# Rheological Behaviour of Polypropylene Blends utilized in Foaming Process

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*Abstract:* Morphological structure of polypropylene foams represented by the size of the bubbles and bubbles density is significantly affected by rheological properties of the source materials. Various blends of high molecular weight and high melt strength polypropylenes were prepared in a twin screw extruder, and subsequently foamed. Their shear flow behavior as well as strain hardening during elongation were found to be the factors of a key importance in foaming process optimization. In addition, pressure dependent shear flow behavior of the tested materials was determined using capillary rheometer modified with backpressure chamber, and obtained dependencies of shear viscosity on pressure conditions were analyzed in order to further tailor blend compositions regarding their following use in foaming processes. It has been demonstrated that foam morphology might be controlled not only through degree of bubble coalescence and nucleation rate by the help of optimizing of material components ratio, but also via setting the proper processing conditions.

*Key-Words:* polypropylene foam, rheology, strain hardening, foam morphology, pressure dependent viscosity

## 1 Introduction

Nowadays, polypropylene (PP) foams become attractive in medical sector due to their superior properties in terms of biocompatibility, high chemical resistance, good stiffness and impact strength combined with reasonable price. Important application advantage of foam products is associated with the possibilities to tailor foam density as well as morphological structure. This goal can be attained by optimizing processing parameters through rheological investigation of PP utilized for foam production.

Generally, viscosity is the crucial characteristic for polymers. Its dependence on temperature is commonly taken into account. In contrast, the effect of pressure on the flow properties of polymer melts is often neglected. This simplification is satisfactory for standard low-pressure technologies, such as extrusion, blow molding, or casting. Nevertheless, in the case of foam extrusion pressure conditions play important role, significantly affecting foam morphology. Hence, implementation of pressure effect into the rheological characterization becomes strengthen.

Polypropylene has rather weak melt viscosity and strength resulting in fractures of thin parts, especially through bubble coalescence and rupture of polypropylene foams. As demonstrated by Münstedt et al. [1] the strain hardening behavior resists the deformation of thin parts of materials during processing. Further, other authors [2-4] pointed out that strain hardening and melt strength tend to prevent bubble coalescence in bubble growth process. Therefore, it is important to optimize rheological properties of PP resins in order to deliver good foam products.

## 2 Problem Formulation

Narrow processing window of PP melt during foam preparation related to the induced foam morphology represents the critical factor requiring extensive understanding of the influence of processing parameters on polymer melt viscosity.

Blends of various polypropylenes could be successful more than neat PP in order to meet the required properties. Several researchers [5-7] improved strain hardening of PP by blending linear and branched PP. Also, Spitael and Macosko [8] reported that optimum composition of linear and branched polypropylenes gives higher bubble density in polymer foams than neat polypropylenes.

Since the effects of viscosity and strain hardening on the foam morphology have not been yet precisely investigated for PP blends, rheological response of blends of linear high molecular weight (HMW) and branched high melt strength (HMS) polypropylenes will be determined and discussed in this work.

## 3 Problem Solution

### 3.1 Experimental

Polypropylenes used in the experiments were a linear HMW type (BE52) with molecular weight about 1,300,000 g/mol and melt flow rate of 0.3 g/min, and branched high melt strength HMS type (Daploy WB130HMS) with a melt flow rate of 2.0 g/min (both supplied by Borealis Polyolefine GmbH, Austria). Their blends containing 30/70 (abbreviated HMW/HMS 3/7) and 70/30 (HMW/HMS 7/3) wt% ratios of linear and branched materials were prepared in a twin-screw extruder Brabender TSE 20/40 (Brabender GmbH & Co. KG).

Shear viscosity was examined using modified capillary rheometer (Göttfert 2001, Göttfert Werkstoff-Prüfmaschinen GmbH, Germany) enabling to measure also pressure-depended viscosity using a backpressure device as described in detail by Sedlacek et al [9]. Apparent shear viscosity was determined in the shear rate range from 35 to 3500 $s^{-1}$. A capillary of the diameter of 1 mm, with the length-to-diameter ratio 20 was employed. True shear rate was determined by the help of Rabinowitch correction.

Elongation viscosity was investigated using extensional rheometer (MCR501 Physica equipped with SER unit, Anton Paar). The experiments were performed at strain rates from 0.1 to 10 $s^{-1}$ at 190 °C under nitrogen atmosphere.

In addition, differential scanning calorimeter (DSC, Pyris1, Perkin Elmer) was used to analyze PPs thermal properties. The samples were tested in the temperature range from 20 to 190 °C at heating rate 10 °C/min. The measurements were conducted under nitrogen atmosphere preventing thermal degradation.

