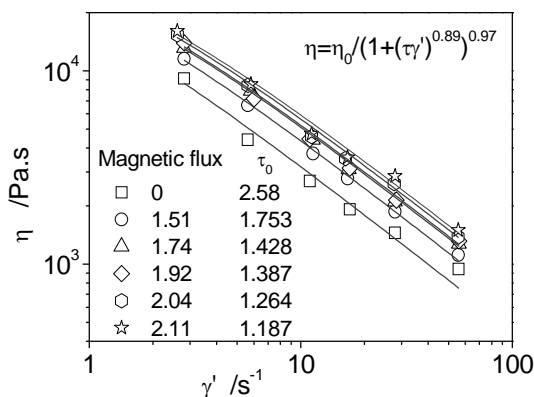


Figure 7 : Shear viscosity of PS in capillary with different magnetic flux density

1.74, 1.92, 2.04 and 2.11T. All tests used PS (Styron 656D 267) in granular form supplied by Siam Polystyrene Co., Ltd (Bangkok, Thailand). Its melt flow index was 7(BS2782 Method 720A, 1979). The employed constant shear rate capillary die was made of mild steel (Grade 1020), 60mm long and 6mm in diameter. The extrudate diameter was dependent on its size when fully swollen, this being about 1–2 inch away from the die exit.

COMPARISON OF THE PREDICTED VALUES WITH THE EXPERIMENTAL DATA

Verification for phenolphthalein poly (Ether Ether Ketone)

Some thermoplastics as PEK-C are sensitive to temperature. The flow behavior was quantified to determine appropriate processing conditions^[26]. The constitutive parameters were obtained and listed by fitting the viscosity at four temperatures as shown in figure 1. Increment of temperature greatly reduced the viscosity at the same shear rate.

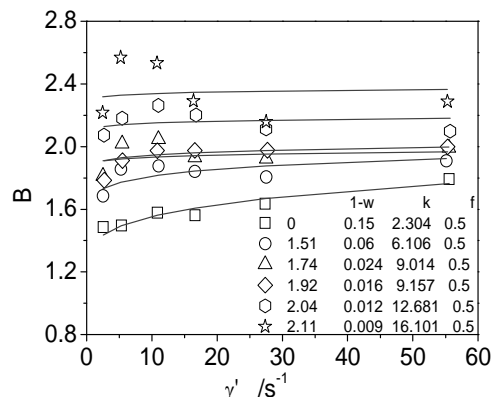


Figure 8 : Die swell ratio vs. shear rate for PS at different magnetic flux density around capillary die

Eq. (7) presented the predict extrudate swell for PEK-C at T= 320°C to be compared with the experimental data in figure 2. It shows that the swell reduced when polymer melt was extruded from longer capillary, in which more of polymer chains were well relaxed. This was illustrated by smaller swell ratio together with smaller k and larger 1-w. Smaller k implied more of the entry effect was removed while larger 1-w represented more of elastic recovery in capillary.

For the extrusion out of capillary with the same length as L/D=20, the swell ratio reduced with increasing temperature as illustrated in figure 3. It was found that k became smaller while 1-w was larger. In the shear field with higher temperature, the uncoiled or disentangled chains in entry region from reservoir were easy to recoil or re-entangled in the capillary.

Verification of the swell equations for PP/organo-bentonite composite

The viscosity for the nanocomposite, polypropylene/5% [C₁₆H₃₃N+(CH₃)₃] bromide modified Na-bentonite compatibilized by 15% polypropylene-grafted

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maleic anhydride, was well fitted by eq. (1) at 190, 200 and 210°C. The fitted parameter values were plotted in figure 4. n and a remained almost constant as illustrated by the parallel viscosity curves while τ_0 and η_0 reduced when heated melt.

In extrusion from the capillary with the length-to-inner diameter $L/D=20/1$, eq. (7) predicted the extrudate swell ratio close to the experimental values. Different from the previous predictions, f is only 0.1 far from the equilibrium value 0.5 while k is by far larger than 1 in figure 5 probably because the test shear rate was higher, at which the relaxation could not fully occurred in capillary. Regardless of this, heating the melt led to the reduction in extrudate swell ratio with smaller $1-w$ (>0.5) and k at the almost constant f . This is different from the observations in figure 3, in which $1-w$ rises (<0.5) when increasing temperature, which originated from the decrement in extrudate swell ratio by filling the bentonite in well compatibilized polypropylene^[25].

The direct correlation of the extrudate swell with temperature was well described by eq. (8). The coefficients α , β , approximately increases with shear rate exponentially as illustrated in figure 6, which was first observed to our knowledge.

$$B = \alpha - \beta T \quad (8)$$

Verification for the polystyrene swell out of magnetic die

Here is to test whether eq. (7) is fitful for the extrudate swell through capillary under magnetic field. Ref.^[27] reported that magnetic field to the die could result in a significant increase in the swelling ratio of the PS extrudate of up to 25%. In experiment, the additional heat due to the induction effect by electro-magnetic field was offset by air cooling. Thus, the increment in swell ratio should be due to magnetic function. The used capillary was short with $L/D=10$.

For emphasis of magnetic effect, the viscosity versus shear rate was drawn again in figure 7. The fitted constitutive values by eq. (1) were also listed. It is noted that n and a remain almost constant as illustrated by the parallel viscosity curves while η_0 are increased instead of decreased τ_0 when the strength of employed magnetic field was enhanced. It seems that the stronger magnetic field was more beneficial for chain relaxation to be quickened.

Eq. (7) crudely predicted the swell ratio illustrating the swell was enhanced by magnetic field. $1-w$ rapid reduces towards zero while k rapid rises far from 1 when keeps f constant. $1-w$ is closer to zero showing the effect of shearing became weaker when enhancing magnetic function, which enlarged the entry effect as representative by larger k . However, our model could not predict the maximum swell ratio at the relatively low shear rate.

CONCLUSIONS

Temperature is one significant operational variable affecting the zero shear viscosity and chain relaxation dynamics, which in turn influences the extrudate swell. One model was used to predict such indirect effects. The variation in die swell due to temperate was quantitatively analyzed for one engineering plastics of Phenolphthalein poly (ether ether ketone), one nanocomposite of organobentonite-filled polypropylene. Similarly, the electro-magnetic field also induced the variations of such material intrinsic properties as relaxation time and subsequently the extrudate swell behavior. One swell instance of polystyrene melt was partially analyzed while the maximum peak in swell ratio can not be forecast.

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