ABSTRACT

Polypropylene (PP) as a linear resin has low melt strength. The melt strength of polymer is the main feature for the success of low density extrusion foam. Use of a high melt strength such as branched PP (Br-PP), is required to achieve large volume expansion by preventing cell coalescence and gas loss. In this paper, the effects of long chain branched polypropylene on melt elasticity and volume expansion in the extrusion process of PP ternary blends are investigated. The equilibrium creep compliance ($J_{e0}$) and damping factor ($\tan \delta$) of melts were evaluated as melt elasticity index by oscillation rheometry. To setup the extrusion foaming process, the Haake 25 L/D single-screw extruder was improved by design and manufacturing to a special 38 L/D screw with a long mixing zone. Extrusion temperatures were optimized to reach a stable foaming process. The consistency of process pressure as a measure of foam extrusion system stability was evaluated. The cell population density and expansion ratio were determined for foam samples. The effects of the blowing agent (BA) on the amount of pressure build-up were measured at various branched PP levels in the blend. The experiments showed that, by increasing the branched PP, $J_{e0}$ increases, and $\tan \delta$ decreases, which is an evidence of improved melt elasticity. The maximum expansion ratio for the blends was achieved at about 55% of branched PP resins and 20% of B.A. The results also showed that, by increasing the branched PP, the cell population density increases to a maximum of $7.5 \times 10^6$ (cell/cm$^3$) and no significant increase was observed at higher branched PP levels.

INTRODUCTION

Polypropylene (PP) foam is a tough, durable, and cost effective material with good mechanical and excellent chemical resistance. The impact energy absorption of PP foam has been put into operation for acoustical applications [1], cushion packaging, and as shock absorber in automotive industries [2].

Polypropylene pre-expanded foam particles are increasingly being used in returnable, and reusable goods in many industries [3-6]. To meet industrial demands, PP resins are being used in multi-layer thermoformable sheets [7,8], or in blends with polyolefin resins.
Polypropylene is a linear polyolefin which shows low melt strength. So far, extensive effort has been extended on increasing the melt strength of linear PP by different methods. The molecular size and molecular weight distribution affect the melt strength of polymers. Broadening the molecular size distribution results in improvement in melt strength. Having the same width of molecular weight distribution and higher average molecular weight results in higher melt strength [12]. There are known limitations in processing high molecular weight resins, with broad molecular weight distribution. Using the bimodal molecular weight PP resins [13], and blending two various grades of linear PP with different average molecular weights (M_w), and various polydispersity have been proposed by Alteeping et al. [14], to increase the melt strength of resin for a stable extrusion foaming operation.

The foaming and thermoforming behaviours of polymers strongly depend on melt elongational viscosity [15]. The effects of molecular size, molecular weight distribution, and long chain branched PP on extensional melt strength (elongational viscosity) behaviour are quite different. The change in weight average molecular weight (M_w) affects melt shear strength, and the elasticity of melt is mainly represented by the Z average molecular weight value (M_z) [16] which can be evaluated by gel permeation chromatography method. Broadening the molecular size distribution results in an improvement in melt strength (melt shear viscosity) and has no significant effect on melt drawability (melt elongational viscosity). High molecular weight PP resins are frequently characterized as “high melt strength” resins, yet fails to yield acceptable foam structure.

Various methods have been used for the evaluation of melt elongational strength. The elastic nature of the melt is considered a measure of melt extensional strength which is directly related to the number of elastically active nodal points of chain entanglements [17]. It is reported that [16], a M_z value above 1×10^6, and M_z/M_w ratio above 3.0 are necessary to yield acceptable foam. The rheological characterization of melts in the linear viscoelastic range of deformation can be used to evaluate the elasticity of resin [18]. Equilibrium creep compliance (J_e0), loss factor (tan δ), and recoverable shear strain (Sr), are factors representing the melt elasticity [19-21]. The various approaches to characterizing the viscoelastic response of melt are usually carried out at single temperature and frequency. In the real foaming process during the expansion, cooling, and stabilization stages, polymer melt experiences a domain of temperature and deformation rate (production rate), therefore it is more preferable to build the master curve for tan δ, and frequency according to the principal of time-temperature superposition [21]. Nevertheless measuring tan δ and J_e0 at a single temperature and frequency can be helpful in making the comparison on elasticity of blends. In this study the creep compliance and tan δ of melt were evaluated for various formulations.