The PP foams were prepared using azodicarbonamide (Sigma-Aldrich Co. Ltd) with concentration of 0.5 phr as a blowing agent on a twin screw extruder (KETSE 20/40, Brabender) with a slit die (designed at TBU in Zlin) having dimensions 2x25x100 mm The die was further modified by insertion of a movable solid valve enhancing the pressure growth on polymer melt. The valve was alternated in three positions; fully open, half open and fully closed. Moreover, the die was equipped with five pressure transducers in order to evaluate shear viscosity from pressure profile inside the die. The screws speed was varied from 5 to 150 rpm. The extruder temperature profile from the hopper to the die was set at 175/180/185/190/190 °C. Extruded PP foams were air cooled at room temperature. Foam density was measured following ASTM standard D792 and foam morphology was examined by means of stereoscopic optical microscope (STM 723).

### 3.2 Results & Discussion

A monotonic decrease of true viscosity (shear thinning behavior), calculated from extrusion data, was observed for all samples as can be seen in Figure 1. It is clear that zero shear viscosity, $\eta_0$, of HMW PP was higher than HMS PP. The viscosities of the blends lie between HMW PP and HMS PP, which implies that the log-additivity rule is obeyed.

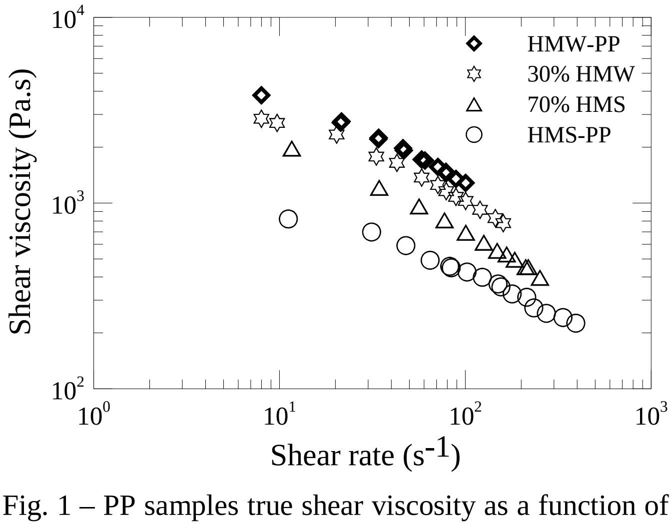

Fig. 1 – PP samples true shear viscosity as a function of shear rate at temperature of 210°C.

The miscibility of the tested blends can be also presumed from the DSC analysis. Clearly, the HMW-PP and HMS-PP have different melting (163.7 °C, and 160.2 °C, respectively) and crystalline (124.4 °C, and 129.7 °C, respectively) temperatures, while their blends showed intermediate melting temperature values. The differences obtained for neat PPs are caused by a positive effect of branching of HMS-PP on crystallinity compared to the negative effect of extremely high molecular weight of linear PP.

Pressure influence on shear viscosity was evaluated through determination of pressure sensitivity coefficient, $\beta$, via fitting the experimental pressure-dependent shear viscosity data with the Carreau model:

$$\eta(\dot{\gamma})=\frac{\eta_0 f}{\left[1+\left(K_1 f\sqrt{2\dot{\gamma}}\right)^a\right]^{\frac{1-n}{a}}} \qquad (2)$$

where $\eta(\dot{\gamma})$ represents shear rate-dependent viscosity, $\eta_0$ means zero-shear viscosity, $\dot{\gamma}$ is shear rate, $K_1$, $n$, and $a$ are empirical constants, and $f$ stands for exponential relation:

$$f=e^{\beta P} \qquad (3)$$

where $\beta$ is the pressure coefficient of viscosity, and $P$ represents gauge pressure.

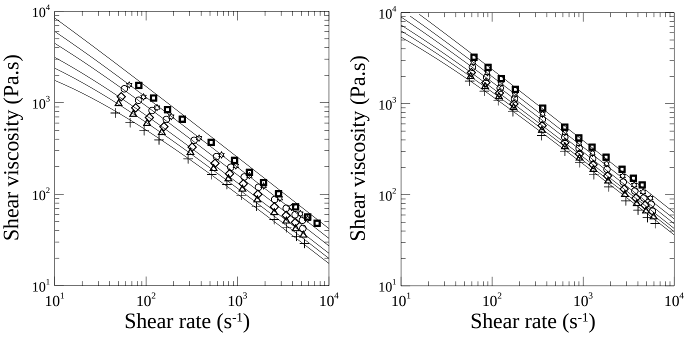

Fig. 2 – Pressure-dependent viscosity vs. shear rate curves of HMS-PP (left), HMW-PP (right) at temperature of 210°C. Solid lines represent data fitting with Carreau model.

Overall, pressure-dependent viscosity of HMS-PP is significantly lower than that of HMW-PP, Fig.2. Variation in zero-shear viscosities of both materials at temperature of 210°C evaluated through the Carreau model exceeded more than one order of magnitude difference as can be seen from the Table 1 summarizing the viscosities and pressure sensitivity coefficients, including the values obtained for PP blends, confirming log-additivity rule validity for the blends. Branched molecules of HMS-PP are almost 1.5 times more sensitive to pressure than linear HMW-PP, which is in agreement with findings reported earlier by Sedlacek et al. [10] for LDPE.

