Interfacial stick–slip transition in hydroxyapatite filled high density polyethylene composite

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Abstract. **Effect of filler addition and temperature on the stick–slip transition in high density polyethylene melt was studied. Results showed that shear stresses corresponding to stick–slip transition increases with the addition of filler. Increase in temperature also increases the shear stresses for stick–slip transition. The features of the flow curves of composites and that of unfilled system remain identical. Filler addition lowers the shear rate at which the transition occurs. The composite extrudate did not show characteristic extrudate distortions associated with the unfilled polymer.**

Keywords. **Stick–slip transition; composite; hydroxyapatite; high density polyethylene; melt fracture.**

1. Introduction

Linear polyethylenes, e.g. high density polyethylene (HDPE) and linear low density polyethylene (LLDPE), are known to exhibit peculiar flow behaviour during extrusion (Bagley *et al* 1958; Lupton and Regester 1965; Blyler and Hart 1970; Ramamurthy 1986; Wang 1999; Münstedt *et al* 2000; Denn 2001; Robert *et al* 2003). The nature of flow curve and instabilities are illustrated with the help of figure 1. While extruding through a capillary die, at sufficiently low shear stresses (or low extrusion rates), the polymer melt is smooth as it exits the die. As the shear stress increases, a series of flow instabilities begin to occur and manifested as extrudate distortions. The first instability that may occur is known as sharkskin or sharkskin melt fracture. The sharkskin formation is characterized by surface roughness and a slope change in a double logarithmic plot of the nominal wall shear rate vs shear stress (Ramamurthy 1986; Wang *et al* 1996). At higher shear stresses, one observes an oscillating stick–slip transition (spurt oscillations or spurt), followed at still higher shear stresses by gross melt fracture in which the polymer is extruded in an extremely irregular fashion.

The flow curve of linear polyethylenes is characterized by two branches of steady flow and a region of discontinuity (figure 1). Characteristics of the discontinuity region are pressure oscillations and a large discontinuous increase in apparent shear rate. During oscillations the flow jumps

from one stable branch to the other making a "flow curve hysteresis cycle" (parallelogram ABCD in figure 1) (Bagley *et al* 1958; Hatzikiriakos and Dealy 1992; Kay *et al* 2003). The amplitude of the pressure oscillations varies typically in the range 1–10 Pa (den Doelder *et al* 1998) and the period of oscillation increases with increase in molecular weight (Hatzikiriakos and Dealy 1992). They describe the phenomenon in detail as given below.

As the wall shear stress increases and reaches an upper critical value, t_{c1}, (point A on branch I), the flow rate suddenly jumps to point B on branch II. What happens if the stress is further increased depends on the mode of operation of the rheometer. In pressure controlled rheometers further increase in pressure causes flow rate to increase along branch II. On decreasing the pressure the flow rate decreases continuously until it reaches a lower critical shear stress, t_{c2} (point C in figure 1), at which the flow rate suddenly decreases, jumps from C to D, and the system comes back to branch I of the flow curve making a flow curve hysteresis (Bagley *et al* 1958; Hatzikiriakos and Dealy 1992). On the other hand, if it is a piston speed controlled rheometer, for the range of piston speeds corresponding to the shear stresses between t_{c1} and t_{c2}, the pressure and the extrudate flow rate oscillate between limiting values. The frequency of the oscillations increases as the volume of melt in the reservoir decreases. As the piston speed is increased, oscillations continue until the apparent shear rate exceeds the value corresponding to t_{c2} (point C) at which point the oscillations cease, and the curve progresses along branch II of the flow curve. If

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Apparent shear rate
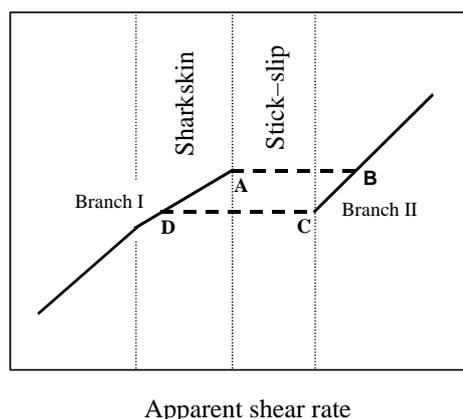
Figure 1. Typical flow curve of linear polyethylene showing the regions for flow instabilities.

the piston speed is now reduced again, the shear stress will continue to decrease in a regular way along branch II of the flow curve until it reaches t_{c2}, when oscillations will again be observed. This behaviour continues with further reductions in piston speed until the apparent shear rate reaches the value corresponding to t_{c1} (point A) on branch I of the flow curve, when oscillations cease and the data follow branch I with further decreases in piston speed. It has been reported that with the decrease in molecular weight of the polymer the stress difference i.e., $t_{c1}-t_{c2}$, also decreases (Hatzikiriakos and Dealy 1992). When $\bar{M}_{w}$ of the HDPE was decreased to 104,700, t_{c1} became approximately equal to t_{c2}. It may be concluded that when $\bar{M}_{w}$ is below this number the flow hysteresis curve would become a plateau. Apart from this oscillatory region, many researchers have reported the presence of a second oscillating area for linear polyethylenes (Li *et al* 1986; Hatzikiriakos and Dealy 1992; Piau *et al* 1995; Robert *et al* 2000).

