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# Effect of Side Chain Branched PP, EPDM and HDPE as a Third Component on Melt Extensional Behaviour of Ternary Blends

Yousef Jahani[1*] and Mehdi Barikani[2]

(1) Department of Plastics, Faculty of Processing, Iran Polymer and Petrochemical Institute
P.O. Box: 14965/115, Tehran, I.R. Iran
(2) Department of Polyurethane, Fibres, and Nanomaterials, Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115, Tehran, I.R. Iran

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## ABSTRACT

The effect of some factors, i.e., long chain branches on EPDM and PP backbone and short side chain branches of HDPE on melt extensibility and melt elasticity were studied and compared with those of ternary blends of linear PPs. Long chain branched EPDM, long chain branched PP, and linear PE with small side chains were used to increase the molecular entanglements and melt drawability and to improve melt elasticity. Using three linear PP in the blends, showed a synergistic effect on melt elasticity in a certain percentage of composition. The experimental results have been indicated that both ternary blends of linear PPs and ternary blends containing a branched PP increased molecular entanglements and affected melt elasticity. HDPE as a polyolefin with short side chains showed better effect on melt elasticity and melt drawability than ternary linear PP blends. Long chain branches of EPDM considerably improved its damping factor (tan $\delta$) and steady state creep compliance ($J_{e0}$). The effect of long chain branched EPDM and high molecular weight linear PE with small branches, on melt tension force and damping factor of blends were measured and compared with those of blends containing a long chain branched PP. Long chain branched PP showed a distinct effect on melt extensibility of blends. The most significant effect is observed by using PE and long chain branched PP, both.

Key Words:
branched PP;
melt extensibility;
equlibrium creep compliance;
ternary blends;
melt damping factor.

## INTRODUCTION

Polypropylene is a linear polyolefin that shows low melt extensibility and low melt strength. The foaming and thermoforming behaviour of polymers strongly depends on their melt extensibility and melts drawability. The melt strength and melt drawability are important factors where deformation is substantially elongational, and tensile stresses are present [1].

Due to wide range of properties necessary for these processes, and in order to be capable to balance the

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(*)To whom correspondence should be addressed.
E-mail: y.jahani@ippi.ac.ir

melt drawability and final properties of products, using linear and branched PP in a blend has been of interest in some recent research works [2, 3, 12]. Using the bimodal molecular weight PP resins in a blend may cause higher melt strength and also with higher melt extensibility [3,4]. To overcome the low melt strength of PP, Alteeping and Nebe [5] used a binary blend of two various grades of linear PP with different weight average molecular weight ($M_W$) of 1,800,000 and 280,000, and poly dispersity of 2.5 and 5, respectively. It is observed that high melt strength PP resins and long chain branched ones, have improved foamability and thermoformability [6,7].

In the past few years different companies have made a lot of efforts to evaluate the possibilities and potentials of the post reactor modification of polypropylene [8, 9]. Recently various grades of long chain branched PP (lcb PP) have been presented to market [10]. The effect of molecular size, molecular weight distribution, and lcb PP on extensional and melt strength behaviours are quite different. The broadening of the molecular size distribution, improves melt strength and has not significance effect on drawability. By having almost the same width of molecular weight distribution, the higher the average molecular weight (low melt flow index), the higher the melt strength [11].

By introducing or creating long chain branch on polypropylene backbone, entanglements of branched chains give rise to improvement of melt extensibility.

Blending of standard PP and high melt strength PP together with lcb PP cause many sites for entanglements, and need much energy to be extended. In this way, the melt strength and melt extensibility can be balanced in a tailor made mixture for certain applications. It is preferred not to use pure lcb PP alone, because of peice and processing limitation. Some efforts have been made to blend branched and linear resins [2,12].

PPs with broad molecular weight distribution has many short friction sites, while lcb PP resins have long chains on backbone that affect more the melt elasticity. The branched structure introduces some physical molecular entanglements that will prevent or retard the slippage of molecules on each other.

Extensional properties and elastic nature of the melt are considered as a measure of melt strength and melt extensibility that are directly related to the number of elastically active nodal points of chain entanglements.

## Background to Molecular Structure of HDP, Lcb EPDM, and Lcb PP

The schematics of molecular structure of HDPE, lcb EPDM, and lcb PP are shown in Figure1.

HDPE is a linear polymer with short side chains. The higher the molecular weight, the more opportunities there are for entanglements. The entanglements persist when the material is melted, and its high viscosity makes it more difficult to be shaped. Different grades of HDPE resins have different average molecular weights; represent compromise between solid strength and viscosity to suit various applications [13].

Ethytene-propylene copolymers are essentially linear in structure. Copolymerization with Ethylidene norbornene (ENB) or dicyclopentadiene (DCPD) as third monomer will give rise to branching reactions at these polyfunctional entities. Branching by polymerization is due to Ziegler reactions at both double bonds of the diene. The longer the polymer molecules, the more likely these reactions occur. They result in a broadened molecular weight distribution (MWD), with long chain branched, i.e., supermolecules [14].

