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ORIGINAL PAPER

Influence of branching on the rheology and morphology of melt state long-chain branched polypropylene/polybuten-1 blends

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ABSTRACT

In this study, the compatibility of polypropylene (PP)/polybutene-1 (PB-1) homopolymer blends before and after a long-chain branching process was studied. The blends were prepared and long-chain branched directly via a reactive extrusion process in the presence of a free radical initiator and trimethylolpropane trimethacrylate (TMPTMA) poly functional monomer. The optimum percentage of TMPTMA and PB-1 resin was determined by measuring the grafting efficiency and by studying the rheological behavior in steady state shear and transient extensional mode and the morphology of samples was investigated by scanning electron microscopy (SEM). The morphology observations, which were also approved by rheological data, demonstrated an enhanced compatibility for the blend branched with 1.5wt% of TMPTMA and 10wt% of PB-1 resin. The highest grafting efficiency of 37% and branch index of 5.2 were achieved for this blend composition. The zero-shear viscosity (η_0) of PP increased from 4500 Pa.s to 6800 Pa.s after branching process, and further enhanced to 2400 Pa.s by using 10 wt% PB-1 resin. The long-chain branched structure of blend resulted in a prominent higher zero-shear viscosity, a longer relaxation time and a pronounced strain-hardening behaviors. The branch index of blend samples were determined, and their branching behavior was quantified using extensional viscosity data. **Polyolefins J (2019) 6: 1-11**

Keywords: Long-chain branching; extensional rheometery; polybutene-1; TMPTMA; branching index.

INTRODUCTION

Isotactic polypropylene (PP), a fast growing commodity resin with many desirable and beneficial physical properties, including high stiffness, resistance to corrosive chemicals, low specific gravity and good processability with reasonable prices is widely used in different industries like automotive, packaging, home appliance, fiber industries and etc. [1]. Such desirable properties have made it one of the most widely used thermoplastics since Ziegler-Natta discovery in 1955, especially when it is compared with other commodity thermoplastics, such as polyethylene, in all its forms, and PVC. It costs less to produce and does not have the difficulties often present in recycling of PVC [2]. However, in commercial linear polypropylenes, absence of side branches leads to low melt strength. As a result, its use has been limited to such applications as extrusion coating, blow molding, profile extrusion, and thermoforming [1, 2].

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Long branches on PP backbone increase molecular entanglements and enhance melt strength. Numerous attempts have been made to produce long-chain branched polypropylene directly using constrained metallocene catalysts [3, 4, 5] or by grafting process. Grafting of long chain branches onto linear backbone is the most commercially attractive and efficient way to enhance the melt strength of linear polymers like poly (ethylenetherphetalate) [6] and polypropylene [7, 8]. It can be carried out by using ionizing irradiation, such as electron beam or gamma ray radiation [6] or with using peroxides and free radical co-agents via reactive extrusion process [7, 9]. Chain-scission, crosslinking and grafting are the competing reactions during grafting process, resulting in branching structures. It has been proposed that the chain-scission and degradation reactions in the radical functionalization of PP can be controlled by using co-agents, such as furan and thiophene derivatives. It is found that these agents significantly prevent the decrease in molecular weight of PP by grafting onto the backbone and promote the reaction with the macro-radicals formed through H-abstraction [10, 11].

A vast number of researches have been carried out on the modification of PP to achieve low-density foam parts and to improve in-mold foaming behavior of expanded polypropylene beads (EPP) [11, 12, 13]. The molding of EPP requires high steam pressure to melt the surface layer and to allow diffusion and sintering of pre-expanded beads to enhance the quality of parts. With the use of PP derivative or its copolymers with double melting peak [14, 15] or by using the multilayer beads expandable at low steam pressure [16] it is possible to expand the beads at lower steam pressures.