The extrudate obtained during one cycle in the oscillatory extrusion consists of two segments of distinctly different appearance. According to Wang and Drda (1996a) the extrudate had a bamboo like appearance. Hatzikiriakos and Dealy (1992) noted that when the system is following branch I of the flow curve, i.e. when the pressure is rising, the extrudate generally exhibits sharkskin. However, the extrudate that appears after the jump to branch II may be much rougher, leading to a description of the extrudate in the rising-pressure portion of the cycle as relatively smooth. On the other hand, if in branch II part of the cycle the extrudate was smooth, branch I part of the material may be described as relatively rough, because of the presence of sharkskin.

Though considerable work has been done to study the flow instabilities in unfilled polyethylenes, hardly any work was reported on the effect of fillers on stick–slip fracture. Hydroxyapatite (HA) ceramic filled high density polyethylene (HDPE) composites have been used in a number of clinical applications (Downes *et al* 1991; Tanner *et al* 1994; Dornhoffer 1998). HA is a bioactive ceramic material that when incorporated into a polymer matrix (e.g. HDPE)

results in composites that bond with bone tissues upon implantation. This paper reports the stick–slip fracture phenomenon observed in HA–HDPE composite system. The paper addresses the effect of filler content and temperature on the stick–slip behaviour of HA filled HDPE composite.

2. Experimental

Injection moulding grade high density polyethylene, HD6070EA, was obtained from BP Chemicals Ltd., UK. The weight average molecular weight ($\bar{M}_{w}$) and number average molecular weights, $\bar{M}_{n}$, were determined using a high temperature gel permeation chromatograph (Waters 150 CV). Synthetic hydroxyapatite, obtained from Plasma Biotal Ltd., UK, was characterized for particle size, size distribution (Malvern Mastersizer-E, Malvern Instruments, Malvern, UK) and specific surface area (Gemini 2370 V5.00 model, Micromeretics, UK).

HDPE was obtained as pellets and ground cryogenically, using liquid nitrogen as coolant, in an ultra centrifugal mill (Retsch, Germany). This powder was blended with pre-dried HA powder and then compounded in a co-rotating twin-screw extruder (Betol BTS-40L). The extrudate was cooled and pelletized using a Betol pelletizer, and later dried in an air oven at 60°C. Composites containing 20 and 40 vol% HA fillers were prepared.

The shear rheology of the composites was studied using a twin bore (RH7) precision advanced capillary extrusion rheometer (Rosand Precision Ltd., UK) using version 6·10 software. One bore of the rheometer was fitted with a capillary die of length to diameter (L/D) ratio, 16 and the other bore was fitted with a short die. The bore diameter of both capillary dies was 1 mm; with die entry angle of 180° while the lengths were 16 mm and 0·25 mm for the long and short dies, respectively. The Bagley (1957) correction was applied by the following method: The pressure recorded at the long die was designated as P_{L} and that at the short die as P_{S}. The pressure drop at $L/D = 0$ (i.e., P_{0}) was determined by plotting P_{L} and P_{S} against corresponding L/D ratios. The Bagley corrected wall shear stress (t_{w}) and the apparent shear rate (g_{a}) were obtained from the following equations (Cogswell 1981):

$$t_{w} = \frac{(P_{L} - P_{o})R}{2L},$$

$$g_{a} = \frac{4Q}{pR^{3}},$$

where R is the capillary radius and Q the volume flow rate. The control software was programmed with pre-compression and melt pause times in addition to the desired shear rate sequence and defined pressure equilibrium conditions. The material was subjected to a total preheating time of 9 min when it had been through different stages of melt

compression before commencement of the test. The control software collected data from the transducers, and variations of pressure with rate of piston movement in both dies at the set temperatures were converted into shear stress and shear rate data. The shear behaviour of the composites and unfilled HDPE were studied at the melt temperatures, 200, 230 and 250°C.

3. Results and discussion

The properties of HDPE used in this study are given in table 1 and that of HA in table 2.