By introducing or creating branches on polypropylene backbone, the entanglement of branched chains gives rise to improvement in melt extensibility [22,23]. Because of price and processing limitations, it is preferable to use pure branched polypropylene (Br-PP) in conjunction with other materials. Some efforts have been made to blend branched and linear resins to produce low density foam [24,25]. Reichelt et al. [9] studied the foaming behaviour of blends of Br-PP and linear PP block copolymer, at various processing conditions using a single-screw tandem foaming extruder. The similarity in melt flow index (MFI) of blend couples was the criteria for linear PP selection [25], for proper mixing of resins. In the previous reports, Naguib et al. [24,25] used a linear PP with MFI of 2.5 g/10min for blending with Br-PP with similar MFI.

The objective of this work was to use two linear PP with different molecular weights in blend with Br-PP, which is a novel method to increase molecular entanglements and improve melt fracture. The PP resins with a higher molecular weight may show more sites for chain entanglements with Br-PP resins and require much energy to be expended to benefit the foam production. Alternatively the high molecular weight linear resin and also Br-PP both are prone to melt fracture. The lower molecular weight PP resin (higher MFI) in the blend is selected to play the role of a rheological modifier to prevent melt fracture of the blend.

The rheological characterization of binary blends (linear + Br-PP), and ternary blends (linear 1+ linear
2+ Br-PP) showed preference for ternary blends [26]. The rheological characteristics and extrusion foaming behaviour of linear and branched ternary blends are studied in this work.

**EXPERIMENTAL**

**Materials**

The materials used in this study are listed in Table 1. PP1 is a standard injection grade polypropylene block copolymer. PP2 is a low MFI, high molecular weight block copolymer, with broad molecular weight distribution which is usually used for thick wall pipe application. Profax PF 814 is a long chain branched PP with high melt strength. n-Pentane was used as blowing agent. A small amount of talc as a nucleating agent, and glycerol monostearate master batch, as a diffusion retarder, were used in all formulations.

**Blend Preparation**

The polypropylene pellets with 0.8% talc, and 2 phr (part per hundred part of resin) of glycerol monostearate master batch were dry blended according to six separate formulas, which were sequentially coded TB-1 through TB-6 (Table 2). The PP1 to PP2 ratios were kept in the range of PP1/PP2 = (1.2±0.3) in the formulation to reach a MFI range of 2.5±0.7 g/10min, which is close to MFI of pure Br-PP. The physically blended mixtures were mixed, in a Dr. Collin twin-screw extruder set at 150 rpm, and with a temperature profile of 195°C to 220°C, from the barrel to die exit. The extrudate was changed to cylindrical shape granules in a strand pelletizer. The produced granules were used in the foaming process.

| Table 1. Experimental raw materials used in the study. |
|-----------------|-----------------|------------------|------------------|
| Materials       | Description     | Supplier             | Specification    |
| PP1             | Moplen EP C40R  | Arak Petrochemical Co. | *MFI = 7        |
| PP2             | Moplen EP D60R  | Arak Petrochemical Co. | *MFI = 0.4      |
| Br-PP           | Profax PF814    | Basell Polyolefine   | *MFI = 2.5      |
| Talc            | Luzenac 1445    | Luzenac France       | 10 μm           |
| n-Pentane       | Industrial grade| --                 | 99.5% pure      |
| GMS Masterbatch | Glycerol monostearate | DEP Co. | 20% rich |

(*) MFI (g/10min) at (230°C, 2.16 kg).

| Table 2. Blend recipes and relevant MFI data. |
|-----------------|-----------------|-----------------|
| Code            | Composition (wt%) | MFI* |
|                 | PP1 | PP2 | Br-PP |
| TB-1            | 40  | 45  | 15    | 1.7 |
| TB-2            | 37  | 38  | 25    | 1.9 |
| TB-3            | 30  | 30  | 40    | 2.2 |
| TB-4            | 25  | 20  | 55    | 2.6 |
| TB-5            | 20  | 15  | 65    | 2.9 |
| TB-6            | 15  | 10  | 75    | 3.2 |

(*) MFI (g/10min) at (230°C, 2.16 kg).

