Rheological Evaluation of Electron Beam Irradiated Polypropylene in the Presence of a Multifunctional Monomer and Polybutene Resin

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ABSTRACT: In this research, the rheological properties of electron beam irradiated polypropylene homo polymer (PP) containing Polybutene (PB) resin and Trimethylol Propane Trimethacrylate multifunctional monomer is studied. The effect of PB resin in inducing long chain branches on the PP backbone are evaluated by various viscoelastic parameters. The zero shear viscosity (η_0) of samples containing 5% PB resin considerably decreased to 5500 Pa s, from $\eta_0 = 11,500$ Pa s, which indicates the plasticizing effect of PB resin on the ease of movement of PP macromolecules. It is found that the presence of PB resin enhanced the branching by facilitating the movement of PP macromolecules in solid state and increasing the recombination efficiency of PP macro radicals. The mobilizing effect of PB resin also reduced chain scission and degradation of PP resin which is traced by shifting the cross over frequency. The PB free radicals formed during the irradiation process can bound to PP free radicals and suppress the degradation process. The evaluation of zero shear viscosity ratios and crossover point ratios of irradiated samples to un-irradiated ones confirmed that using small amount of PB resin increase branching efficiency, which is the evidence of mobilizing effect of PB resin. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2036–2041, 2012

Key words: polypropylene homopolyme; polybutene; electron beam; branching; mobilizer

INTRODUCTION

Polypropylene (PP) is a widely using commodity plastic due to its excellent properties in balance with low price. It is a linear polyolefin with low extensional melt strength that do not exhibit strain hardening behavior as a vital characteristic is the processes such as thermoforming and foaming.[1,2] The long chain branches on the PP backbone effectively increase the melt strength and melt extensibility and can be created industrially by electron beam irradiation of PP in solid state[3,4] or by the chemical modification through a reactive mixing process.[5,6] PP structure is prone to chain scission which in both of the aforementioned processes, compete with grafting and crosslinking reaction. Multifunctional monomers generally use to improve the efficiency of branching and to decrease the degradation of PP.[5–7] The chain scission, branching, and crosslinking are main phenomena in irradiation process which can take place simultaneously in the PP. Controlling the irradiation condition, sample atmosphere, and using multifunctional monomers can inhibit degradation and may change the condition in favor of generating long chain branches.[4,8] It has been reported that using Pentaerythritol Triacrylate together with a peroxide through reactive mixing process, increased the branched structure in PP.[9]

The irradiation of neat PP resin without any additives despite formation of few branches predominantly leads to significant decrease in molecular weight due to β-chain scission.[3] To increase the efficiency of branching in irradiation process, several researches has been performed by using Trimethylol Propane Trimethacrylate (TMPTMA) as a multifunctional monomer,[10] and irradiation of PP in solid state in an acetylene atmosphere.[1]

The PP architecture can also be modified in melt state. Grabling, used the Tetra Ethyl Tiuram Disulphide (TETDS) as an Iniferter with peroxide and TMPTMA multifunctional monomer to create branches on PP backbone through reactive extrusion. It is believed that TETDS reacts with the free radicals produced during the process, and this dominates the formation of branched structure over the degradation process.[11] The use of mobilizers has been attempted to decrease the degradation of polymers irradiated by high energy rays.[12] The mobilizers are low molecular weight substances

which increase the free volume and facilitate the movement of molecules in the amorphous portion of semicrystalline polymers. The mobilizing effect of this material minimizes degradation during and after the irradiation and prevents the loss of properties due to irradiation process.[12–14]

In this research, Polybutene (PB) oligomer for the first time is used as a mobilizer and oxidation depressant in the branching process of PP in the presence of TMPTMA by electron beam irradiation. PB resin can play the role of a mobilizer and oxidation suppressant simultaneously. The viscoelastic parameters obtained by rheological measurements are used to evaluate the effect of PB resin in the formation of long chain branches on the PP backbone. The complex viscosity data of samples at various irradiation dose rates showed a good coincidence with Cross equation.

EXPERIMENTAL

Materials

The Isotactic PP homo-polymer in this study was the commercial grade Moplen HP500H, supplied by Arak Petrochemical Company, Iran, with melt flow rate of about 2.15 g/10 min (230°C, 2.16 kg) according to ASTM D1238. The PB oligomer, PB2400, supplied by Daelim Company, Korea. The PB oligomer is a water white nonpolar resin with low molecular weight (Mn = 2450 g/mol) and high viscosity. It is hydrophobic and impermeable to water vapor or gas. TMPTMA is a trifunctional monomer supplied by Aldrich Company, Germany.