Polybutene-1 is a polyolefin showing typical properties of commodity polymers, as well as some properties of engineering polymers. It can be used as a blend component to improve the properties of other polyolefins. In PE films, polybutene-1 can improve sealing performance, the ability to peel with controlled force, flexibility, and temperature strength [17]. Polybutene-1 can improve the impact strength, tear strength, puncture resistance, optical properties [17,18,19], flow characteristics, creep, ultimate elongation, heat seal ability [19,20] and weld line strength [1] of PP. There are relatively few studies on polypropylene/polybutene-1 blends and their crystallization and morphology behaviors. It has been found that the main effect of irradiation on polybutene-1 is chain scission [20, 21]. Solid state blending of PP/PB-1 and the role of PB-1 on the long chain branching of PP by electron beam irradiation in solid state, and the melt viscoelastic and dynamic viscoelastic behaviors of polypropylene/polybutene-1 blends and their correlation with morphology have been studied [22]. The miscibility and compatibility of PP and PB-1 blends was the subject of various investigations [21, 22]. It has been reported that there are not any specific interactions between PP and PB-1 in their blends, and the balance between the dispersive and entropic driving forces implies miscibility in some compositions [22]. The miscibility and compatibility of PP/PB-1 blends have been evaluated by measuring glass transition temperature, T_g, using dynamic mechanical analysis (DMA) [23]. As it was observed a single glass transition temperature over the entire composition ranges, it could be concluded that these two polymers were miscible [23]. It is necessary to note that the T_g of PP and PB-1 is close to each other and their difference is less than 20°C, about 13–16.5°C [19], and due to the broadness of PB-1 damping peak, DMA method is not capable to differentiate the damping peaks of these two polymers, and consequently it is not accurate enough to announce their miscibility and compatibility. In another study, according to the results obtained by differential scanning calorimetry (DSC), thermo mechanical analysis (TMA), and based on the statistical calculations, it was concluded that the PP and PB-1 are compatible [23]. The depression of the melting temperature and crystallization rate of PP were used to study the compatibility of this blend. It was concluded that PB-1 as a miscible diluent affected the crystallization behavior of PP and the two components were compatible in the amorphous phase [22-23]. There are also some contradictory reports on the miscibility of PP/PB-1 blends [22]. In one study, it was detected two glass transition temperatures (T_g) in ultra-quenched samples prepared by compression molding process. According to these observations it could be concluded that, PP and PB-1 were highly compatible but the miscibility was difficult to obtain by ordinary melt mixing processing. The percentage of PB-1 may also affect the miscibility and compatibility of the components [23]. It was shown that the blends were miscible in PB-1 content of less than 20 wt % or higher than 80 wt %, and were immiscible in the middle composition range. As the DSC and DMA techniques are incapable to detect the micro-heterogeneities smaller than 50 nm in the blends, observing a single T_g for a blend cannot be attributed to the miscibility in molecular level, therefore, it should be confirmed by other analytical methods. Although, the melt blending of PP/PB-1 is an effective method to produce a new high melt strength PP base resin, there is no any publication or open literature survey regarding to melt state branching of PP/PB-1 blends and the role of PB-1 in branching process. The novelty of this investigation lies in the effect of PB-1 on the branching of PP prepared by reactive extrusion in the presence of a multifunctional monomer, a primary antioxidant and a peroxide, likewise studying the effect of the additive that participating in chemical reaction of branching process.

EXPERIMENTAL

Materials and methods

The PP homopolymer used in this work was a Moplen HP500H of Shazand Petrochemical Company, Iran, and the polybutene-1 homopolymer (PB 0110M) of Lyondell Basell, Germany with density of 0.914 g/cm3, both as pellet form with a melt flow rate of 2 g/10 min (230°C; 2.16 kg). The polyfunctional coupling agent, tri-methylol propane tri-methacrylate (TMPTMA), and dicumyle peroxide (DCP) were obtained from Aldrich Company.

All blends were prepared in different compositions of PB-1 (0, 10, 20, wt %) along with different percentages of TMPTMA (0.5, 1, 1.5, 2, 3wt %) and DCP (0.03, 0.05, 0.07, 0.1wt %). The physically hand mixed components were blended in a L/D 40 co-rotating lab twin-screw extruder Brabender, Germany. The mixing was carried out at 80 rpm and the temperature profile of 180–200°C from the hopper to die. The same compounding conditions were applied to neat PP and PB-1 resins, and also to the blends, to ensure a unique thermo-mechanical history. The prepared samples were injection molded at melt temperature of 185°C.

Gel fraction was measured gravimetrically by immersing the samples in xylene at 140°C for 12 h. The residue was dried to a constant weight during 1 hr at 150°C in a vacuum oven. Three pieces were used to determine the average gel content for each sample (ASTM D 2765).

MFI of the samples was measured with an MFI instrument (Zwick 4100, Germany) at 230°C under a loading of 2.16 kg (ASTM D 1238).

The rheological measurements were carried out using a Rheometrics Mechanical Spectrometer, RMS 800, Anton Paar, Germany, on a 25-mm diameter disc obtained from 1.5 mm sheets in the oscillation mode. The linear viscoelastic behavior of the samples was investigated in a frequency range of 0.01–600 rad/sec with the strain amplitude of 5% which was determined by strain sweep test at a frequency of 10 rad/sec at 180°C. Continuous nitrogen purging of the environment chamber was necessary to inhibit oxidative degradation of the blends.

Samples were also rheologically characterized in simple extension mode using SER Universal Testing Platform that was used with MCR301 rheometer and CTD450 convection oven (Anton Paar). Extensional viscosity was measured at constant Hencky strain rates of 0.01–1 1/s at 180°C on samples with dimension of 15×1.0×0.5 mm^3.

The extent of grafting was evaluated by FTIR spectra obtained using a Bruker-IFS 48 instrument, Germany. To purify samples before the test, they were dissolved in hot xylene at 140ºC and precipitated by methanol and filtered to extract the non-grafted polymerized monomers from the PP/PB-1 and PP/PB-g-TMPTMA blends. To remove the residue of solvent, the samples were dried in a vacuum oven at 70ºC to constant weight and hot pressed to thin films at 180ºC.