**Preparing the Test Specimens**

Specimens for tensile, and oscillation rheometry tests were prepared by injection moulding machine, set at temperatures of 175°C to 195°C, from hopper to nozzle. The tensile test was carried out on Zwick Z020 universal testing machine, on 5 sample bars (type I) at 50 mm/min according to ASTM-D638 test method.

**Crystallization Study**

The crystallization behaviour of the blends was investigated using PL differential scanning calorimeter (DSC) at 10°C/min. The samples were heated to about 250°C and then after 5 min holding, were cooled down to room temperature under a nitrogen blanket.

**Oscillation Rheometry**

The viscoelastic characterization of melt was conducted by a Paar Physica Modular Compact Rheometer MCR 300, and a TC30 temperature control unit. To prepare the samples, injection moulded
sheets with 1.2 mm thickness were stamped out with a 25 mm diameter circular die. The creep compliance of melt was measured at 210°C for 150 s test duration, using 25 mm parallel plate geometry with a 1 mm gap, at constant stress of 100 Pa.

**Extrusion Foaming Setup**

The schematic of the experimental extruder setup for foaming resins is shown in Figure 1. The Haake 19.1 mm, 25 L/D single-screw extruder is modified by designing and manufacturing a long 38 L/D mixing screw, with 13D length for injection and a mixing section on the end head. The extended barrel section, equipped by two heating elements, was controlled by the spare control channels of Haake HBI SYS 90 control system. The blowing agent was injected into the melt by a Knauer 6400 high pressure pump. A stable processing condition was established, before the randomly selected foam samples were tested by Nikon optical microscope. Magnification of the lens was recorded for the calculation according to eqn (3). The number of cells (n) was counted from the pictures on the monitor. The foam density was determined by measuring the weight and volume of samples.

**RESULTS AND DISCUSSION**

**Mechanical and Rheological Properties**

The melt flow index test was used for rheological evaluation of polypropylene polymers in this study. The inverse MFI as an index of viscosity was plotted against temperature and are shown in Figures 2 and 3.

PP2 is a high molecular weight PP resin with a broad molecular weight distribution, therefore shear viscosity is more sensitive to temperature and shear stress than PP1 and Br-PP. At 230°C (mixing temperature for blend preparation) the viscosities of PPs are closer to each other, and due to molecular structure similarity of PPs, they can easily be blended in the twin-screw extruder. Because of analogous chemical structure of linear PPs, the resins with higher viscosity ratio [27], can be mixed in the compounding machines.

The strength of a thin layer of material of the cell wall, and its crystalline structure, has a major effect on foam specifications. The tensile strength, modulus and yield strain of blends are illustrated in Table 3. By increasing the Br-PP content in the blends, the crystallization heat, and consequently degree of crystallinity increases. By increasing the heat of crystallization, the elastic modulus and yield stress increased and yield strain decreased. Br-PP is a homopolymer and its tensile strength and also elastic modulus are higher than block copolymers PP1 and PP2.

