A Study on the Onset Surface Melt Fracture of Polypropylene Materials with Foaming Additives

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ABSTRACT: The melt fracture behaviors of linear and branched polypropylene resins with foaming additives were investigated. The effects of branching, processing temperature, additives, and blowing agent on the surface melt fracture of polypropylene materials were thoroughly studied. A CCD camera was installed at the die exit to precisely observe the onset of surface melt fracture of extruded foams. The critical wall shear stress was determined for various linear and branched polypropylene resins using a capillary die. It was found that the branching required to foam polypropylene resins also promotes melt fracture: the critical shear stress was decreased by 0.0175 MPa with an increase of 0.1 n/1000c in long-chain branching. It was also observed that the dissolved blowing agent (butane) significantly suppressed the melt fracture of both linear and branched polypropylene resins. On the other hand, a noticeable increase in the critical shear stress of branched polypropylene materials was observed with the nucleating agent (talc) and the aging modifier (glycerol mono stearate), whereas almost negligible effect of the additives on the critical shear stress was observed for linear polypropylene materials. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3571–3577, 2008

Key words: poly(propylene) (PP); foam extrusion; visco-elastic properties; rheology

INTRODUCTION

Extrudate distortion or melt fracture is considered to be one of the major factors for determining foam quality. It is defined as nonuniformity and irregularities of the extrudate shape along its length. At early stages, extrudate distortion starts as surface roughness or sharkskin, and then it turns to gross melt fracture, which results in a completely distorted extrudate. Extrudate distortion occurs when the wall shear stress at the die land exceeds a critical value.[1,2] There are many factors affecting the extrudate distortion in polymer processing,[3] including flow rate, die geometry, molecular weight, molecular distribution and the chemical nature of polymer.

Polypropylene or propylene materials have been regarded as good candidates for foam materials because of their outstanding mechanical characteristics, thermal stability, and chemical resistance.[4] However, polypropylene materials have not been used much in foam processing compared to other plastics because of their weak melt strength. In this context, long-chain branched polypropylene materials with high melt strength have been developed as a foam-able grade.[5–8] But the effect of branching on the melt fracture of polypropylene materials has not been studied much yet. Although the dissolved blowing agent is expected to influence the critical shear stress, its effect on the melt fracture has not been studied extensively.

BACKGROUND

A number of studies have been attempted to investigate the melt fracture behavior of polypropylene. Sammler et al.[9] investigated the extrudate distortions of polypropylene using two types of isotactic polypropylene resins of identical melt flow rate. They observed ''spurt'' melt fracture behaviors in the case of high melt strength polypropylene. They claimed that the long-chain branching is the most probable molecular origin of ''spurt'' melt fracture of these polypropylene resins. Baik and Tzoganakis[10] studied the melt fracture characteristics of controlled-rheology polypropylene, using a capillary rheometer. They investigated the effects of shear rate and die geometry on the melt fracture behavior. They observed that there was no surface melt fracture and the extrudate distortions decreased when the shear rate was increased for a given material and processing conditions. Also, they found that the severity of melt fracture reduced with increasing the L/D ratio. Kazatchkov et al.[11] investigated the melt fracture behavior of molten polypropylene, using a capillary

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rheometer. They observed a sudden transition from a smooth extrudate to a highly distorted one in the case of polypropylene unlike in the case of polyethylene. They claimed that the onset of gross melt fracture was detected to occur at critical shear stresses in the range of 0.14–0.15 MPa. Also, they noted that both the critical apparent shear rate and critical shear stress decreased with increasing the L/D ratio. In addition, Tao and Huang[12] studied the melt fracture behavior of polypropylene resins in capillary flow. Previous studies have considered other systems such as polyethylenes,[13–20] whereas others[21–24] investigated the effect of additives on the sharkskin and gross melt fracture. But very few considered polypropylene, and to our knowledge none studied foaming systems.

An experimental investigation is conducted in this paper to measure the critical wall shear stress (the onset of surface melt fracture) of polypropylene materials. The effects of branching, processing temperature, foaming additives, and blowing agent on the critical wall shear stress of polypropylene materials were studied.

DESIGN OF EQUIPMENT

An experimental setup is designed to investigate the surface melt fracture behavior of polypropylene materials melts and polypropylene/butane solutions under various conditions. Figure 1 shows a schematic of the designed experimental setup.