Table 1 – Zero-shear viscosity and pressure sensitivity parameters derived from viscosity data at temperature of 210°C via Carreau model.

| Material | $\eta_0$ (Pa.s) | $\beta$ (GPa$^{-1}$) |
|---|---|---|
| HMS-PP | 2240 | 55.2 |
| HMW/HMS 3/7 | 5650 | 52.3 |
| HMW/HMS 7/3 | 13600 | 50.1 |
| HMW-PP | 39200 | 38.2 |

From the strain hardening observed at elongational viscosity data (Fig. 3) for HMS-PP and its blends with HMW-PP the prevention of bubble coalescence during expansion step in polymer foaming processes might be expected.

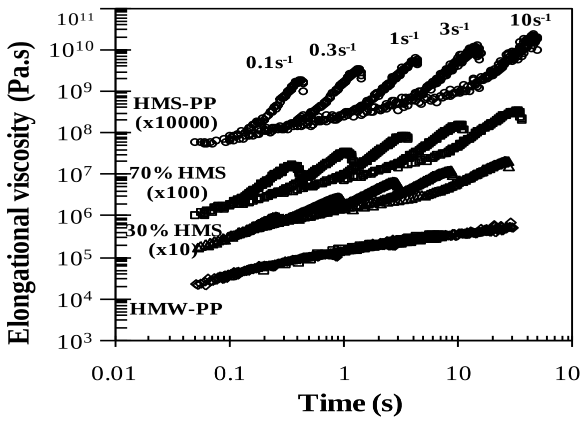

Fig. 3 – Elongational viscosities of HMW-PP, HMS-PP and their blends at temperature of 190 °C.

Bubble densities of PP foams as a function of blend composition are depicted in Figure 4. The bubble density of HMW-PP foams was significantly lower due to its linear molecular structure resulting in bubble coalescence during the bubble growth process. The insufficient strain hardening in this case caused pure resistance of cell walls against the bubble fracture.

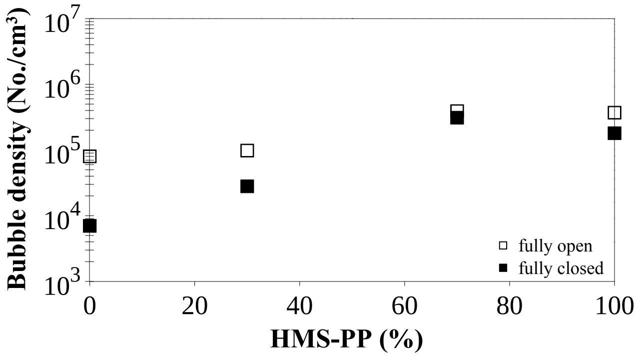

Fig. 4 – Bubble density of HMW-PP foams as a function of HMS-PP addition at screws speed of 20 rpm and various position of restriction valve.

However, this rupture involved bubble sizes propagation as can be seen from Fig. 5 showing large bubble sizes of HMW-PP. In other words, strain hardening behavior of HMS-PP enhanced cell density by preventing bubble rupture and coalescence. Hence, the blends containing HMS-PP component possessed higher bubble densities than that of pure HMW-PP.

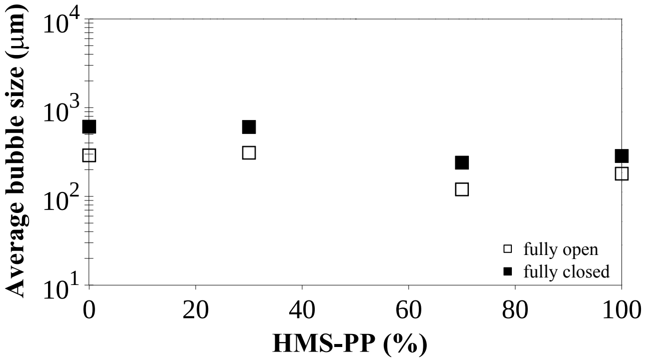

Fig. 5 – Average bubble size of HMW-PP foams as a function of HMS-PP addition at screws speed of 20 rpm and various position of restriction valve.

## 4 Conclusion

High molecular weight (HMW-PP) and high melt strength (HMS-PP) polypropylenes, and their blends in compositions containing 30/70 HMW-PP/HMS-PP and 70/30 HMW-PP/HMS-PP were foamed utilizing a special designed slit die with a pressure valve.

It was found that polypropylenes composition as well as shear and elongational viscosities significantly influence foam morphology in terms of bubble density and size.

Furthermore, an increasing use of computer simulations for both tools design and processing parameters optimization demand precise specification of materials properties. Therefore, evaluation of shear and elongation viscosities was supplemented with evaluation of pressure influence on flow properties of both polypropylenes and their blends.

Pressure sensitivity coefficients derived from Carreau model, which fitted precisely the experimental data, revealed that flow behavior of branched (HMS-PP) polypropylene is more influenced by pressure than linear one (HMW-PP).

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