The lcb PP has improved melt strength. There are different methods to develop branched PP. Daploy is a process which involves the modification of PP by a combination of peroxide and coupling additives [11]. The PP chains are broken by peroxide and recombined by coupling agent of defined functionality to create a long chain branch structure (Figure 2). The next method to develop lcb PP is usually an electron beam radiation process [15-17]. The most possible reaction

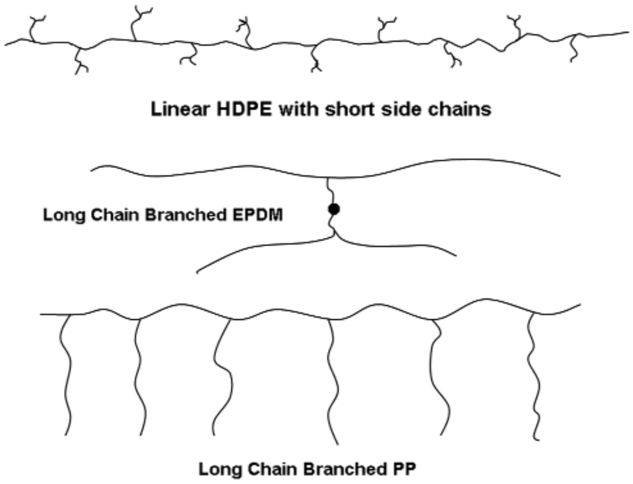

**Figure 1.** Schematics of molecular architectures of HDPE, lcb EPDM, and lcb PP.

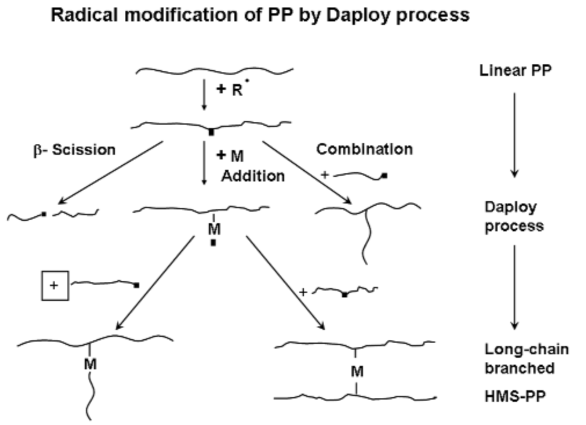

**Figure 2.** Schematic of Daploy process.

of this process is shown in Figure 3 [11].

## EXPERIMENTAL

### Materials

The materials used in this study are shown in Table 1. PP1 Is a standard injection grade with high MFI (ISO 1133 at 230°C/2.16 kg) of about 7.0 g/10min. PP2 And PP3 are low MFI grade, high molecular weight, with various molecular weight distributions.

PP1 Is usually used for thick wall pipe application. PP3 Is introduced to the market as a high melt strength PP for blow molding applications [18]. Profax PF 814 is a lcb PP supplied by Basell polyolefine.

### Polymer Mixing

To study the effect of side chain branch on melt strength and melt drawability, three sets of blends are prepared according to recipes mentioned in Table 2, 3 and 4. The polypropylene pellets with 0.8% talc as nucleating agent were dry blended. No antioxidant additives are used in the formulations. The physically blended mixtures were compounded in a Dr. Collin twin screw extruder at 120 rpm. The temperature profile of 195 to 220°C is set from barrel to die exit. The die used was a 3 mm round die and the strand was changed to cylindrical shape granules in a strand pelletizer.

To study the side chain branch effects on rheological properties of polymer melt, three sets of experi-

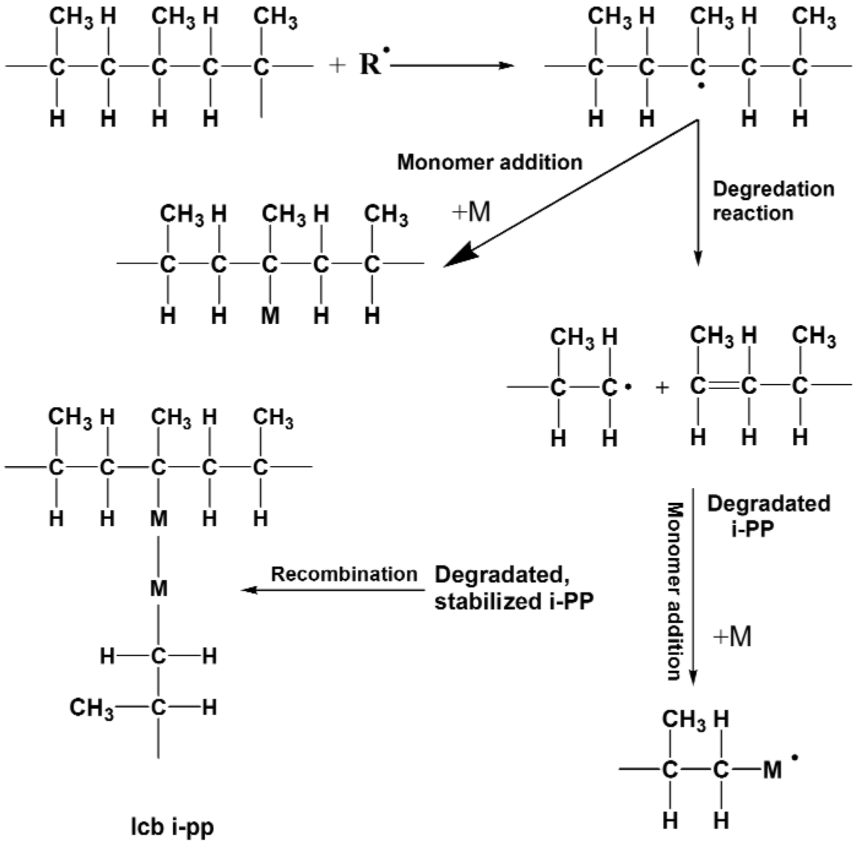

**Figure 3.** Formation of lcb PP by radical reaction on PP homopolymer bellow 80°C.

**Table 1.** Experimental raw materials.

| Materials code | Grade name | Description | MFI (g/10min) (230°C,2.16kg) |
|---|---|---|---|
| PP1 | Moplen EP C40R | Standard injection grade | 7 |
| PP2 | Moplen EP D60R | Low MFI pipe grade | 0.3 |
| PP3 | Moplen EP Q30R | High melt strength for blow molding | 0.8 |
| LCBPP | Profax PF814 | Long chain branch PP | 2.5 |
| PE | Hostalen 5010T | Pipe grade HDPE | 0.5<br>(190/2.16kg) |
| EPDM | Royalene 8340A | Controled lcb EPDM | - |