<table>
<thead>
<tr>
<th>Blend code</th>
<th>Blend code</th>
<th>Modulus (MPa)</th>
<th>Yield stress (MPa)</th>
<th>Strain-at-yield (%)</th>
<th>ΔH_crys. (mcal/mg)</th>
<th>T_s (°C)</th>
<th>T_peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB-1</td>
<td>40/45/15</td>
<td>1230</td>
<td>26.5</td>
<td>0.73</td>
<td>35</td>
<td>16.6</td>
<td>133.5</td>
</tr>
<tr>
<td>TB-2</td>
<td>37/38/25</td>
<td>1250</td>
<td>27.0</td>
<td>0.70</td>
<td>31</td>
<td>9.0</td>
<td>15.8</td>
</tr>
<tr>
<td>TB-3</td>
<td>30/30/40</td>
<td>1270</td>
<td>28.5</td>
<td>0.75</td>
<td>30</td>
<td>8.0</td>
<td>17.0</td>
</tr>
<tr>
<td>TB-4</td>
<td>25/20/55</td>
<td>1350</td>
<td>30.0</td>
<td>0.80</td>
<td>25</td>
<td>8.0</td>
<td>18.5</td>
</tr>
<tr>
<td>TB-5</td>
<td>20/15/65</td>
<td>1550</td>
<td>32.0</td>
<td>1.17</td>
<td>30</td>
<td>8.0</td>
<td>18.5</td>
</tr>
<tr>
<td>TB-6</td>
<td>15/10/75</td>
<td>1620</td>
<td>33.0</td>
<td>1.23</td>
<td>39</td>
<td>7.5</td>
<td>18.8</td>
</tr>
</tbody>
</table>

*Table 3. Mechanical properties of blends.*
The creep compliance, $J(t)$, is given in the following equation by [28,29]:

$$J(t) = \frac{\gamma(t)}{\delta_0} = Je_0 + \left(\frac{t}{\eta_0}\right)$$

where $\gamma(t) = \text{strain; } \delta_0 = \text{stress; } Je_0 = \text{equilibrium creep compliance; } \eta_0 = \text{zero shear viscosity; and } t = \text{time.}$

The strain as a function of time is divided by the stress given to $J(t)$. $Je_0$ is the intercept of $J(t)$ versus time plot.

The damping factor, $\tan \delta$, was calculated by measuring the viscous ($G''$), and elastic component ($G'$) of the melt, in the linear viscoelastic range of deformation in an oscillation frequency of 1 rad/s. The equilibrium creep compliance ($Je_0$) of the blends shown that by increasing Br-PP in the ternary blends, $Je_0$ increases (Figure 4). Higher $Je_0$ is evidence of increased elastic melt. However, $\tan \delta$ of the blends TB-1 and TB-6 with 15% and 75% of Br-PP are quite different, there was not a meaningful difference observed in $\tan \delta$ of middle range (25-60 wt%) of Br-PP content blends.

**Optimization of Heating Setup**

Temperature has a major role in the stability of the extrusion foaming process [7,8]. Viscosity is a function of temperature, and decreases by increasing the temperature. The injected $n$-pentane is a foaming agent is mixed with polymer, and reduces the melt viscosity even more. Conversely, temperature directly affects vapour pressure of the blowing agent and increases the system pressure, and thus promotes instability of the extrusion process. By increasing the temperature, with thermodynamic instabilities, the foaming agent partially vapourizes, and viscosity increases proportionally, and the foaming agent will not be liquid or be able to be mixed with polymer melts.

The heating setup of the extruder barrel and die section and the processing conditions affect the stability of the foaming process. Variations of extruder and die pressure and fluctuations in output are the signs of

<table>
<thead>
<tr>
<th>Heating programme</th>
<th>Melting zone (°C)</th>
<th>Pressurizing zone (°C)</th>
<th>Injection &amp; mixing zone (°C)</th>
<th>Mixing zone (°C)</th>
<th>Die head (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T1</td>
<td>T2</td>
<td>T3</td>
<td>T4</td>
<td>T5</td>
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<td>190</td>
<td>190</td>
<td>185</td>
<td>175</td>
<td>163</td>
</tr>
</tbody>
</table>
system instability. In an unstable extrusion foaming process, the foaming agent losses escaping from the die exit reduces the die pressure and output simultaneously. Endothermic evaporation of gas out of the die removes the heating energy, reduces the temperature, increases viscosity, and builds a resistance to flow accordingly.