Sample preparation and tests

Mixing of materials according to the formulations of Table I was performed using Internal Mixer (Haake SYS 90-Germany) with Banbury blades at 180°C and 60 rpm. PB was added to PP melt and after 4 min TMPTMA is fed into the mixing chamber. The total mixing time for samples was 9 min.

Electron beam irradiation

The samples were irradiated by a high power industrial Electron Beam Accelerator of the Rhodotron type in Yazd Radiation Processing Center. The energy of accelerated electrons was 10 MeV with 4 mA beam current. The high energy of the accelerated electrons enhances the penetration of beam within the samples.

Oxygen during irradiation accelerates the chain scission reactions in PP and PB and leads to severe degradation. The granules and dumbbells of samples were packed in the five layers polyamide—polyethylene bags with the thickness of 0.8 mm, and then

TABLE I
Formulation of Samples

Sample	% wt		
	PP	PB	TMPTMA
PPT	99.6	0	0.4
PBaT	94.6	5	0.4
PBbT	89.6	10	0.4
PBcT	84.6	15	0.4

vacuumed up to 99%, and sealed after purging with pure Nitrogen gas by means of a Henkeleman food packaging device.

The packed samples were irradiated in different doses, 25, 50, 75, and 100 kGy at room temperature. To avoid temperature increase of the samples, the irradiation at higher doses was performed with step by step, change of 25 kGy in each step. After irradiation, the samples were annealed under Nitrogen atmosphere for 30 min at 80°C, to enhance the mobility of free radicals and then 90 min at 130°C to deactivate the residual free radicals.

Oscillation rheometry

Oscillatory shear rheological analysis was performed with a Paar Physico Modular Compact Rheometer MCR300. The angular frequency range was 0.01–600 rad/s, and the temperature was 180°C. Strain was kept at 5% in the linear viscoelastic range of deformation. The measurements were conducted under dry Nitrogen environment to prevent degradation. The sample with 25 mm diameter and the thickness of 1.5 mm were prepared by compression molding at 180°C.

Thermal stability of the irradiated samples was checked by time sweep test at a constant angular frequency of 1 rad/s and strain amplitude of 1% and temperature of 180°C to ensure the consistency of the molecular structure during the time of experiments.

Gel content

Gel content of the samples was determined by extracting the soluble components in boiling Xylene for 18 h. Then the residue was dried to constant weight during 1 h at 150°C. (ASTM D2765-95). The gel content was calculated by a weight ratio of the dried gel to the irradiated samples.

RESULT AND DISCUSSION

Gel content

Under the experimental condition used, the modified PPs are gel-free, revealing no crosslinking in the samples.
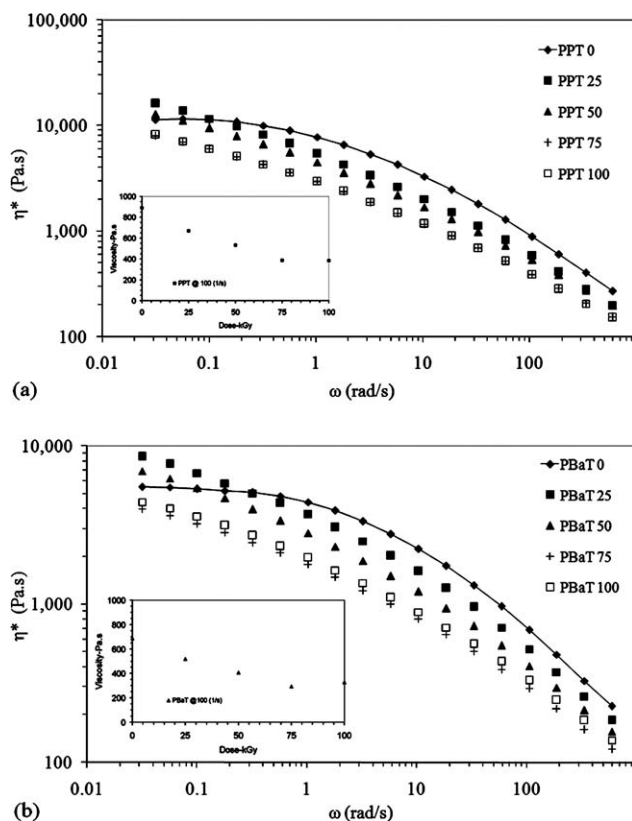
Figure 1 Complex viscosity of the un-irradiated and irradiated samples against angular frequency: (a) PPT samples and (b) PBaT samples.