**Table 2.** Linear PP Blends formulations and properties.

| Blends No. | Blends desig. | PP1 (%) | PP2 (%) | PP3 (%) | MFI (210 °C,2.16 kg) |
|---|---|---|---|---|---|
| A-1 | R-1 | 70 | 30 | - | 3.0 |
| A-2 | R-2 | 50 | 50 | - | 1.6 |
| A-3 | R-H-2 | 50 | 35 | 15 | 2.1 |
| A-4 | H-R-1 | 50 | 25 | 25 | 2.3 |
| A-5 | H-R-2 | 50 | 15 | 35 | 2.5 |
| A-6 | HMS-2 | 50 | - | 50 | 2.1 |

ments were designed. In the experiments, 50% of PP1 is used, and PP2 or PP3 were replaced with high density polyethylene, lcb EPDM, and lcb PP.

### Thermal Analysis

Since the deformation of thin layer of melts (e.g., in foam cell wall or deep thermoforming process) stops just at the moment of crystallization, understanding the crystallization behaviour of blends is important in this study. The crystallization behaviour of the blends was investigated using a PL differential scanning calorimeter (DSC) at 10°C/min heating and cooling rate. The samples were heated to about 250°C and then after some minutes were cooled down to room temperature, under nitrogen blanket.

### Melt Extensibility

To study the melt extensibility and melt strength of blends, two different methods were used. In the first method, the universal testing machine equipped by hot chamber is used to evaluate the extensional behaviour of resins at high temperature. The strips of 10 × 4 × 70 (mm), as the samples of this test, stamped out from injection molded sheet. The circulating chamber of tensile test

**Table 3.** Blends, specification containing HDPE.

| Blends No. | Blends desig. | PP1 (%) | PP2 (%)<br>PP3 (%) | PE | MFI (210 °C,2.16 kg) |
|---|---|---|---|---|---|
| B-1 | H-PE-1 | 50 | -<br>15 | 35 | 2.3 |
| B-2 | PE-H-2 | 50 | -<br>25 | 25 | 2.2 |
| B-3 | PE-R-2 | 50 | 15<br>- | 35 | 1.9 |
| B-4 | R-PE-1 | 50 | 25<br>- | 25 | 1.9 |

**Table 4.** Formulations of blends containing lcb EPDM and lcb PP.

| Blends No. | Blends desig. | PP1 (%) | PP2 (%)<br>PP3 (%) | PF814 (%)<br>EPDM (%) | MFI (210 °C, 2.16 kg) |
|---|---|---|---|---|---|
| C-1 | R-L-1 | 50 | 25<br>- | -<br>25 | 2.5 |
| C-2 | H-L-1 | 50 | -<br>25 | -<br>35 | 3.3 |
| C-3 | H-L-2 | 70 | -<br>15 | -<br>15 | 4.0 |
| C-4 | B-60-1 | 50 | 25<br>- | 25<br>- | 2.4 |

machine is set on 180°C and the samples left for 20 min to reach to test temperature. To find the differences between melt extensibility and melt extensional strength of samples, various test speed of 300, 400, and 500 mm/min were used. The gage length was fixed on 20 mm for all the samples. In the second method an instrument is designed and manufactured that is schematically shown in Figure 4. It consists of a small laboratory screw extruder with 19 mm screw diameter and 25 L/D and a proper take-off system. This apparatus can easily be used to obtain repeatable results. The applied torque to draw the melt strand as a measure of melt strength is recorded at various velocities of rollers.

Polymer melt strength is usually measured by a Gottfert$^{TM}$ Rheoten melt tension instrument [19]. In this instrument the polymer strand is produced by a plunger type extruder at very low output rate.

**Oscillatory Rheometry**

The viscoelastic characterization of melt was conducted by a Paar Physica Modular compact rheometer MCR 300, and a TC 30 temperature control unit. Two approaches are used to characterize the viscoelastic responses of polymer melts by this equipment. In the first approach the creep compliance of melt at 210°C for 150 s test duration was measured. To prepare the samples, pellets were compression molded into sheet of 1.2 mm in thickness. Sheets were stamped out with 25 mm diameter circular die. Tests were conducted at 210°C using 25 mm parallel plate geometry with 1 mm gap, at constant stress of 100 (Pa) for 150, and 300 s start delay time.

Another method of measuring the viscoelastic behaviour of molten polymers is measuring the damping factor (tan $\delta$) of material using a dynamic mechanical spectrometer. The parameter of tan $\delta$, as a measure of melt elasticity, was calculated via $G''$ divided by $G'$. This method involves measuring the torque resulting from an induced oscillatory strain on a molten polymer sample at 190°C. Once the sample is heated to a desired temperature for testing, one of the surfaces is then rotated relative to the other in a frequency of 1 rad/s. Maximum strain on the sample is usually limited to 10 percent to prevent strain induced effects by impacting the results. The time induced torque resulting from the induced strain is measured. The viscous or loss component of melt, $G''$ and the elastic component of it, $G'$ are measured accordingly.