RESULTS AND DISCUSSION

Formulation Design

In branching of polypropylene through a reactive extrusion process, peroxide and polyfunctional monomers are two major chemical agents which affect the branching efficiency and architecture. Three competing reactions, including degradation or scission, crosslinking and grafting control the branching process. DCP was used to make the chain scission and macro-radicals, while TMPTMA a three functional acrylic-base monomer was used as grafting promoter, and irganox1010, a primary antioxidant was used to control the degradation. Hence, as Fig 1-a shows, the increase in DCP content lonely increases the vis-breaking of PP, but when DCP is used with a multifunctional monomer like TMPTMA, the MFI value changes moderately since the grafting reactions which leads to form the branches occurs simultaneously.

The DCP content of the formulation is selected based on the target MFR of around 7±1 g/10 min for the final branched product. In this regard, PP was reactively mixed with various amounts of DCP in the extruder and the MFR of samples was determined. As seen in Fig.1-a, a target MFR of ≈ 0.07 wt% is required for DCP.

TMPTMA as a polyfunctional monomer (PFM) promotes the branching as well as crosslinking reactions. The TMPTMA content of samples was optimized based on the minimizing of the crosslinking of PP. To reach the optimum DCP and TMPTMA content, PP was branched with various amounts of TMPTM and DCP and the gel content of samples was determined. The formulation of 24 samples and their gel contents are surveyed in Table 1. For a gel-free sample with a required MFR, the required TMPTMA content is around 1.5 wt%.

Optimization of TMPTMA content

The amount of TMPTMA was optimized by measuring grafting efficiency and rheological data. In this regard, PP and its blend with 10wt% of PB-1 were branched with various amounts of TMPTMA from 0.5 up to 2 wt% at a fixed DCP content of 0.07 wt%.

Table 1. Effect of peroxide and polyfunctional monomer percentages on the gel content.

TMPTMA	Gel Content (wt %)			
wt%	0.03%DCP	0.05%DCP	0.07%DCP	0.1%DCP
0.0	0.00	0.00	0.00	0.00
0.5	0.00	0.00	0.00	0.00
1.0	0.00	0.00	0.00	0.00
1.5	0.00	0.00	0.00	0.8±0.1
2.0	0.00	0.00	0.5±0.1	1±0.1
3.0	0.00	0.65±0.1	1.8±0.1	3.5±0.1

The grafting efficiency (GE) can be measured by various methods, such as titration [24], gravimetrically [25] or by using FTIR technique [23]. A good agreement has been reported for grafting of a vinyl monomer onto PP between the results obtained by these methods [26]. The FTIR results sometimes are preferred because of large experimental error involved in measuring the weight increase after grafting [27]. In this study, the extent of grafting has been quantified by FTIR spectra of samples by using a calibration curve [28]. The calibration curve (Figure 1-b) was built by calculating the ratio CI=A1735/A1464 as carbonyl index of different blends obtained by melt mixing of PP and TMPTMA, where A1735 belongs to IR absorbance peak area of the stretch vibrations of carbonyl group of TMPTMA, and A1464 belongs to the area of the peak of CH_3 groups of PP and PB-1[29]. As seen in Table 2, the highest grafting efficiency belongs to PB10/T1.5/D0.07 sample with 1.5 wt% monomer.

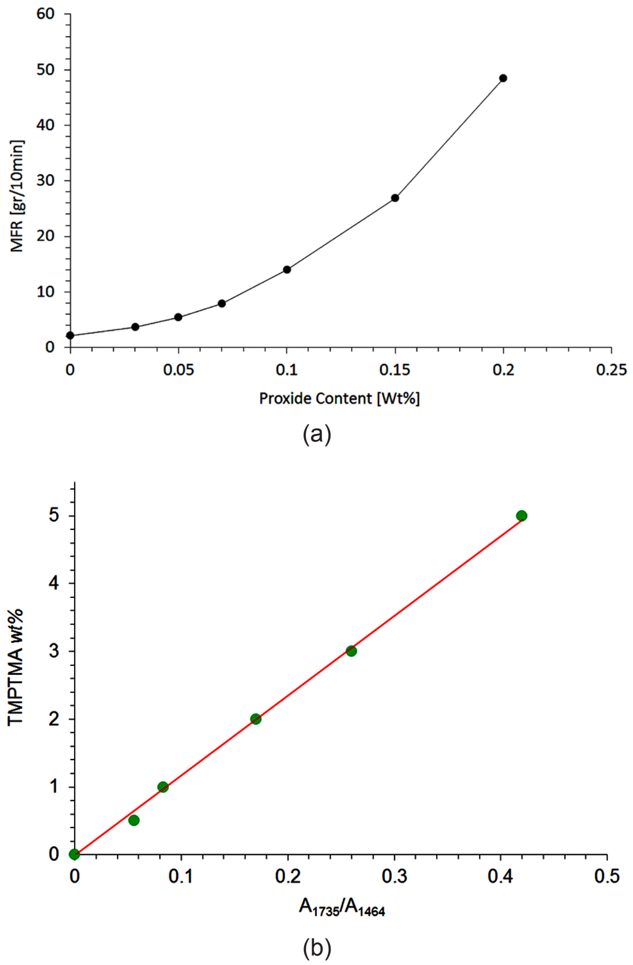


Figure 1. a) effect of DCP wt% on the melt flow rate of PP, b) Correlation of carbonyl index and TMPTMA wt%.