Complex viscosity

The dynamic shear viscosity (η^*) of samples against angular frequency (ω) at various irradiation doses are shown in Figure 1(a,b). The un-irradiated samples showed Newtonian-plateau at low frequencies, which is broader for the samples treated by PB resin. The zero shear viscosity (η_0) of samples containing PB resin considerably decreased for example from $\eta_0 = 11,500$ Pa s for PPT0 to $\eta_0 = 5500$ Pa s for PBaT0, indicating the plasticizing effect of PB resin on the ease of movement of PP macromolecules.

By increasing irradiation dose the complex viscosity of samples at medium and high range of shear rates are decreased. The increase of viscosity at 100 kGy is more significant for the samples containing PB resin. By increasing irradiation dose to 100 kGy, the PP molecules divide to smaller species which promote the recombination efficiency of macro radical. This effect is more pronounced in the presence of PB resin due to its mobilizing effect. The chain ends of PB resin contribute free volume. The extra free volume associated with chain ends improves chain mobility of PP molecules.

The rheological behavior of materials at low frequency is sensitive to their molecular architecture. Small amount of long chain branches affect zero

shear viscosity, and the shear thinning behavior in comparison with linear polymer with similar molecular weight.[15]

The inducing of long chain branches on the PP backbones has two controversial effects.[15] First, the radius of gyration decrease compared with that of the linear chain of the same molecular weight. The decreased radius of gyration results in fewer entanglements and a lower viscosity.

The second effect of branching occurs when the branch length is sufficiently long for entanglement. This happens when the molecular weight of branches becomes comparable with critical molecular weight for entanglement of linear chains. The enhanced entanglement of branches, longer than the critical entanglement length, causes a large increase of η_0 at high molecular weight and long branches.[16]

As is seen, the transition from Newtonian-plateau to shear thinning, power-law region are shifted to lower frequencies that is the evidence of long chain branches in polymer structure.[17]

The complex viscosity of samples can be correlated to frequency by Cross equation:[9]

$$\eta^*(\omega) = \frac{\eta_0}{1 + (\lambda\omega)^{n'}} \tag{1}$$

where λ is relaxation time which inversely related to ω at the onset of shear thinning region and n' is shear thinning index. In Table II, the values of n' and λ are shown. As is seen, η_0 and λ of irradiated samples are higher, and shear thinning index is lower than its un-irradiated counterparts. The complex viscosity of irradiated samples at low frequencies is higher than un-irradiated ones, while they are

TABLE II
Cross Rheological Model Parameters and Terminal Slops

| Sample	n'	η_0(Pa.s)	λ (s)	Terminal slope
PPT0	0.69	11,400	0.36	1.52
PPT25	0.62	17,500	2.23	0.81
PPT50	0.57	16,000	3.6	0.87
PPT75	0.53	13,800	7.88	0.85
PPT100	0.53	14,800	8.08	0.85
PBaT0	0.64	5510	0.23	1.6
PBaT25	0.6	9950	1.7	0.93
PBaT50	0.54	8980	3.1	0.93
PBaT75	0.51	6900	5.2	1
PBaT100	0.5	7500	6.9	1
PBbT0	0.64	4420	0.2	1.65
PBbT25	0.58	6200	0.95	1.1
PBbT50	0.52	4500	1.2	1.25
PBbT75	0.45	3200	1.8	1.37
PBbT100	0.45	2900	3.5	1.47
PBcT0	0.62	3620	0.2	1.65
PBcT25	0.56	3800	0.48	1.3
PBcT50	0.5	1700	0.3	1.4
PBcT75	0.42	900	0.27	1.55
PBcT100	0.44	2000	0.94	1.37
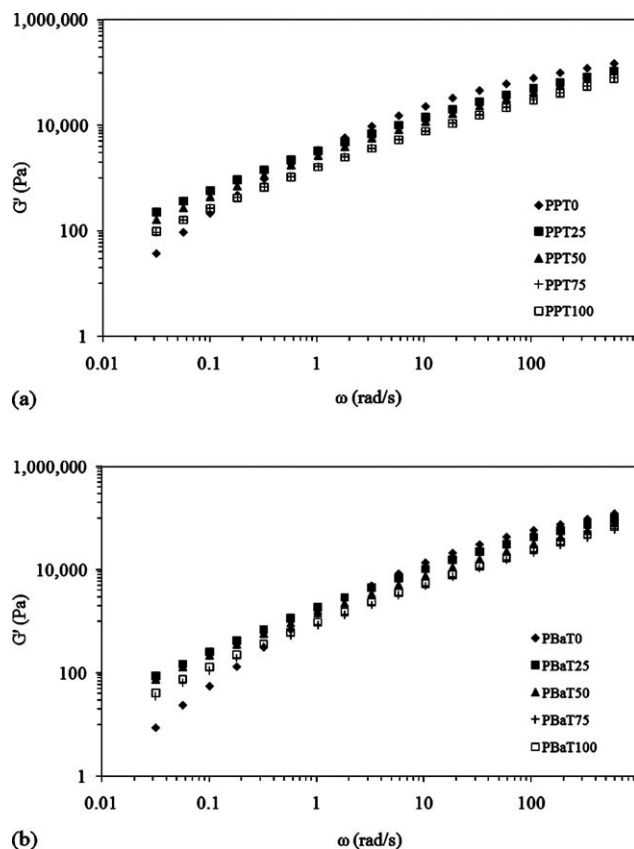
Figure 2 Storage modulus of the un-irradiated and irradiated samples against angular frequency: (a) PPT samples and (b) PBaT samples.