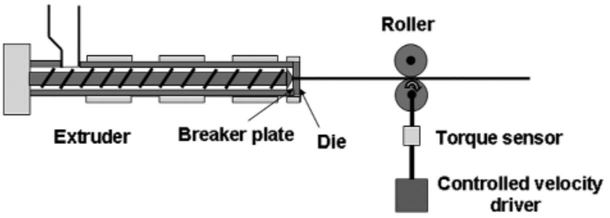

**Figure 4.** Schematic drawing of melt extension tester.

## RESULTS

The melt extensibility and melt strength of ternary blends of three standard linear polypropylene samples with different MFI were measured by two different methods. Hot tensile test was the first method that was used to study the behaviour of melt against tensile elongation force. The tests were conducted at 180°C and various crosshead speeds of 300, 400 and 500 mm/min. Figure 5 shows the effect of test speed on tension behaviour of melt. As it was expected increasing the test speed increases the tension forces.

The results at 500 mm/min were selected to investigate the melt strength of polymers. Figure 6 shows the hot tensile test results of three different blends. Melt tension instrument, which measures the torque required to pull out a strand of polymer melt from a die at a certain temperature were used for this measurement. The test results are summarized in Figures 7-12.

Figure 7 shows the melt extensibility of linear PP

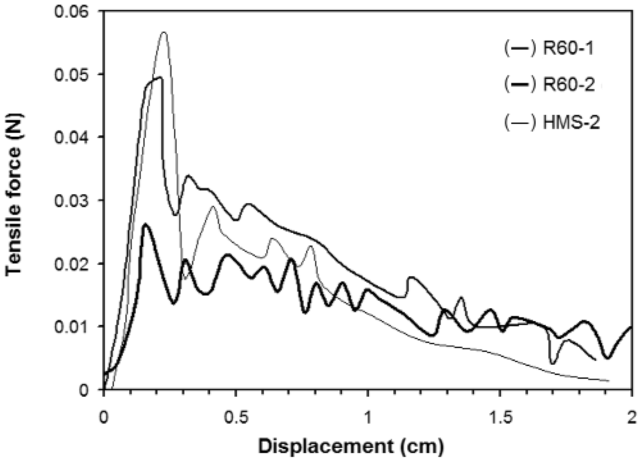

**Figure 5.** Effect of crosshead speed on hot tensile behaviour.

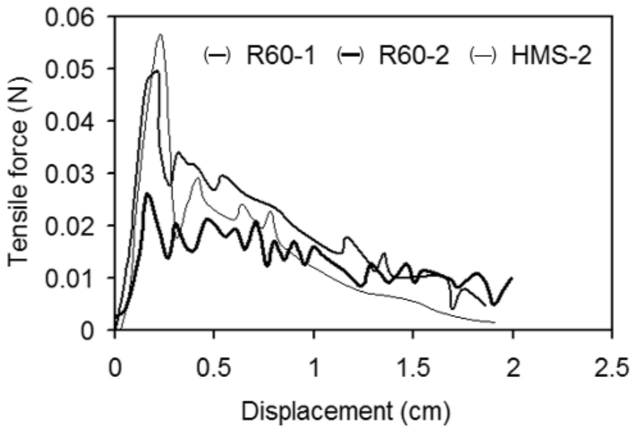

**Figure 6.** Hot tensile test for three PP blends.

blends. No significant difference was observed in the required torque to draw the strand for all formulations. It was observed that the blend (A-4) showed lower melt strength than what was expected and as the roller velocity is increased, the measured torque remained nearly constant.

It means that melt strength of linear pp ternary blends were nearly the same at different draw velocity, but the blend (A-4) showed higher extension rather than the other blends .The melt extensibility of this blend at high velocity of roller showed no break down of strand. The roller at high speed was not capable enough to pull out any of the small diameter fibril shape of extruded strand, and the torque values were not correct enough to be recorded.

To investigate the effect of short side chains of HDPE, the blends (B-1, B-2) and (B-3, B-4) were prepared. In these blends high molecular weight linear, PP2 and PP3, were replaced by low MFI high density polyethylene. Figures 8 and 9 show the melt extensibility of blends (B-1, B-2) and blends (B-3, B-1) respectively, By increasing the PE content from 25% to 35%, the melt drawability is improved and no significant effect on melt strength was observed. The curves of B-1 and B-3 in Figure 9 are nearly the same. These two blends have the same composition of PP1 (50%) and HDPE (35%) but in B-1 PP2 (15%) is replaced by PP3.

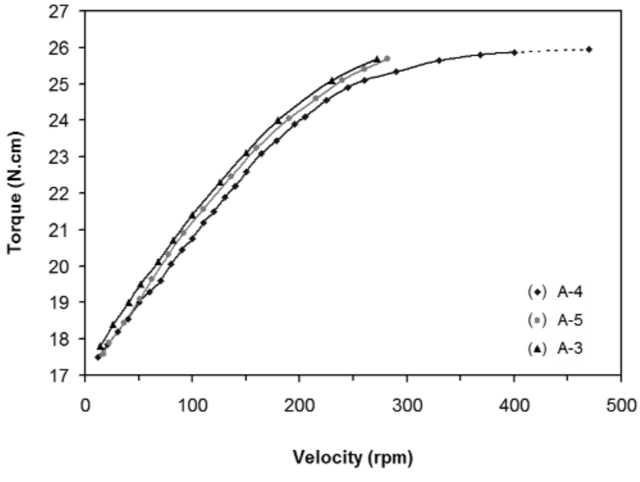

**Figure 7.** Melt strength study of linear PPs ternary blends.

As the molecular weight of two linear PP are nearly the same and the percentage of these two linear PP are not so much (15% and 25%), the melt strength graph of blends (B-1, B-3) that contain equal amounts of PP1 and PP2 are the same.