To investigate the effect of dissolved blowing agent on the melt fracture, a foaming extrusion system is utilized and a homogeneous and uniform single-phase solution of polypropylene materials and butane is formed. Formation of a single-phase polypropylene/butane solution requires injection of a soluble amount of butane into the molten polymer with the assistance of a convective diffusion device.[25,26] The amount of butane is metered by a microprocessor-controlled syringe pump, which supplies the gas at a fixed rate into the plasticated polymer stream in the extruder. As the polypropylene/butane mixture is conveyed in the extruder barrel, the shear fields generated by the plasticating screw and irregular mixing blades stretch the gas bubbles under high pressure, ultimately breaking them into smaller stretched bubbles. This process eventually leads to dissolution of the supercritical fluid into the polymer matrix.

To accurately control the temperature of polypropylene materials melts (or polypropylene/butane solutions), a second extruder in a tandem line and a heat exchanger consisting of a cooling channel and a homogenizing static mixer are used. The temperature of the polymer melt flowing out of the plasticat-
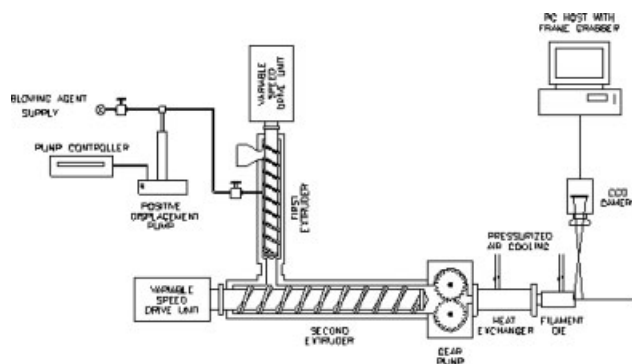

Figure 1 Experimental setup.

ing extruder (i.e., the first extruder) is typically very high. This high melt temperature can be lowered uniformly while maintaining a high pressure within the second extruder. The cooling of melt using the second extruder in a tandem system is known to be effective.[27] A heat exchanger with a static mixer can also be utilized to further lower and/or homogenize the temperature of the polymer.

To disperse the foaming additives uniformly in the polymer matrix, master pellets containing 20 wt % additives are produced with a linear polypropylene material carrier using an intensive twin-screw compounder. The master pellets are then dry-blended with linear or branched polypropylene material and fed into the first extruder through the hopper. The additives well dispersed in the master pellets become distributed uniformly in the polymer melt because of the mixing action of the screw in the extruder.[28]

Because of the difficulties in determining the onset of melt fracture for polymer foam, a CCD camera is installed at the die exit and the foam extrudate is carefully monitored. In the case of foaming extrusion, the skin of extruded foam is stretched as the expansion occurs. As a consequence, the foam skin becomes shiny as along as the expanded foam does not contract due to gas loss.[29] Even if melt fracture occurs and sharkskin developed on the extrudate surface, the foam expansion of extrudate causes the foam skin to be stretched, and thereby, the trace of the sharkskin gets easily removed. Therefore, it is very difficult to detect the onset of melt fracture by simply checking the surface of the fully expanded foam. However, it is believed that the onset of surface melt fracture can be observed by monitoring the early stage of extrudate using a CCD camera before it gets expanded.

A capillary die of length L and radius R is used to calculate the critical shear stress at which melt fracture occurs.[3] A pressure transducer is mounted in the die before the capillary section. To minimize the entrance effect, the L/D ratio was chosen to be 35,

TABLE I
Material Properties of Linear and Branched Polypropylene Materials

Material	MFR (g/10 min)	M_w (kg/mol)	M_n (kg/mol)	LCB degree (n/1000c)
Branched P1	2.3	418	31.7	0.21
Branched P2	4.8	416	48	0.17
Branched P3	3.1	427	46.5	0.13
Linear P1	11	360	70	0
Linear P2	2.8	500	97	0

and the wall shear stress is calculated in terms of the die pressure, P_d, and the die geometry[3]:

$$\tau_w = \frac{P_d R}{2L} \tag{1}$$

The corresponding wall shear rate, $\dot{\gamma}_{app}$, is determined by[3]:

$$\dot{\gamma}_{app} \equiv \frac{4Q}{\pi R^3} \tag{2}$$

The polymer flow rate is controlled by the rotational speed of the gear pump regardless of the temperature and pressure fluctuations in the barrels.