Table 2. Effect of PFM content on the grafting and shear thinning behavior.

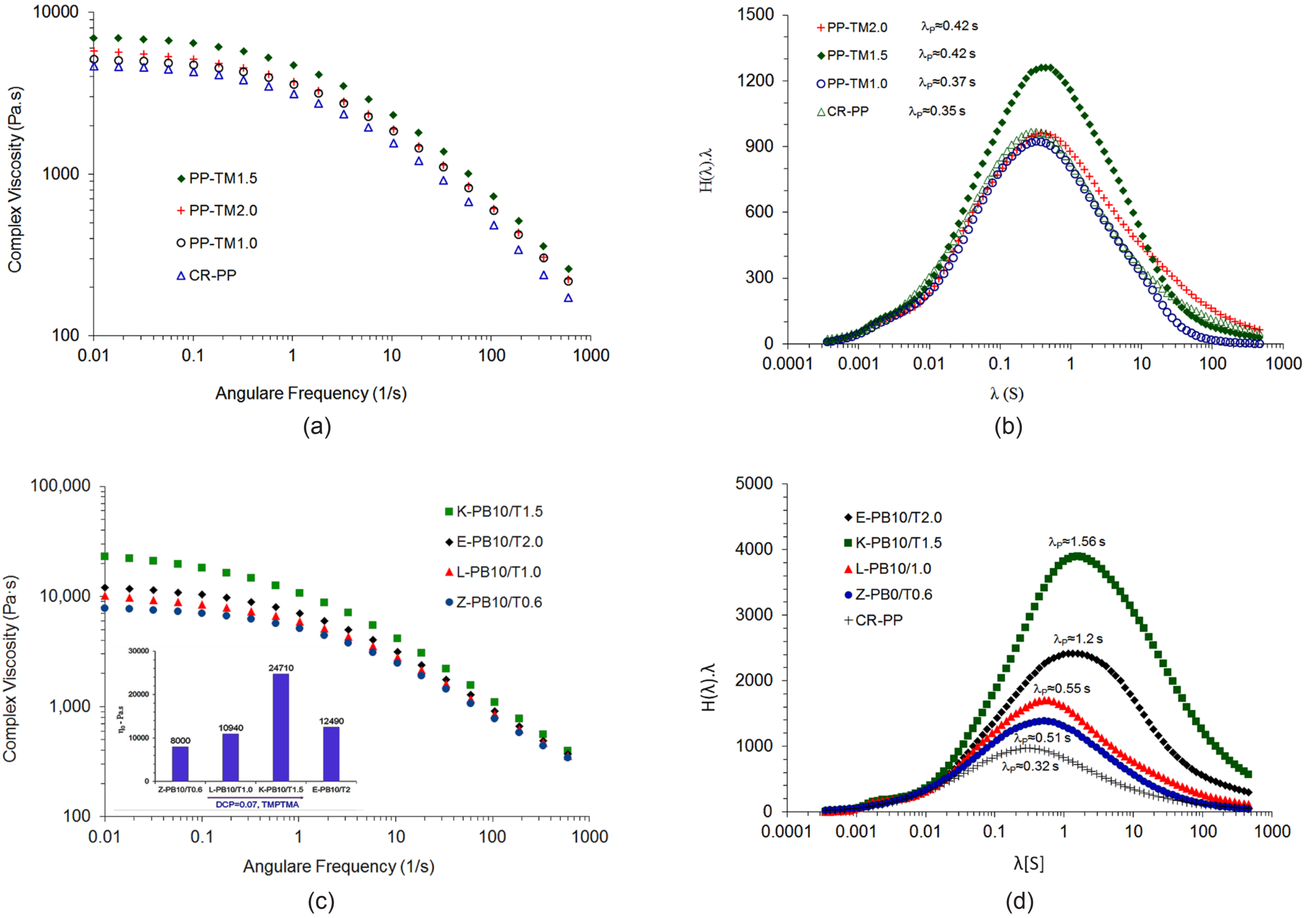
Sample	PFM	A1735/ A1464	GE %	Shear Thinning Index-n'
Z-PB10/T0.6	0.6	0.007	12.8	0.58
L-PB10/T1.0	1.0	0.012	13.2	0.54
K-PB10/T1.5	1.5	0.049	36.9	0.49
E-PB10/T2.0	2.0	0.025	14.1	0.49

The complex viscosity (η*) at various angular frequencies, η_0 and relaxation time spectrum of branched PP and branched PP+10wt%PB-1 blends are shown in Figure 2a-d. It can be seen that for both PP and its blend with PB-1, the complex viscosity and relaxatin time of samples grafted by 1.5 wt% of TMPTMA is above those of other samples. The η_0 of samples was determined by fitting the experimental data to the Cross equation. The samples branched with 1.5 wt% of TMPTMA showed maximum zero shear viscosity of 7100 Pa.s and 24700 Pa.s for PP and PP/PB-1 blends respectively.