In Figures 10 and 11, the effect of three modal

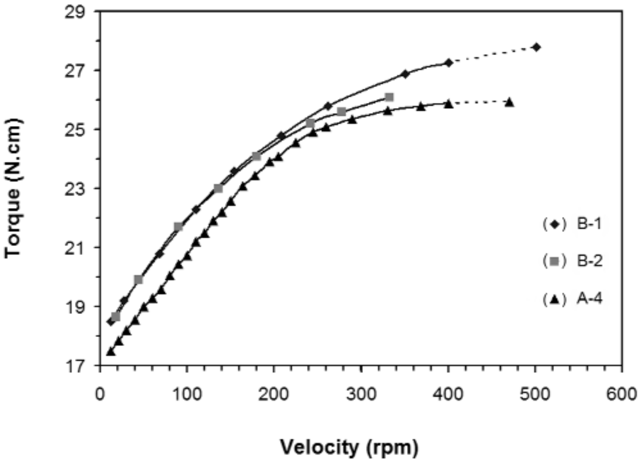

**Figure 8.** Effect of PE content on melt strength.

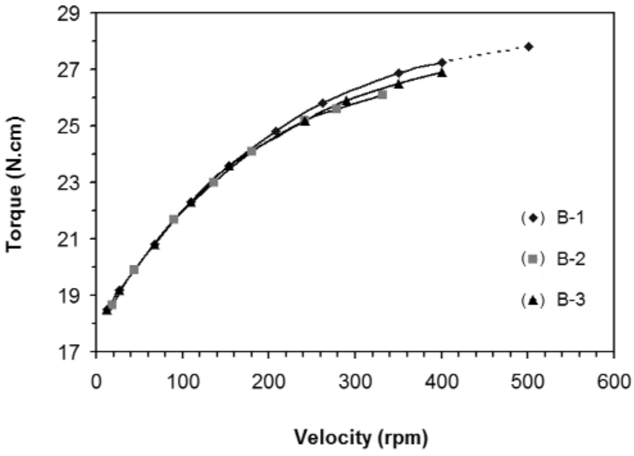

**Figure 9.** Effect of linear PP2 and PP3 on melt extensibility of blends.

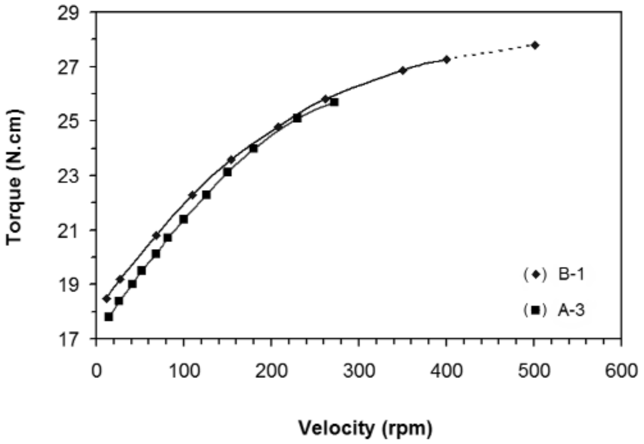

**Figure 10.** Effect of short side chain of PE to three modal molecular weight on melt strength.

molecular weight distributions on melt strength and melt drawability are shown and compared with side chain branch effect of PE on molecular entanglements.

The lcb EPDM has a flexible backbone with long side branches, which can play as nodal points for chain entanglements. In addition, lcb PP which was used in the blend (C-4) was a PP homopolymer that was changed to long chain branched structure via a post reaction treatment. Effect of molecular entanglements of these two polymers on melt strength and melt drawability of blends are shown in Figure 12.

By using constant amounts of PP1(50%) and PP2(25%) in the blends and adding PP3, HDPE, branched EPDM, and lcb PP, in the B-4, A-4, C-1, C-4 respectively, it is obvious that the blends with more elastic points of entanglements show higher melt drawability. Blend C-4 in Figure 12 that contains lcb PP showed superior melt extensibility.

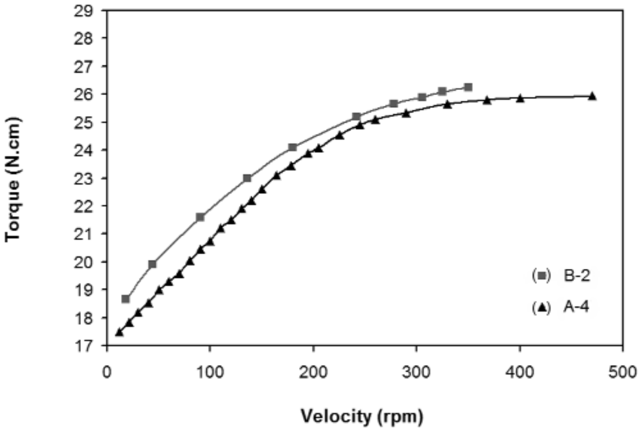

**Figure 11.** Effect of PE on melt extensibility comparing to HMW linear PP.

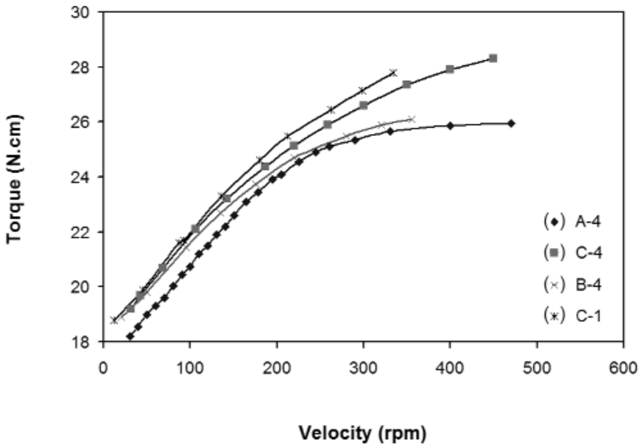

**Figure 12.** Effect of lcb EPDM, lcb PP, and PE on melt strength of blends.

As all the blends were designed for extrusion process, the target MFI was 3±1.5 g/10min. In this range of MFI, the melt strength of all blends has no significant difference, but the drawability was increased by increasing the PE and lcb PP. The same effect was observed in a certain percentages of linear PP in blend (A-4). We found that in this specific formula, the three modal molecular weight distribution showed a synergistic effect on melt strength and melt drawability. To interpret this phenomena, crystallization behaviours of blends were studied.