smaller at higher frequencies in power-law region. This is typical behavior of long chain branched polymers.[18]

The formation of branched structure is evident in the viscosity behavior. The Newtonian-plateau disappeared by forming branched structure and the onset of shear thinning is shifted to lower frequencies. A similar behavior has been reported elsewhere.[19]

The shear thinning behavior is practically an important aspect of materials. The shear thinning index of samples (Table II) is changed considerably for the samples irradiated at 25 and 50 kGy, and no more significant changes were observed at higher dose rates than 75 kGy. The branching process often broadens the molecular weight distribution and in this respect, it is difficult to separate the effects of these two.[20]

It has been shown that, the polydispersity of isotactic PP homopolymer do not change very much and showed an slight decrease (narrower molecular weight distribution) by the irradiation from 4.2 to 3.6 ± 0.2 depending on dose rates.[3] Therefore the changes in rheological parameters of PP can be attributed to induced branching effect of irradiation process.[3]

Storage modulus-G'

Branching also may affect the storage modulus.[18] The G' of samples against angular frequency is shown in Figure 2(a,b). In the terminal zone, the behavior is dominated by the longest relaxation time and storage modulus and loss modulus (G'') of linear polymers follow the well-known frequency dependency.[16,21] The terminal behavior can be seen in Figure 1(a,b) for un-irradiated samples of PPT0 and PBaT. The G' of all irradiated samples were increased at low frequency and were deviated from terminal behavior. The deviation from terminal behavior of irradiated samples can be attributed to longest relaxation time of long chain branched structure formed by recombination of macromolecules generated by high energy electron beam. The terminal slope of G' before and after irradiation is shown in Table II. The higher terminal slope of PBaT and PBbT samples comparing with PPT is because of PB resin which its molecular weight decrease more by irradiation of electron beams.

Effect of the quantity of PB resin

The amount of PB resin in the formulations affects the zero shear viscosity ratio (the ratio of η_0 of irradiated sample to its un-irradiated counterpart) of samples (Fig. 3). The best result is obtained for the PBaT sample that its viscosity ratio is bigger than other samples. Thess results show that using small amount of PB resin increase branching efficiency, which is the evidence of mobilizing effect of PB resin. At higher PB resin content, its plasticizing effect is more pronounced than its effect on branching, and their viscosity ratio is lower than untreated PPT sample.