The effect of adding filler on the nature of the flow curve at 200°C is given in figure 2. The flow behaviour observed in all the systems appear similar in that the flow

curve consists of three regions: a pseudoplastic region at low to moderate shear rates (corresponding to branch I in figure 1), a plateau corresponding to oscillating stick–slip transition and a second pseudoplastic region (corresponding to branch II in figure 1) at high shear rates. Here the particular shear stress at which the stick–slip plateau appears is termed critical shear stress (t_c). It is found that t_c has substantial dependence on filler content as an increase in HA content increases the value of t_c. Increased resistance to flow by increased amounts of filler pushes the formation of stick–slip plateaux to lower shear rates. For example, for unfilled HDPE, the stick–slip plateau occurred in an apparent shear rate range of 7000–10,000 s^{-1}. When the HDPE is filled with HA (20% by volume of composite), the stick–slip plateau occurred in the range 2500–4000 s^{-1}. For 40 vol% composites, it occurred in the range 250–2500 s^{-1}.

Table 1. Properties of HDPE used.

Commercial name	Rigidex HD6070EA
Melt flow rate* 2·16 kg load (g/600s)	7·6
Annealed density (kg m^{-3})*	960
$\bar{M}_w$	72,350
$\bar{M}_n$	12,650
Polydispersity	5·7
Mark Houwink Alpha	0·77
Mark Houwink log K	− 3·72

*Data taken from manufacturer's product data sheet.

Table 2. Properties of hydroxyapatite used.

Commercial name	Density (kg m^{-3})	Specific surface area (m^2 g^{-1})	Mean particle size ($d_{0.5}$) (μm)
P205	3160	13·2992	4·02

Figure 3. Flow curve of HA–HDPE composite at 230°C. The numerals 0, 20 and 40 in the inset indicate the volume fraction of HA (%) in the HDPE matrix.
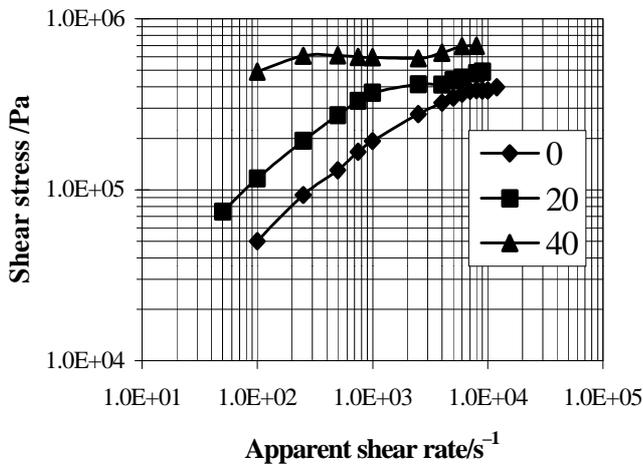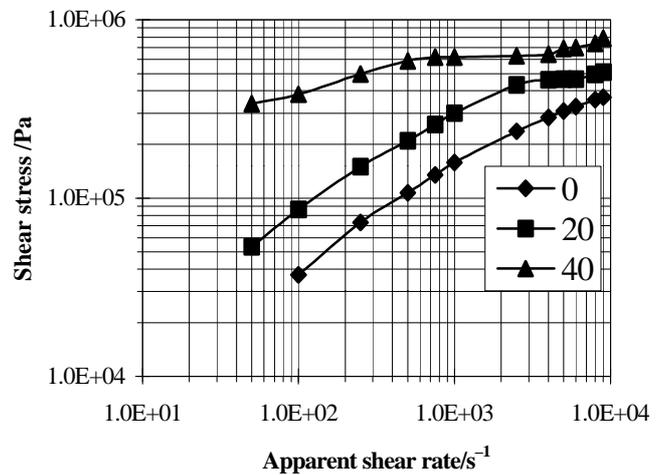

Figure 2. Flow curve of HA–HDPE composite at 200°C. The numerals 0, 20 and 40 in the inset indicate the volume fraction of HA (%) in the HDPE matrix.
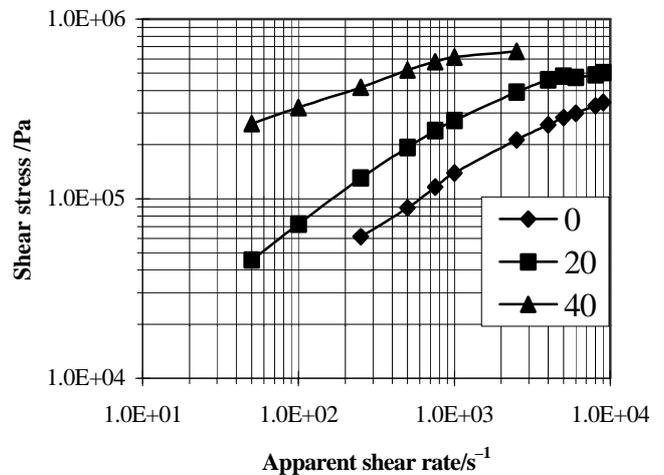

Figure 4. Flow curve of HA–HDPE composite at 250°C. The numerals 0, 20 and 40 in the inset indicate the volume fraction of HA (%) in the HDPE matrix.