## Crystallization Study of Blends

The heat of crystallization ($\Delta H_{crys}$) and the peak tem-

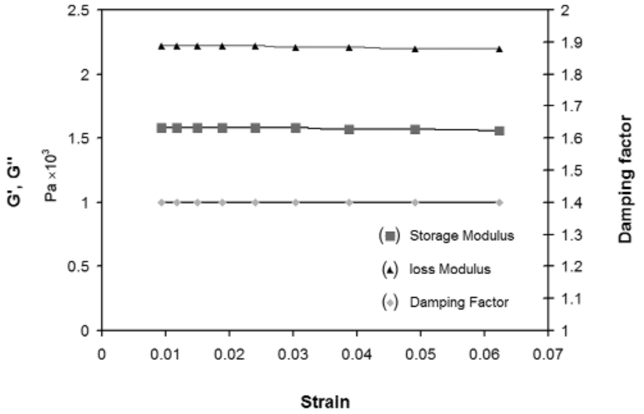

**Figure 13.** G′, G″ and Tan δ of polymer melt via dynamic mechanical spectroscopy analysis.

**Table 5.** Properties of linear PP Blends.

| Blends No. | Blends desig. | DSC | | Melt viscoelasticity | |
|---|---|---|---|---|---|
| | | $\Delta H_{cry}$ (mcal/mg) | $T_{Peak}$ (°C) | $J_{e0} \times 10^{-4}$ (1/Pa) | Tan δ |
| A-2 | R-2 | -14.1 | 112 | 1.5 | 2.35 |
| A-3 | R-H-2 | -13 | 118 | 2 | 2.33 |
| A-4 | H-R-1 | -11 | 112 | 3 | 2.31 |
| A-5 | H-R-2 | -20.1 | 121 | 2 | 2.32 |
| A-6 | HMS-2 | -15.6 | 110 | 2 | 2.32 |

**Table 7.** Properties of blends containing lcb EPDM and lcbPP.

| Blends No. | Blends desig. | DSC | | Melt viscoelasticity | |
|---|---|---|---|---|---|
| | | $\Delta H_{cry}$ (mcal/mg) | $T_{Peak}$ (°C) | $J_{e0} \times 10^{-4}$ (1/Pa) | Tan δ |
| C-1 | R-L-1 | -13.2 | 116.5 | 4.5 | 2.15 |
| C-2 | H-L-1 | -12.4 | 118.5 | 4.0 | 2.23 |
| C-3 | H-L-2 | -13.1 | 118 | 2.0 | 2.45 |
| C-4 | B-60-1 | -14.6 | 122.5 | 7.0 | 1.96 |
| - | PF814 | - | - | 14 | 1.4 |

perature ($T_{Peak}$) of all samples were measured that are presented in Tables 5, 6, and 7.

The heat of crystallization of blend (A-4) shows a minimum of 11 (mcal/mg) at specific blends compositions of 50/25/25.

## Elastic Behaviour of Melts

The damping factor and equilibrium compliance of blends, measured by dynamic mechanics spectroscopy method are summarized in Tables 5, 6, and 7. Both elastic and viscous nature of polymer melts were measured at frequency of 1 rad/s at 190°C, and maximum strain of 10 %. A sample graph of G′ and G″ are shown in Figure 13.

The changes of damping factors for the first set of experiments at different blend compositions were shown in Figure 14. It is found that the three modal molecular weight compositions have an effect on minimizing the tan δ at a certain level of composition. The lower tan δ means higher elasticity of melt and is more favoured in the above mentioned processes.

**Table 6.** Properties of blends containing HDPE.

| Blends No. | Blends desig. | DSC | | Melt viscoelasticity | |
|---|---|---|---|---|---|
| | | $\Delta H_{cry}$ (mcal/mg) | $T_{Peak}$ (°C) | $J_{e0} \times 10^{-4}$ (1/Pa) | Tan δ |
| B-1 | H-PE-1 | -17.5 | 116.5<br>111 | 4 | 2.1 |
| B-2 | PE-H-2 | -16.2 | 116<br>111 | 3.5 | 2.2 |
| B-3 | PE-R-2 | -18 | 116<br>111 | 4 | 2.11 |
| B-4 | R-PE-1 | -16.5 | 116.5<br>111 | 3.2 | 2.25 |

The steady state (equilibrium) compliance of melts were measured at a constant stress of 100 Pa at 210°C, for a period of 0-15 s. The compliance $J_{(t)}$ is given by (20) :

$$J_{(t)} = \gamma_{(t)}/\delta_0 = J_{e0} + (t/\eta_0)$$

Where:

$\gamma_{(t)}$ =strain

$\delta_0$ =stress

$J_{e0}$ =equilibrium creep compliance

$\eta_0$ = zero shear viscosity

The equilibrium compliance $J_{e0}$ is a measure of melt elasticity and is determined by first plotting strain vs. time at constant stress. The strain as a function of time is divided by the stress to give $J_{(t)}$. $J_{e0}$ is the intercept of $J_{(t)}$ against time plot (Figure 15).