EXPERIMENTATION

Experimental setup

Based on the design described in the previous section, an experimental setup is constructed to study the effects of branching, processing temperature, additives, and blowing agent on the surface melt fracture behaviors of polypropylene materials melts and polypropylene/butane solutions. The setup consists of a 5 hp extruder driver with a speed control gearbox (Brabender, Prep Center), a $^3/_4''$ extruder (Brabender, 05-25-000) with a mixing screw of 30 : 1 L/D ratio (Brabender, 05-00-144) as the first extruder, a $1\,^1/_2''$ extruder with a built-in 15 hp variable speed drive unit with a 18 : 1 L/D ratio (Killion, KN-150) as the second extruder, a positive displacement pump for injecting the blowing agent into the polymer melt, a static mixer (Omega, FMX-84441-S) as a diffusion-enhancing device, a gear pump (Zenith, PEP-II 1.2 cc/rev), a heat exchanger (for cooling the polymer melt) which contains homogenizing static mixers (Labcore, Reading, PA, Model H-04669-12), a capillary die of 0.1 cm diameter and 3.0 cm in length, and a cooling sleeve for the precise control of die temperature. A CCD camera (Pulnix, San Jose, CA) is mounted at the exit of the die and connected to a computer processor to accurately visualize and monitor the onset of melt fracture.

Experimental materials

The materials used in this study were two linear standard polypropylene resins and three high melt strength (HMS) branched polypropylene resins supplied by Borealis AG. They are denoted in this paper as Linear P1, Linear P2, Branched P1, Branched P2, and Branched P3, respectively. The materials properties, including MFRs (ISO 1133, 230°C/2.16 kg), molecular weights and numbers (M_w, M_n), and the degrees of long chain branching per 1000 carbon atoms (LCB), are summarized in Table I. The foaming additives used in this study were talc and glycerol mono stearate (GMS) as the cell-nucleating agent and the aging modifier, respectively,.[30] The blowing agent used in the experiments was n-butane, C.P. (Matheson, 99.0%).

Experimental procedure

The polypropylene resins were processed in the extrusion setup and the onset of melt fracture was investigated by observing the die pressure, the surface quality of extrudate, and the image of the extrudate from the CCD camera.

First, experiments were conducted without gas injection for investigating the effects of branching, melt temperature, and foaming additives on the melt fracture. Branched materials with various degree of long chain branching were used to investigate the effect of branching on the melt fracture. For investigating the effect of processing temperature, the melt temperature was precisely controlled using the tandem extrusion system. Various amounts of talc and GMS were added to the polypropylene materials to investigate the effects of foaming additives on the surface melt fracture of the extrudate. The onset of surface melt fracture was determined by both directly observing the surface quality of the extrudate and by analyzing the image of the extrudate. As the die pressure increased by increasing the gear pump speed, the occurrence of melt fracture was detected. When melt fracture occurred, the critical shear stress was calculated by reading the corresponding die pressure.

Secondly, experiments were conducted with gas injection to study the effect of dissolved gas on the
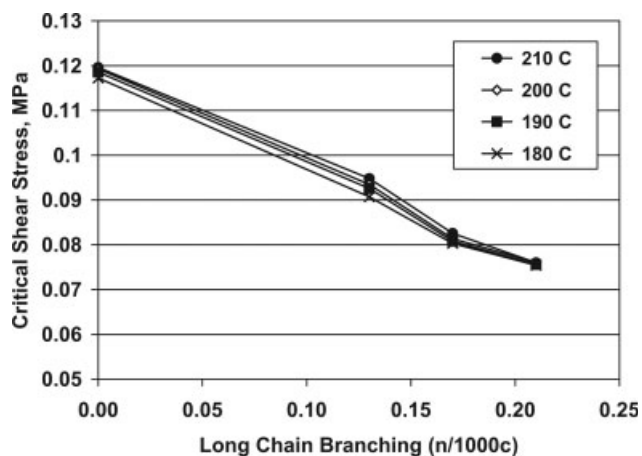
Figure 2 The effect of long-chain branching on the critical shear stress.