Compatibility Evaluation

The morphology of the blends before and after branching can be seen in the SEM images shown in Figure 3-a and b, respectively. At 10 wt% of PB-1, the blends before branching (Figure 3 a1) show a droplet matrix morphology, which changed to a nearly continuous phase after branching [30]. The rheological test results approved the increased homogeneity at the low PB-1 percentage. By increasing the percentage of PB-1, the size and the number of droplets decreased. This decrease was more pronounced for the sample containing 30 wt% PB-1 as compared to other samples.

A number of attempts have been proposed to correlate and quantify the long chain branch numbers to shear rheology data [31, 32, 33, 34]. The change in η_0 of linear samples in comparison to its branched counterpart with similar molecular weight has been pro-



(a) (b)

(c) (d)

Figure 2. Effect of TMPTMA wt% on the a) complex viscosity of PP, b) relaxation spectrum of PP, c) complex viscosity of (PP+10wt% PB-1), d) relaxation spectrum of (PP+10wt% PB-1).

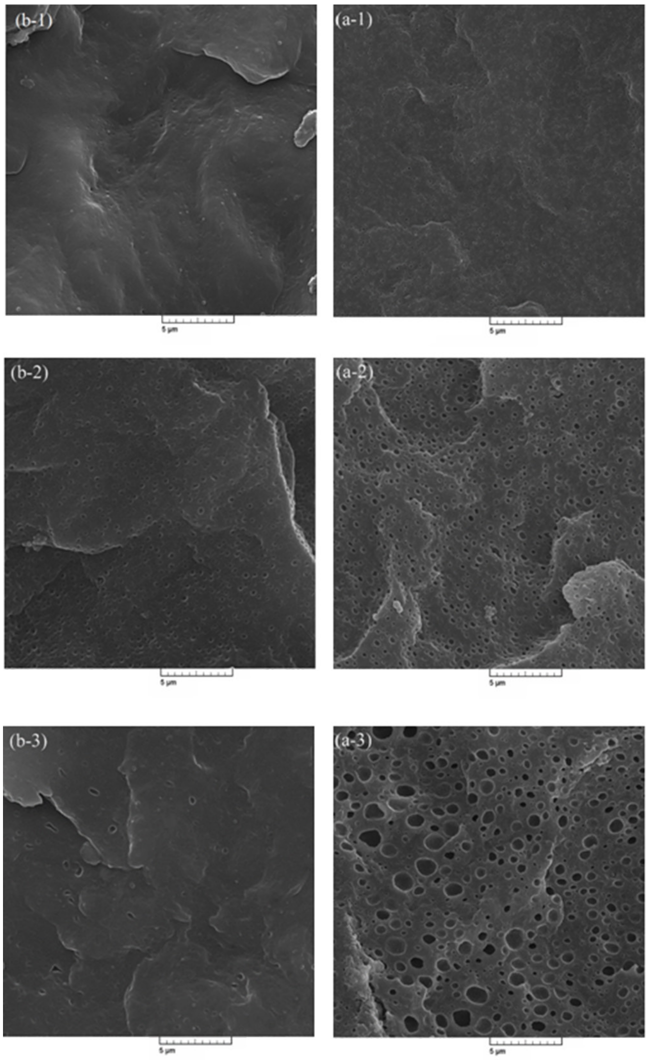


Figure 3. SEM images of samples a)before branching and b) after branching for 1- 10, 2- 20 and 3- 30 wt% of PB-1.