The effect of chain branching of PE on melt elasticity was shown in Table 5. By increasing the PE content in the blends, the elasticity of melts was increased (lower tan δ), and the compliance measurement

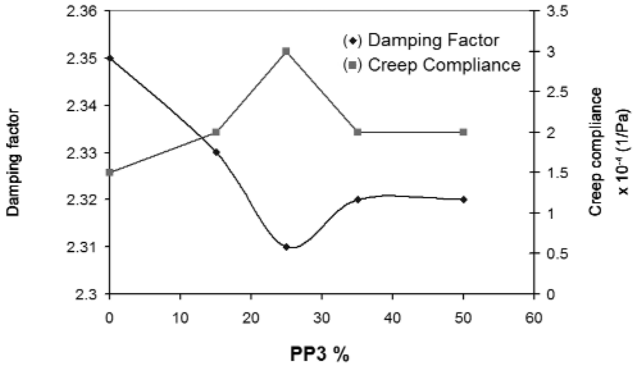

**Figure 14.** Tan δ and $J_{e0}$ of linear PPs ternary blends.

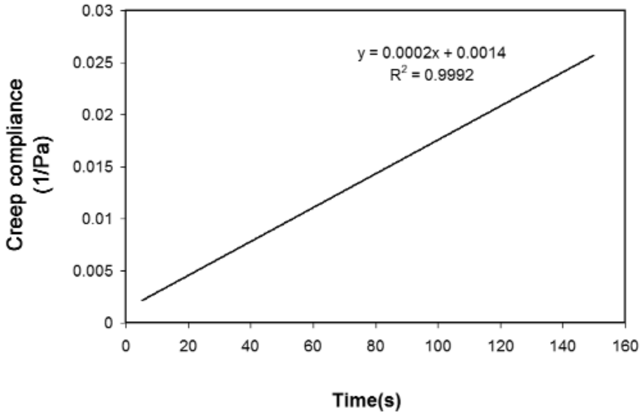

**Figure 15.** Calculation of equilibrium compliance by dynamic mechanical spectroscopy of polymer melts.

confirmed the tan δ results (Table 5).

Effect of long chain branch of EPDM on the melt elasticity (damping factor and compliance) of melts is shown in the Table 6.

At the same composition level, the lcb EPDM have better effect on the melt elasticity ($J_{e0} = 4.5 \times 10^{-4}$ ($Pa^{-1}$) for 25 wt% lcb EPDM) than polyethylene ($J_{e0} = 3.3 \times 10^{-4}$ ($Pa^{-1}$) for 25 wt% PE) . But it reduces the tensile strength and tensile modulus of resin significantly that is not acceptable for some applications.

The same behaviour is observed in the measurement of loss tangent of the blends. The loss tangent of the blends with lcb EPDM is tan δ = 2.11, compared to tan δ = 2.2 for the blends containing PE. Referring to longer chain branches on EPDM, the elasticity of melt is higher than standard PP and even higher than blends containing PE (with short side chains).

The melt elasticity of ternary blends containing lcb EPDM and two standards linear PP with different molecular weight was strongly depends on the EPDM rubber content. By decreasing the EPDM content to 15% in blend (C-3), the damping factor increased to tan δ =2.45, and the compliance decreased to $2 \times 10^{-4}$ ($Pa^{-1}$).

## DISCUSSION

Melt extensibility and melt strength is a consequence of the elastic behaviour of a material in melt state. The property is directly related to the numbers of elastically active nodal points, such as chain entanglements which prevent polymer chains from moving past each other in the melt state by applying stress or strain.

In melt tension test, the polymer melt being stretched undergoes uniaxial extension and offers resistance that is a consequence of molecular entanglements. Figure 1 shows schematic pictures of molecular architecture of standard linear PP, lcb EPDM [14], lcb PP, and HDPE [21].

Tensile test at high temperature was a time consuming method that could not distinguish the samples with small melt strength differences. As it was expected, by increasing the PP2 content in the blends, the melt strength is increased. Increasing the PP2 content in R-2 leaded to decrease the MFI. MFI is an index of shear viscosity. Tensile viscosity is at least 3 times (for Newtonian fluids) to a few hundreds (for none Newtonian fluids) higher than the shear viscosity [22].

The melt tension test by the manufactured equipment was a useful method to obtain rational comparisons among the melt extensibility behaviour of different polymers.

Melt strength and melt drawability are not well defined rheological properties [23], because during the stretching of the polymer neither the strain nor the temperature are uniform. Melt strength is also a function of temperature, so all the tests were conducted at constant temperature.

Three type of linear standard PP that was used in the first series of experiments have various molecular weight and distributions. Effect of bimodal molecular weight distribution on the melt strength and foamability of polymer resins were studied by blending two linear PP with different viscosities and molecular weight characteristics [5].

There are not any big differences between elasticity factors (i.e, tan δ, $J_{e0}$) of binary blends. To evaluate the effect of various linear high molecular weight PP on melt elasticity, the ternary linear PP blends were prepared and studied hereafter. It is found that at a specific proportion of components (blend A-4), the melt elasticity increases and the heat of crystallization decreases. It is believed that the higher intermolecular friction forces due to higher molecular weight, and possible molecular entanglements prevents the free movement of chains to go to lamellas to build a crystal structure.

Experiments showed that selection of suitable low and high molecular weight components in the blends and their relative proportion are important to improve the melt elasticity by molecular frictions.

By refering to the result of melt tension tests, no significant difference in melt strength was observed between the different blends. The blend (A-4) showed the same melt strength but higher melt drawability.

Lower heat of crystallization of A-4 is an evidence of higher proportion of molecules in amorphous phase, which is due to resistance of molecular ties to move in to crystals. Lower heat of crystallization can also addresse to weak nucleation effect in the blend (A-4). The blend compositions can affect crystallization of resins. Higher heat of crystalisation of A-5 can be due to nucleating effect of PP3 in the blend.