Figure 3 The effect of processing temperature on the critical shear stress.

melt fracture. A metered amount of blowing agent was injected and dissolved into the polypropylene melt to form a single-phase polypropylene/butane solution. The formed single-phase polypropylene/gas solution entered the die and foaming was allowed. The onset of melt fracture on the foamed surface was carefully observed using the CCD camera as the die pressure was increased with a higher speed of gear pump.
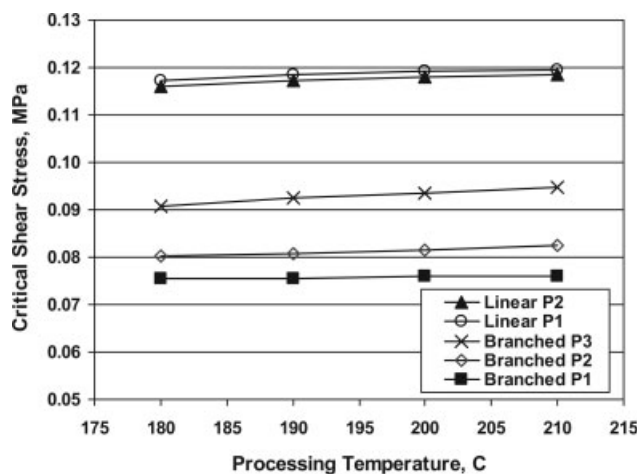
RESULTS AND DISCUSSION

Effect of branching on the critical shear stress

The effect of branching on the surface melt fracture behavior of polypropylene resins is shown in Figure 2. In this experiment, no additives were used. It was observed that the critical shear stress linearly decreased with an increase in the degree of long chain branching. In other words, the surface melt fracture of polypropylene resin becomes promoted by branching. This indicates that the introduction of branching required for foaming of polypropylene resin accompanies a side effect of promoting surface melt fracture. According to the experimental results, the critical shear stress decreased approximately by 0.0175 MPa with an increase of 0.1 n/1000c in long chain branching. The decrease of critical shear stress may be attributed to the increase of melt elasticity as the degree of long chain branching increased. An increase in melt elasticity can increase the slip at the die wall, and hence promote surface melt fracture.[9]

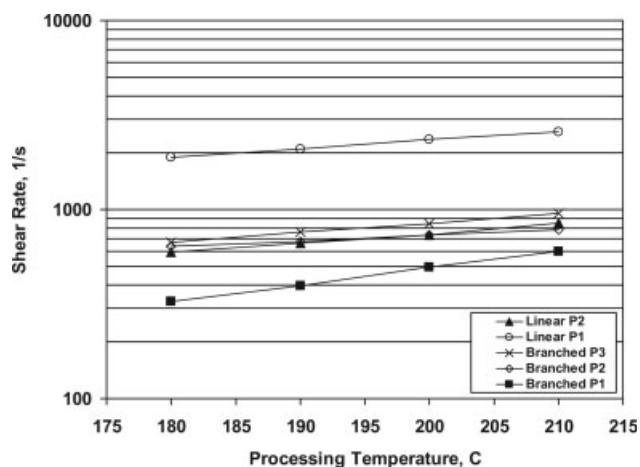### Effect of processing temperature on the critical shear stress

The effect of processing temperature on the surface melt fracture behavior of polypropylene resins is shown in Figure 3 for all the linear and branched

materials. In this experiment, the processing temperature was varied from 180 to 210°C. It was observed that the critical shear stresses of linear and branched polypropylene resins were almost insensitive to the processing temperature in the range of 180 to 210°C. Especially, when the LCB degree is high (Branched P1), the shear stress was barely affected by the temperature. Except Branched P1, the critical shear stress increases with temperature, even though it is small amount.

The critical shear rate at the onset of surface melt fracture was also calculated as a function of the processing temperature. Figure 4 shows that the apparent shear rate at the onset of surface melt fracture linearly increased as the temperature increased from 180 to 210°C for all the polypropylene resins. The rate of increase, contrary to the case of shear stress, has the highest when Branched P1 material is used. Also, the shear rate shows to be proportional

Figure 4 The effect of processing temperature on the critical shear rate.
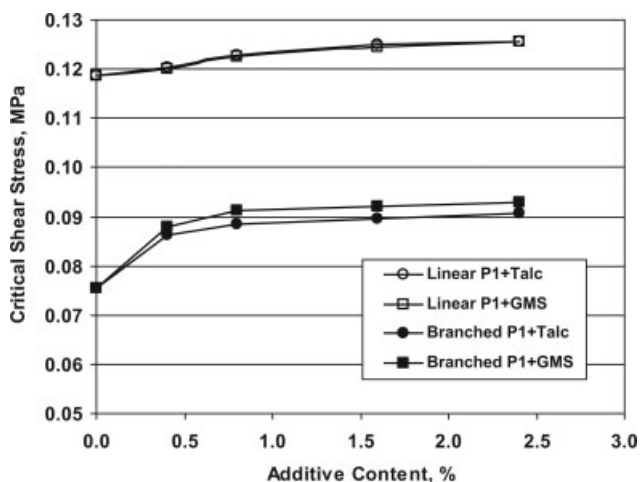
Figure 5 The effect of foaming additives on the critical wall shear stress.