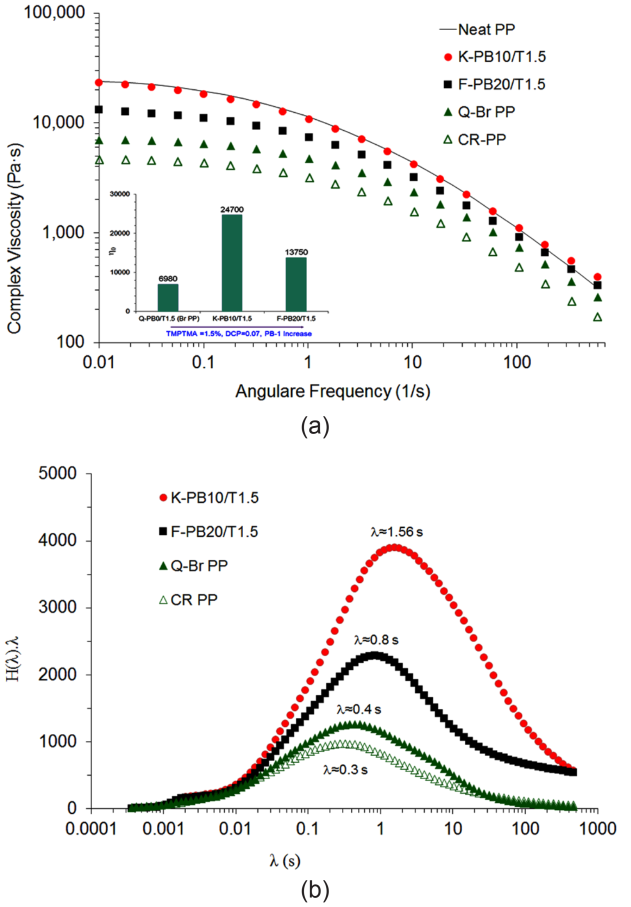
posed as an index for long chain branching [35]. These efforts have been extended in some studies even to the cases that the molecular weight changes [36].

The complex viscosity at a wide range of frequencies are shown in Figure 4-a for neat PP resin (one time extruded), peroxide-treated PP (CR-PP), and PP branched in the presence of 10wt% PB-1 (K-PB10/T1.5) and 20wt% PB-1 (F-B20/T1.5). It can be seen that the η_0 of linear PP increases from 4600 Pa.s to 6950 Pa.s after branching process, and to 24000 and 12000 Pa.s by using 10 and 20 wt% of PB-1, respectively. Long chain branches (LCB) may affect η_0 in two competing aspects [37]: first, it can increase the possibility for entanglements in the polymeric melt leading to increase zero shear viscosity, and second, the radius of gyration decreases compared with that of the linear chain with the same molecular weight [38].

It is found that the maximum increase in η_0 after branching process belongs to the PP +10wt% PB-1 blends. The optimum weight fraction of 10% PB-1 has been found also for solid state branching of PP by electron beam irradiation [22].

The long chain branches structure can be specified also when the length of branches is more than 2.5 times of the molecular weight at the onset of entanglement M_c [39]. The increased number of entanglement due to long chain branch structure further improves the melt elasticity and enhances the relaxation time. The relaxation time spectra of linear PP and branched samples containing up to 20 wt% PB-1 are compared in Figure 4-b. It is seen that due to branching, the peak of the curves has shifted to longer times, obviously, for the blend containing 10wt% PB-1.

In the branching of PP/PB-1 blends, a complicated set of reactions, schematically shown in Figure 5, may happen.



(a)

(b)

Figure 4. Effect of PB-1 resin on the a) complex viscosity, and b) relaxation time spectrum of branched PP.

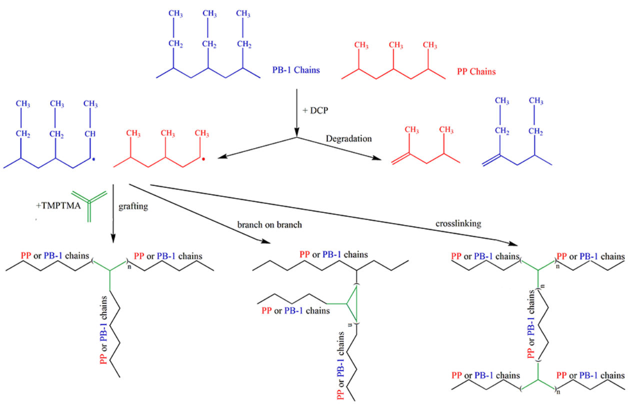


Figure 5. Schematic of possible reactions of branching process.

PP and PB-1 may a) branch separately, b) they may graft on each other, c) a long chain of PB-1 may graft onto the PP backbone or d) a long chain of PP may graft onto the PB-1 backbone. The PB-1 macromolecules grafted on the PP backbone, or vice versa, can play the role of an efficient compatibilizer and affect the rheology and morphology of the blends.

Optimization of monomer and PB-1 content by branching efficiency

Many efforts have been made to investigate the efficiency of branching process by shear rheology data and also by transient elongational flow behavior. Schreiber [35] proposed the $\frac{\eta_{0,lin}}{\eta_{0,br}}$ ratio simply as an index of long-chain branching. In the study of mPEs [34, 37] it has been found that at low levels of branching the η_0 increases with branch number and reaches a maximum and then decreases at higher values of branch number. This is while the shear thinning becomes stronger by increasing the branch number. The higher shear thinning index of PB10/T1.5, compared with that of PB10/T2.0, revealed the higher branching number at 1.5 wt% TMPTMA, approving its higher grafting efficiency (Table 2) [40,41]. The TMPTMA polar monomer is not soluble enough in the PP a polar polymer [41]. It is believed that the extra amount of monomer with limited solubility in polymer promotes