The (Haake) 25 L/D single-screw extruder was improved by design and manufacturing with a special 38 L/D screw with a long mixing zone. The screw should be capable to prevent escape of the blowing agent back to the hopper by a built in a melt seal in the first melt pumping section, and before the liquid injection point. It is necessary to optimize the melt temperature before and after the liquid injection point for a stable and efficient system. The length of the first pumping section of the screw is 4.5 D. The experiments showed that each pitch (D) of this zone can generate a pressure of about 3.0 MPa at 180ºC. The pressure before the die section increases to a maximum of 13 MPa for the experimental setup of this study, and drop down, in an unstable process. Following frequent test runs, the heating programme no 1 are selected (Table 4) for the extrusion foaming process.

**Effect of Blend Composition on Melt Fracture**

The surface quality and distortion of rod shape extrudate were studied visually on Br-PP and its blends. According to the previous studies, the extrudate obtained from pure Br-PP [25] and its blends with one linear polymer [24] show non-homogeneous swelling by distorting the extrudate. In the ternary blends of this study, PP2 is a high molecular weight resins (low MFI). This resin could promote the molecular physical entanglements, induced by long chain branches of Br-PP, and leads to strong melt elasticity, with poor homogeneous swelling. The lower molecular weight PP1 resin with higher MFI affects the relaxation of entangled branched molecules and improved the melt distortion in the die exit. With the combination of PP1 and PP2 resins, the molecular entanglements and die swell of extrudate can be controlled by extrusion system setup. It is observed in this study that, by increasing Br-PP in the blends from TB-1 to TB-6, the PP1/PP2 ratio should increase from 0.9 to 1.5 to prevent melt fracture and extrudate distortion.

**Effect of the Amount of Foaming Agent on Die Inlet Pressure**

The amount of foaming agent affects the die pressure...
and system stability. The variations of die pressure at different amounts of \(n\)-pentane and Br-PP are shown in Figures 5 and 6.

It is observed that die pressure is reduced by increasing the amount of \(n\)-pentane and also branched PP content in the blends. Die pressure is reduced because of reduction of viscosity of the mixture by increasing the pentane content, and also increasing the MFI of blends, and because of the MFI of Br-PP and PP1/PP2 ratio in the blends.

**Theoretical Calculation of Foaming Agent**

The maximum theoretical expansion ratio of foam is estimated by eqn (2) [30]:

\[
V_T = \frac{\text{Polymer volume} + \text{Gas volume}}{\text{Polymer volume}}
\]

\[
V_T = 1 + \frac{m_g / \rho_g}{m_p / \rho_p}
\]

where, \(\rho_g\) is the density of foaming agent at polymer crystallization temperature, \(\rho_p\) is polymer density at room temperature and, \(m\), is weight percent. The DSC study of blends (Table 3) showed that the crystallization of blends starts at about 135ºC. The specific volume of \(n\)-pentane at 135ºC is 446 cm\(^3\)/g [30]. Butane, isopentane, and \(n\)-pentane are long chain blowing agent, which are commonly used in low density foam processing. The foaming agent should be able to be mixed with polymer, and preferably have large molecules to reduce the diffusion out of nucleated cell walls to the atmosphere.

The theoretically required amount of \(n\)-pentane in the absence of any loss is about 5 wt% for a foam density of 0.045 g/cm\(^3\) (20 times expansion ratio). This calculation is a theoretical basis for estimation of maximum expansion ratio at a certain percentage of blowing agent. Practically, some parts of blowing agent losses are out of the foaming process, depending on the type of blowing agent and foaming process setup.

**Effect of the Amount of Blowing Agent on the Blends Foaming Behaviour**

The blowing agent injected in the melt convectively diffuses, and dissolves in the polymer melt in the extruder barrel. The polymer-blowing agent solution destabilizes thermodynamically by passing out of the die and removing the pressure. Low pressure at the die exit, reduces the solubility of the blowing agent in the polymer and changes the homogenized polymer-blowing agent solution in a two-phase system. The volume expansion ratio of foam is calculated as the ratio of pure PP density to the density of the foam sample and it is shown in Figure 7. It is observed that the expansion ratio increases by increasing \(n\)-pentane up to about 20% and decreases sharply at higher amount of blowing agent. This is because of a decrease in viscosity by increasing \(n\)-pentane which facilitates rapid expansion and promotes the cell coalescence. The high concentration of foaming agent, also plasticizes the polymer melt and reduces the viscosity of the mixture. The soft material in the foam’s cell walls cannot resist the vapour pressure of \(n\)-pentane and promotes the cell coalescence and gas loss.