to the MFR. The shear rates behavior observed in this study conform to the behavior observed in other studies.[10,11]

Effects of foaming additives on the critical shear stress

The effects of the dispersed foaming additives, i.e., talc and GMS, on the critical shear stress of polypropylene resins were also investigated. All the experiments were conducted at 190°C. Figure 5 shows the critical shear stress as a function of the contents of talc and GMS for Linear P1 and Branched P1 materials. For both talc and GMS cases, it was observed that the critical shear stress of Branched P1 increased sharply as the amount of dispersed additive increased from 0 to 0.4 wt %. A further increase in the amount of dispersed additives, the critical shear

stress slightly increased. Also, the critical shear stress was augmented more by GMS than talc. By contrast, the critical shear stress of Linear P1 did not change much with the foaming additives. For both talc and GMS, the critical shear stress increased slightly ($\approx$ 0.007 MPa) as the concentration of additives increased from 0 to 2.4 wt %. Also, there was no significant difference in the effect of additive between talc and GMS.

It was surprising to observe that the commonly well-known lubricating effect of GMS was not distinguished in this study.[31] On the other hand, the lubricating effect of talc, as a cell nucleating agent, for the branched polypropylene materials was also surprising whereas the lubricating effect of boron nitride, which is another well-known cell nucleating agent in foam processing, has been reported before.[18] It is speculated that there may be some relationship between the cell nucleating ability of additive and its lubricating effect. Further study needs to be conducted to clarify this issue.

Calibration of the CCD camera image for detecting the onset of surface melt fracture

To precisely determine the effect of dissolved gas on the onset of surface melt fracture of polypropylene materials, the image captured from a CCD camera of extrudate for the early stage of foaming was carefully analyzed. Figure 6 shows the CCD images of the effect of gas contents on the melt fracture of Branched P1 at various temperatures. It was observed for a pure polymer melt without any dissolved gas that the extrudate was steadily coming out of the die exit before the onset of surface melt fracture. In this case, the extrudate shape was uniform and smooth. However, at the onset of surface
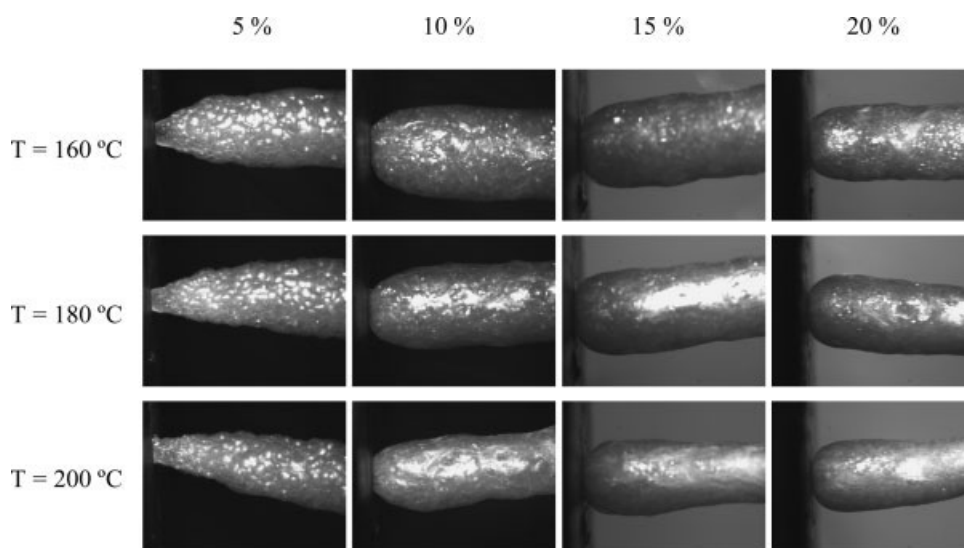
Figure 6 CCD images of Branched P1 at various temperatures and gas contents.

melt fracture, the extrudate coming out of the die started to oscillate vertically in a direction perpendicular to the flow. It was also confirmed that surface irregularities started to appear on the surface of the extrudate at this moment. Because the amplitude of oscillation was very small at the onset of surface melt fracture, the oscillation of extrudate could be detected only by the magnified image of extrudate from the CCD camera.