Flow curves obtained when the melt temperatures were 230 and 250°C are given in figures 3 and 4. Branch II portion of 40 vol% composite at 250°C could not be determined as the pressure oscillations were too high above 2500 s^{-1} and the machine did not stabilize. Rheological data obtained at higher temperatures (figures 3 and 4) showed that the temperature has a clear influence on t_c. Increasing the temperature increased t_c and shifted the onset of t_c to higher shear rates. For example, when the melt temperature was increased to 230°C the inflection point for the onset of stick–slip plateau for 40 vol% HA–HDPE composite shifted from 250 to 750 s^{-1}. The increase in t_c with temperature is consistent with the observation made by Hatzikiriakos and Dealy (1992) for unfilled HDPEs.

Table 3 lists the t_c values obtained for the composite and unfilled polymer. The results clearly demonstrate that the shear stress corresponding to the stick–slip transition (t_c) increases with temperature and filler content in the matrix. t_c of the unfilled polymer could not be determined at 230 and 250°C because of the shear rate limitation of the machine. And the shear stress build up by the matrix resin was low. However, in the case of composites, t_c occurred at sufficiently lower shear rates and could be measured easily. It can be seen that when the volume fraction filler in the matrix was low the increase in t_c is lower (~ 8%) probably due to the resistance offered by the filler being low at lower concentrations. However, when the filler content increased from 20 to 40 vol%, increase in the value of t_c is substantial (37–46% depending on the temperature) at all temperatures. This is probably due to the increased resistance to flow offered by the filler particle agglomerates.

The existence of plateau in the composite demonstrated that nature of flow curve in the composite is largely controlled by the matrix and whatever features shown by the matrix are also shown in the composite.

Wang and Drda (1996a) had reported that extrudate in the stick–slip transition region appeared 'bamboo' like. However, the composite extrudates did not display the characteristic 'bamboo' like appearance discussed in the literature. The extrudate of 20 vol.% composite appeared to be slightly wavy. This waviness could, perhaps be due to the presence of HA in the composite, which interferes with the elastic strain recovery of HDPE at the stick–slip region.

The composite filled with 40 vol.% of HA did not display any visible melt fracture and had a glossy appearance at all shear rates tested. In this case also higher filler content would have interfered with the elastic strain recovery of HDPE molecular chains and arrested molecular parameters causing the surface roughness from the bulk. However, migration of filler particles away from the die wall leading to the formation of a thin HDPE rich layer on the wall causes glossiness. Yilmazer (1998) reported that for moderately filled polymer melts, the migration effect increased with increasing shear stress. This explains why 40 vol.% HA–HDPE composite appears glossier than 20 vol.% HA–HDPE system in the stick–slip region.

A number of reasons have been put forward to explain stick–slip transition in the literature. Blyler and Hart (1970) suggested that melt elasticity is responsible for capillary flow instability and that extrudate distortion is due primarily to uneven elastic strain recovery. Some researchers believed that the fundamental reason for the onset of flow instabilities was slip of the polymeric liquid at the die wall (Lupton and Regester 1965; Ramamurthy 1986). Wang and Drda (1996a, b) proposed that stick–slip transition was largely interfacial and was due to complete disentanglement of the adsorbed chains from free chains at the melt/wall interface at and beyond the plateau region. The increase in t_c with filler content can also be explained based on this argument. Higher filler content effectively increases the viscosity of this interface layer and hence a higher stress is needed to produce the onset of this phenomenon.

4. Conclusions

Following conclusions can be drawn from this study:

(I) The flow curves of the composite and the unfilled high density polyethylene melts exhibited similar features, viz. an initial pseudoplastic region, a plateau corresponding to stick–slip transition, and a second pseudoplastic region.
(II) Shear stress plateau corresponding to stick–slip transition increased with increase in filler content and temperature.
(III) Increasing the filler content lowered the shear rate at which the plateau appears.

Acknowledgements

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Table 3. Effect of temperature and filler content on t_c.

Polymer/composite	t_c/MPa at temperatures		
	200°C	230°C	250°C
Unfilled HDPE	0·38	NA	NA
20 vol.% HA composite	0·41	0·46	0·48
40 vol.% HA composite	0·60	0·63	0·66

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