The higher compliance of $3 \times 10^{-4}$ ($Pa^{-1}$) and lower tan $\delta$ of 2.31 compared to other blends of ternary linear PPs (Table 5) are evidence of higher intermolecular force in blend (A-4). The test result of damping factor and steady state compliance of ternary blends of liner PPs showed improved properties but it is not good enough for extrusion foaming. The tan $\delta$ and $J_{e0}$ of pure branched PP (Hifax Pf 814) based on the measurement of this study were 1.4 and $14 \times 10^{-4}$ ($Pa^{-1}$), respectively (Table 7). It is reported different tan $\delta$ and $J_{e0}$ for lcb PP [24] based on homopolymer, block, or random copolymers. For a conventional PP block copolymer with MFI = 0.4 (Profax7823), it is reported tan $\delta = 1.63$ [25]. The tan $\delta$ of conventional linear PP2 measured in this study was 1.96. In addition, for the same grade of lcb PP which is used in this study tan $\delta$ of 1.2 is reported [25].

In some other studies the $J_{e0} =(3.3\text{-}3.7) \times 10^{-4}$ ($Pa^{-1}$) for a linear PP and $J_{e0} =(14.0\text{-}22.0) \times 10^{-4}$ ($Pa^{-1}$) for various grades of high melt strength PP were reported [4] .The differences of measured tan $\delta$ and $J_{e0}$ between our study and literatures is probabably due to various test parameter setting, and also the higher thickness of samples of 1.75 mm comparing to 1.0 mm in this study. Park et al. [26] disclosed that by the resins with tan $\delta$ of 1.69 (about 38% higher tan $\delta$ than 1.22 of lcb PP) still can make a closed cell and low density foams, while resin with tan $\delta$ =1.83 failed to be foamed in the same process. The equilibrium compliance $J_{e0}$ also can be used as an index for melt elasticity and melt strength study.

When polymer melts are deformed, polymer molecules not only slide past each other, but they also tend to uncoil or at least they are deformed from their random coiled-up configuration. On releasing the deformation stresses these molecules tend to revert to random coiled-up forms. Since molecular entanglements cause the molecules to act in a co-operative manner because of recoiling, some recovery of the shape occurs corresponding to the elasticity of melts.

The total deformation of a melt during the flow, composed of viscose flow and a high elastic deformation due to chain uncoiling [24]. An increase in molecular weight, leads to higher viscosity, reduces the rate of viscose deformation, and increases the proportion of deformation due to chain uncoiling. Consequently, elastic effects tend to be more important in high molecular weight materials. The PP3 is a high melts strength high molecular weight linear PP with lower amount of low molecular weights. The PP2 is a high molecular weight linear PP with broad molecular weight distribution. The low molecular weight portions of this material reduce the melt elasticity of the blends. This effect was observed before [26].

However the HDPE improved the factor of melt elasticity, but for lowering tan $\delta$ and elevating $J_{e0}$ values, the PE content of blends has to be increased. Increasing the PE content of blend higher than 35% will decrease the service temperature and heat resistance of blends that may not be convenient for some applications.

The blends (B-3) and (B-4) showed better elasticity factors (tan $\delta$, $J_{e0}$) ,comparing to blend (B-1) and (B-2), it is because of PP3 resin in the blend that contain lower amount of low molecular weight PP.

To investigate the long side branch effect on melt elasticity controlled long chain branched high moony viscosity EPDM and long chain branch homopolymer are used. The long side chain branch of EPDM is connected to main chain via a norbornen group and is more flexible than long chain branches on PP homopolymer.

The standard linear PP2 (blends (B-1), (B-2) and PP3 (blends (B-3), (B-4)) was replaced with a pipe grade HDPE. The HDPE is a linear material which have some short side chains. The MFI of blends are 2.2±0.3 g/10 min. The elasticity of the melts of these blends containing HDPE (at 25% and 35%) are improved and the results confirm that even short branch HDPE improve the melt drawability due to molecular entanglements. The higher melt drawability of blend (B-2) in Figure 8 comparing to B-4, is because of higher tie nodes of molecules. It is also found that PP3 compared to PP2 has better effect on melt elasticity and melt drawability in the blends B-2 and B-4. It is due to higher amounts of low molecular weight molecules in PP2 resin which has a broad MW distribution.

These small molecules make the slippage of other bigger molecules easier in the tension process. Although, they will show higher strength at the start of small deformations, in melt drawability, but by enlarging the deformation, these small molecules can not provide enough interactions to resist versus higher elongational deformation.

## CONCLUSION

The melt extensional characteristics of PP blends containing PE, lcb EPDM and lcb PP were studied and compared. To investigate the effect of side chain branch on molecular entanglements and therefore on melt extensibility, several formulation were prepared. The experimental works in this study lead to the following conclusions:

1- Ternary blends of linear PPs, in a certain composition showed an improvement on melt strength comparing to other proportions. The heat, onset, and peak of crystallization of these blends showed lower values. Despite the better elastic behaviour of these blends in melt state, among the other ternary blends of standard PPs, they were not elastic enough comparing to the blends containing a branched polymer.

2- High molecular weight, high density PE, as a blend's composition showed an improvement on melts strength. The melt extensibility increased by increasing the PE content, and showed an improvement on tan δ and creep compliance as melt elasticity index.

3- Long chain branch EPDM, showed an improvement on melt elasticity indexes on higher percentages of 20%. In this percentages the tensile strength and elastic modulus decrease significantly that is not preferred for many applications. At lower content of 15%, no effect on melt elasticity is observed.

4- Branched PP, showed a distinct effect on melt extensibility and melt elasticity indexes. With the same percentage, the blends containing lcb PP, improved significantly the melt extensibility and melt elasticity indexes comparing to lcb EPDM and HDPE.

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