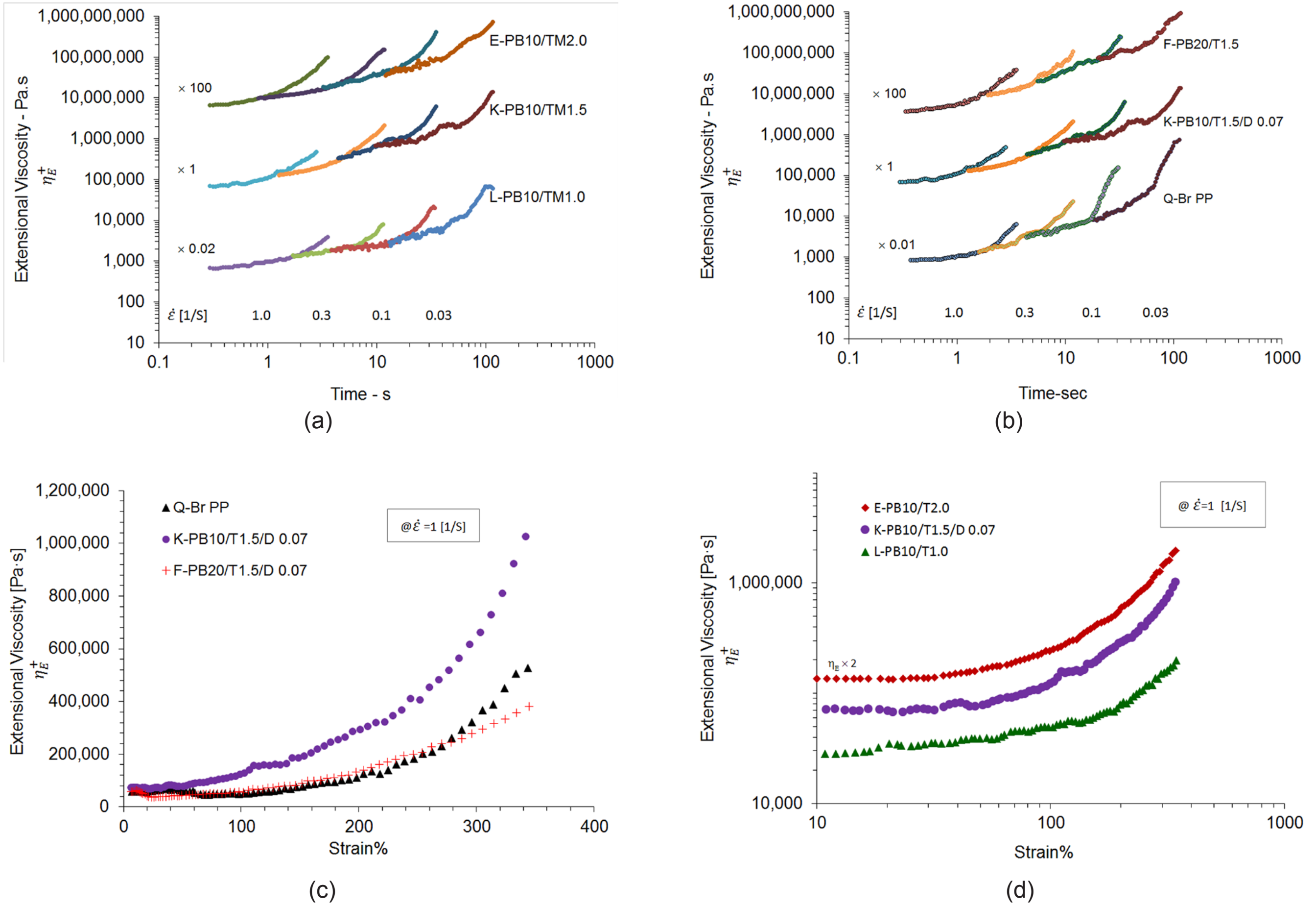


Figure 6. Extensional viscosity of samples a) at various strain rates and wt% of PB-1, b) at various strain rates and wt% of TMPTMA monomer, c) effect of PB-1 on the η_E^+ at $\dot{\varepsilon}$ =1, d)effect of TMPTMA monomer on the η_E^+ at $\dot{\varepsilon}$ =1

Table 3. Effect of PB-1, TMPTMA and DCP content on SHI, BI and onset strain.