Cross over point

The cross over point is a point at which the value of storage modulus equals the value of loss modulus.
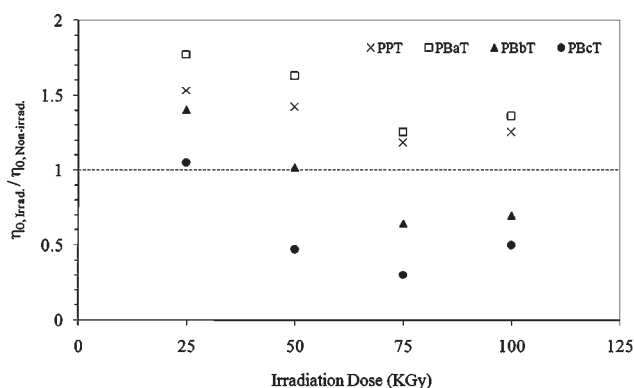

Figure 3 Cross over frequency ratio against irradiation dose of PPT and PBaT samples.
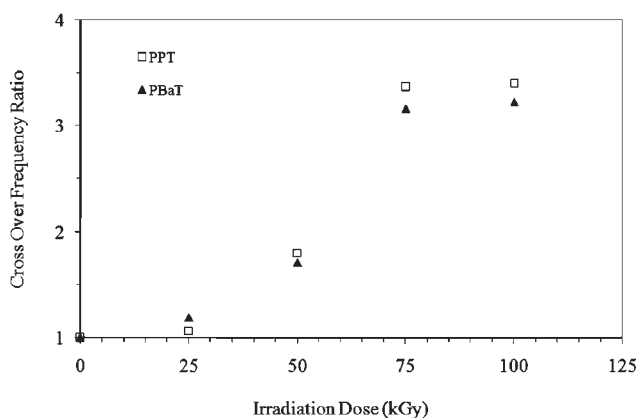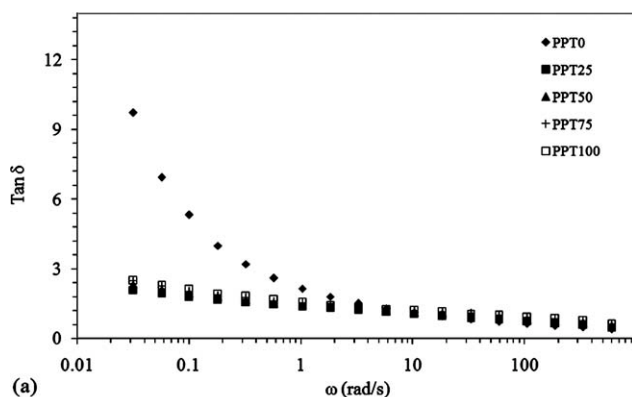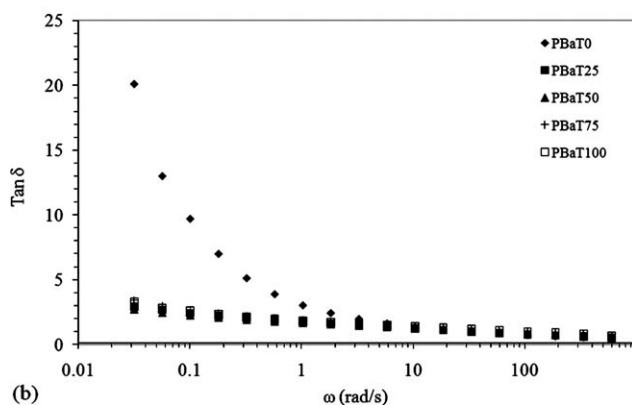
Figure 4 Zero shear viscosity ratio of samples at various irradiation doses.

The cross over frequency (ω_c) moves to lower angular frequencies by increasing average molar mass and enhancing melt elasticity. This is because at higher angular frequencies shorter molecules remain mobile, whereas longer molecules and branched one are immobile even at lower angular frequencies.[3,22] To be able to differentiate between the effect of PB resin and the effect of electron beam irradiation on the molecular mass and molecular topology, the ratios of cross over frequency of irradiated samples to cross over frequency of un-irradiated ones are compared in Figure 4. It is found that samples containing PB resin show lower cross over frequency ratio whose behavior is more significant at higher doses than 25 kGy.

The irradiation of semicrystalline material in solid state affects the amorphous region and the molecules on the surface of crystallites.[23] The PB resin such as plasticizer increase the free volume and serve to mobilize the molecules in amorphous part and enhance branching by recombination of macro-radical and reduce degradation by promoting radical termination reaction consequently. Generally hydrocarbon oil, greases, waxes, and dioctyphetalate may play the rule of plasticizer.[12–14]

Loss tangent and modified Cole-Cole plot

Loss tangent is also a measure of polymer damping behavior which inversely can be correlated to elasticity.[9,24] The tan δ–ω diagram of samples are shown in Figure 5(a,b). It can be seen that the tan δ of irradiated samples show a drastically decrease in all range of applied irradiation. The variation of tan δ of irradiated samples is small and nearly independent of angular frequency for all dose rates. This behavior