On the other hand, when gas was dissolved in the polymer and the expansion of extrudate occurred due to foaming, the appearance of surface melt fracture on the foam surface was not synchronized with the moment when the foam extrudate started to oscillate. In other words, even when the minute-scale oscillation of extrudate was detected from the captured image of CCD camera, there was no visible change on the extrudate surface and the degree of straightness of foam extrudate. It was believed that surface melt fracture actually occurred at the moment of oscillatory motion of the extrudate. But the trace of melt fracture on the foam surface must have been removed because of the stretching of foam skin during expansion. The foam skin at this moment was typically very shiny. By contrast, when the degree of oscillation of the extrudate got bigger to be visible even to the naked eye, the foam extrudate became wavy. However, the foam surface was still shiny and smooth.

In conclusion, the onset of surface melt fracture could be detected effectively using a CCD camera by observing the image of the extrudate shape as it starts to oscillate for both pure polymer and foam.

Effect of blowing agent on the critical shear stress

The effect of the dissolved blowing agent on the critical shear stress of polypropylene resins is shown in Figure 7. It was observed that the critical shear stress increased significantly as the amount of dissolved butane increased. As the butane content increased from 0 to 20 wt % the critical shear stress increased by 0.047 MPa and 0.03 MPa for linear and branched polypropylene resins, respectively. This is evident by the CCD images shown in Figure 6, by increasing the butane content the trace of melt fracture on the foam surface decreased due to the stretching of foam skin during expansion. These results mean that the surface melt fracture is significantly suppressed by the dissolved butane. The decreased critical shear stress of Branched P1 by branching was almost recovered by the dissolved 20 wt % butane. On the other hand, the critical shear stress of Linear P1 was also significantly increased by the dissolved butane.
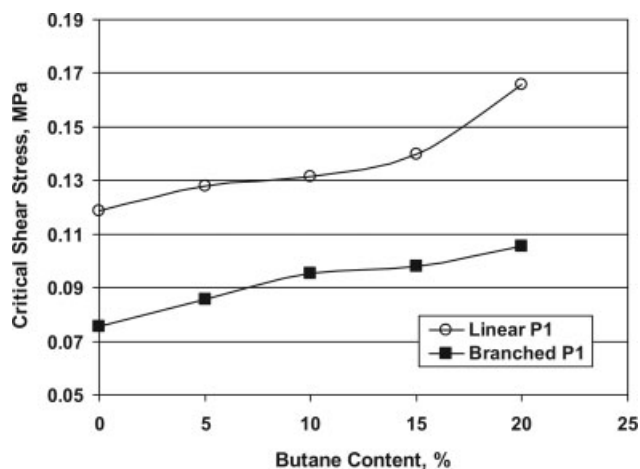
Figure 7 The effect of dissolved butane on the critical shear stress.

SUMMARY AND CONCLUSIONS

Experimental studies were carried out to investigate the effects of branching, processing temperature, foaming additives, and blowing agent on the critical shear stresses of linear and branched polypropylene resins. An experimental setup was designed to investigate the surface melt fracture behaviors of polypropylene melts and polypropylene/butane solutions under various conditions. Efforts were made to accurately control the processing temperature, to well disperse the foaming additives in the polypropylene melt, and to form a single-phase polypropylene/butane solution. A CCD camera was installed at the die exit to precisely monitor and analyze the onset of surface melt fracture of the extrudate at the early stage of foam processing. The experiments conducted in this study lead to the following conclusions:

1. An on-line technique for detecting the onset of surface melt fracture for extruded foam has been developed by visualization of extrudate using a CCD camera.
2. The long-chain branching of polypropylene materials significantly decreased the critical shear stress of the resins.
3. The critical shear stress was almost insensitive to the die temperature; however, the die temperature significantly affected the critical shear rate at the onset of surface melt fracture.
4. The foaming additives of talc and GMS increased the critical shear stress of branched polypropylene materials. However, they did not affect the critical shear stress of linear polypropylene materials much.
5. The dissolved butane significantly increased the critical shear stresses of linear and branched polypropylene resins.

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