	PP/PB wt%	Sample Designation	SHI	BI	
Effect of PB	100/0	Q-Br PP	5.3	3.7	251
(DCP= 0.07 and	90/10	K-PB10/T1.5/D 0.07	9.2	5.2	247
TMPTMA=1.5 phr*)	80/20	F-PB20/T1.5	7.7	3.6	198
Effect of TMPTMA%	90/10	L-PB10/T1.0	10.6	4.7	222
(DCP=0.07 phr*)	90/10	K-PB10/T1.5/D 0.07	9.2	5.2	247
	90/10	E-PB10/T2.0	4.3	2.4	202
Effect of DCP%	90/10	P-PB10/D 0.05	9.9	5.8	238
(TMPTMA=1.5 phr*)	90/10	K-PB10/T1.5/D 0.07	9.2	5.2	247
	90/10	R-PB10/D 0.1	5.6	3.7	253

*Phr: Part hundred resin

the homopolymerization reactions of TMPTMA and does not enhance the branching number.

Transient elongational flow measurement is a known method to study long chain branched structures [42]. Long chain branches increase the number of entanglements in the melt and intensify its strain hardening behavior [43, 44]. Strain hardening is a phenomenon that at a certain Hencky strain-rate the elongational viscosity rises above the linear viscoelastic start-up curve. The effect of PB-1 and TMPTMA monomer on the extensional viscosity of samples at various strain rates are shown and compared in Figures 6-a,b,c and d. As it can be seen, all of the samples show the strain-hardening behavior, revealing the formation of sparsely long-chain branched structures [37, 42].

By increasing the number of long chain branches, the melt strength increases with an enhanced strain hardening behavior. The extent of branching can be quantified by directly measuring the extensional viscosity of the melt at two different strains. The ratio of extensional viscosity at the strain of 3 to the extensional viscosity at the strain of 0.3 in logarithmic scale has been introduced as strain hardening index (SHI) [41]. Recently, in another work, the SHI of long chain branched PP is determined by the slope of tensile stress growth function against Hencky strains in the range of 1 to 3 s^{-1}. It is proposed that this ratio should not be less than 0.15 for a good foaming behavior [45].

The efficiency of long chain branching process, in this work, is evaluated by obtaining the onset of strain hardening behavior as the reference point. In this method, the ratio of extensional viscosity at onset strain to the onset extensional viscosity is considered as branching index for strain hardening behavior at a strain rate of

$$BI = \frac{\eta^{+}_{E,\varepsilon_{onset}} - \eta^{+}_{E,onset}}{\eta^{+}_{E,onset}} \qquad (1)$$

The definition of $\eta^{+}_{E,\varepsilon_{onset}}$ and $\eta^{+}_{E,onset}$ are shown in Figure 7 for a branched sample. The SHI and BI of samples are calculated and surveyed in Table 3. As seen at 10wt% PB-1, the BI and SHI have the maximum values of 5.3 and 9.2, respectively, which confirm the findings in shear rheological behavior. The same trend is observed for the BI of the sample with 1.5 wt% TMPTMA with a maximum BI of 5.2 and a highest

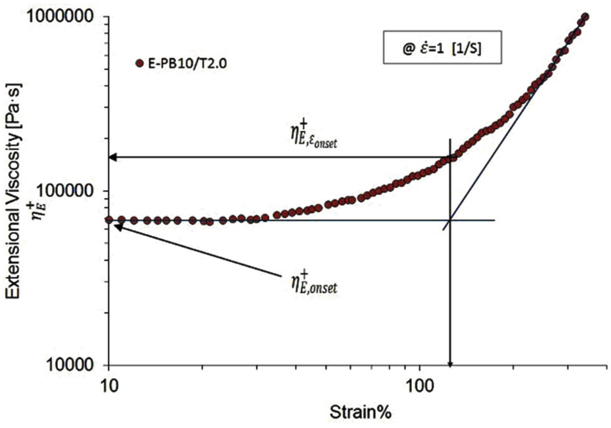


Figure 7. Definition of $\eta^{+}_{E,\varepsilon_{onset}}$ and $\eta^{+}_{E,onset}$.

onset strain of 247. Therefore, BI can predict the strain hardening behavior in a better coincidence with grafting and shear rheological data than the SHI.

CONCLUSION

This study was performed to investigate the effect of long-chain branching on the compatibility of PP with PB-1, and to understand the architecture of polypropylene homopolymer (PP) directly branched via a reactive extrusion process in the presence of polybutene-1(PB-1), DCP-free radical initiator and TMPTMA co-agent. This investigation led to the following conclusions:

It was demon strated that the maximum grafting of TMPTMA monomer onto PP occurred at the beginning of gel formation. By increasing the TMPTMA content, the grafting efficiency increased up to an optimum percentage and declined afterward, and thereby, gel started to form simultaneously.

The optimum percentage of TMPTMA monomer for grafting on the PP polymer backbone was about 1.5wt%. It was concluded that blending of PB-1 with PP did not change the optimum usage level of PFM.

PB-1 resin significantly affected the branching of PP in melt state and enhanced the efficiency of branching.

The SEM images revealed that the melt state branching of PP/PB-1 blends considerably improved the compatibility, a result that is not expected for the solid state branching process.

The enhanced compatibility of the blend branched by 1.5wt% TMPTMA and 10wt% for PB-1 resin was approved by the highest grafting efficiency and branching.

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