Figure 5 Loss tangents of the un-irradiated and irradiated samples against of angular frequency: (a) PPT samples and (b) PBaT samples.
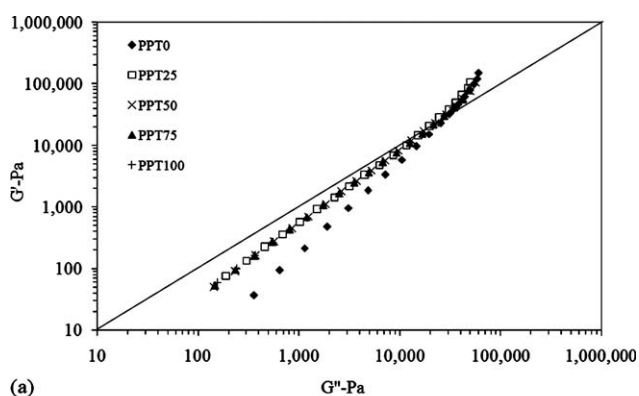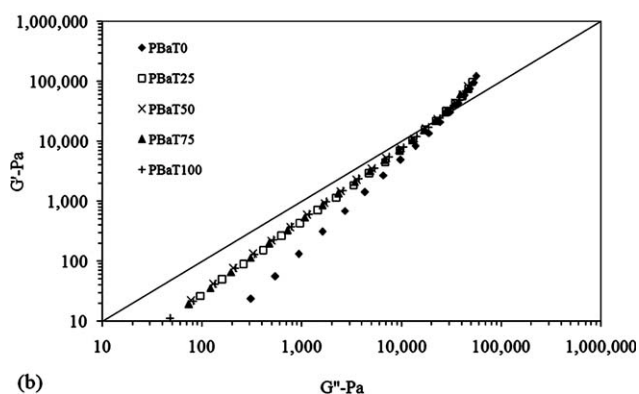
Figure 6 Han plots for the un-irradiated and irradiated samples: (a) PPT samples and (b) PBaT samples.

addresses the increase in elasticity of the melt of irradiated samples.

Modified Cole–Cole diagram—well known as Han plot—is a way to evaluate the change in the elasticity of materials.[2,25] The analysis of viscoelastic properties by Han plot is selected here as it is nearly independent to temperature and also weight average molecular weight which change during the irradiation process. In Figure 6(a,b), G' were plotted against G'' for various samples in PPT and PBaT categories. As is seen, the slope of Modified Cole–Cole plots for irradiated samples were decreased and deviated more toward reference line of $G' = G''$ which is the evidence of enhanced elasticity and longer relaxation mechanism of irradiated samples. The improvement in the elasticity of irradiated samples may be attributed to the presence of long chain branched structures. The simultaneous plasticization effect of PB resin is evident by comparing the slopes of the plots for irradiated samples with and without PB resin in Figure 6(a) (from 1.48 for PPT0 to about 1.2 for PPT50) and Figure 6(b) (from 1.6 for PPaT0 to about 1.2 for PPaT50).

CONCLUSION

This study is peformed to understand the role of PB resin on electron beam irradiation of PP in solid state to prepare long chain branched structure. The architecture of irradiated samples was evaluated by interpreting the rheological data determined by small amplitude oscillation rheometry. This systematic study leads to the following conclusions:

- PP homo polymers become branched in presence of TMPTMA multifunctional monomer, by irradiation with electron beams even at low doses and under Nitrogen atmosphere, without cross linking. According to the gel content measurement, it can be concluded that under the experimental condition of this study the main postreaction is chain branching not crosslinking.
- Adding PB resin to PP extended the Newtonian-plateau, shortened the relaxation time, and decreased the shear thinning index.
- The zero shear viscosity of all irradiated samples increased, and the sensitivity of the storage modulus to shear rate reduced. The longer relaxation time and the decrease in loss tangent, shear thinning index and terminal slop of $G'(\omega)$, are the evidences of long chain branched architecture.
- PB resin as a mobilizer can facilitate movement of PP macro molecules in solid state and simul-

taneously increase the branching efficiency and decreases the chain scission/degradation process in irradiation.
- The zero shear viscosity ratio and cross over frequency ratio of irradiated samples to their unirradiated counterparts show that adding PB resin to PP increase branching efficiency which is the evidence of mobilizing effect of PB resin.

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