The cell population densities (CPD) of foams were determined by eqn (3) [31,32]:

\[
N_o = (nM^2/A)^{3/2} \times 10^{12} \times (\rho_f/\rho_p)
\]

where, \(N_o\) is the CPD (cells/cm\(^3\)), \(n\) is the number of cells on the micrograph, \(M\) is the magnification factor, \(A\) is the area on the micrograph selected for counting the cells (cm\(^2\)), and \(\rho_f\) and \(\rho_p\) are foam and polymer densities, respectively. CPD of foams, calculated by eqn (3) are shown in Figure 8.

The cell population density is determined on the samples with maximum expansion ratio at optimized \(n\)-pentane percentage of 20%. The expansion ratio for
Figure 8. The cell population density of blends at different amounts of Br-PP.

The cell population density of blends at different amounts of pentane is shown in Figure 9.

The higher amount of Br-PP in the blends increased the melt elongational strength, and higher cell population density was achieved by suppressing cell coalescence (Figure 8). The expansion of nucleated cells occurs by vaporizing the blowing agent. The rate of expansion depends on viscosity of thin layer of melts in the cell walls, and also vapor pressure of blowing agents. Higher cell population density by increasing the Br-PP has reported before in the binary blends of linear and branched PP, and has been enhanced by the higher cell nucleability effect of branched PP [25]. The crystallization study of blends showed no evidence for the higher nucleability of linear PP compared to branched ones. However, cell nucleation is one of the main stages in the foam production, but the melt elongational strength of branched PP made it preferable to prevent the cell coalescence of nucleated cells during the expansion process.

The cell population density depends on higher cell nucleation and lower cell coalescence. Higher cell nucleation does not necessarily lead to higher expansion ratio, because of cell expansion dynamic and possibly, because of deterioration of the thin layer of polymer film in cell walls. It is believed that larger cells expand faster than smaller bubbles, and the rate of cell expansion increases rapidly with time [15].

By increasing the amount of Br-PP in the blends, the melt elasticity (Figure 4), and expansion ratio increased. The expansion ratio shows a maximum at about 65% of Br-PP levels, and decreases at higher Br-PP content without large changes in cell population density. It indicates that, the expansion force of n-pentane is not able to increase the expansion ratio of blends with higher melt extensional strength. For the blends with higher Br-PP levels, blowing agents with higher vapour pressure are more effective.

The best results are achieved by higher cell nucleation and lower cell coalescence in the presence of efficient blowing agent. It is found in this study that, the best results can be obtained by 55-65% Br-PP for simultaneous optimum expansion ratio and cell population density.

CONCLUSION

In this study the ternary blend of two linear PP block copolymers with Br-PP resin were being used to optimize the properties and processability in foam extrusion. The experimental work carried out in this study led to the following aims:

- The ternary blends of two linear PP resins with a Br-PP lead to successful optimization of melt elasticity and melt fracture.
- The high molecular weight and low MFI resin promote molecular entanglement induced by long chain branched PP. The second linear PP is an injection grade resin, with higher MFI and lower molecular weight used as a modifier for melt fracture and extrudate distortion. The cell population density
(CPD) and expansion ratio increased by Br-PP content up to 65%. At higher Br-PP content, the expansion ratio showed small decrease at nearly constant CPD. The incorporation of a higher amount of Br-PP, up to 65% in the blends, caused the cell population density to increase, and a higher expansion ratio due to lower cell coalescence was achieved.

- The n-pentane blowing agent is not effective to generate adequate foam bubbles with adequate internal pressure to overcome the strength of thin layer of melt in the cell walls. An efficient method is found to obtain optimum temperature settings for a stable and efficient extrusion foaming process. The plasticizing effect of excess blowing agent is accompanied simultaneously with extra evaporation and heat removal from the die section. In this study we found it was not necessary to change the optimum temperature setting at a higher blowing agent content.

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