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The characterization of rheological properties of melt grafting polypropylene for foaming

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Abstract Large enhancements of the melt strength of polypropylene (PP) were achieved by the introduction of specific unsaturated linear polyester (ULP) branches using melt grafting. The transient torque curves and optical rheology microscope images indicated that branching reactions took place and the ULP had been grafted onto the PP backbone. Shear rheological behaviors of three kinds of PP were investigated using rotational rheometer under dynamic shear mode with periodic shear rate. These PP samples are foamable PP (FPP) with sparse branches obtained by grafting ULP, commercial high melt strength PP (HMS PP) for foaming and conventional linear PP (EPS). It was found that the rheological properties of FPP, the HMS PP, were distinctly different from those of conventional PP. Storage modulus, steady state compliance and zero shear viscosity increased in comparison with EPS, while shear viscosity decreased. This result implied the presence of branching structures that was not revealed in conventional PP. In melt flow measurements, extrusion swell that was a prominent behavior of branching PP was observed also for FPP and PF. Compared to linear PP, FPP and PF showed distinct sag-resistant property and lower melt flow index. On the other hand, to estimate the extent of branching, a detailed method was applied using the obtained zero shear viscosity. The result showed that FPP was grafted by sparse ULP. From these results, it was found that FPP showed obvious enhancements in rheological

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M. Xiao · H. Xiao Department of Chemical Engineering, University of New Brunswick, Fredericton, NB E3B 6C1, Canada behaviors similar to PF, although its melt strength was lower than that of PF due to the presence of shorter branching chains grafted on the backbone of FPP.

Keywords Melt grafting · Polypropylene · Rheological property · Melt elasticity · Melt strength

Introduction

Polypropylene (PP) has various properties, such as higher melt point, lower density, excellent chemical resistance and relatively low price; therefore, large amounts have been produced and used. Also, PP is a superior material for the reusing and recycling of plastics. Several methods have been applied to PP fabrication, such as injection moldings, foaming, compression and film extrusion. On the other hand, as a conventional PP composed of linear chains with relatively narrow molecular weight distribution (MWD), it exhibits low melt strength and weak strain-hardening behavior. Therefore, it is unsuitable for linear PP for blow molding, foaming, extrusion coating and thermoforming processes. In order for PP to be used in wider domain, modifications are needed to enhance the strain hardening behavior of its melt in such flows. Even though a very broad (e.g. bimodal) MWD can improve strain-hardening behavior [1], the most efficient approach to increase melt strength is to produce PP with long chains branching structure. If an appropriate method can be found to improve the melt strength of conventional PP, its market position will become even more prominent and replace other thermoplastics (e.g., polyethylene, polystyrene) in forming domain, because it is more friendly to the environment and heat resistant.

High melt strength Polypropylene (HMS PP) is the commercial term which is used for long chain branching PP. The introduction of long chain branches on the PP backbone may be one of the alternatives to improve its melt strength [2-6]. There are several possible methods to obtain branching PP. HMS PP can be commercially available (e.g. Profax[®] by Basell and Daploy[®] by Borealis) and has been successfully applied in foaming, blow molding, thermoforming and extrusion coating products. Most of commercial grades are produced using electron beam (EB) irradiation [7]. EB irradiation will cause scission of the PP chains, which is followed by crosslinking, leading to long chain branching [8-10]. Furthermore, it is known [11] that the use of high-energy radiation produces branching confined for the most part to the amorphous phase of the semicrystalline PP, since it is in this region that the segmental mobility and free volume are sufficient for macroradicals formed on irradiation to approach one another and form branches. In principle, branches can also be introduced onto the PP backbone by post-reaction modification. Kim et al. [12] produced model HMS PP by reactive extrusion of randomly functionalized PP with polyfunctional monomers. It was found that as a result of branching both storage modulus and gel content was increased. Another alternative to branching PP may be through the recombination reaction in which PP molecules react with a polyfunctional monomer, having more than two double bonds, in the presence of peroxide [13–17]. Wang et al. [18] found that the amount of macrogel in the modified PP increased with increasing PETA and peroxide concentrations and it could be minimized by using low concentrations. Therefore, due to the presence of macrogel in PP melt, some applications of modified PP were limited, such as forming and blow molding.

One of the objectives of our current work was to develop a kind of HMS PP without the formation of PP macrogel using commercial linear PP by melt grafting. In practice, melt grafting is one of the most effective techniques to increase the melt strength of commercial linear PP. Meanwhile, the characterization of branching structures and melt properties of modified PP was carried out for evaluating the enhancements of melt strength. In this study, the unsaturated linear polyester (ULP) was introduced onto PP backbone to obtain a kind of applicable HMS PP in extrusion foaming. In order to evaluate the potential application of the modified PP, the commercial available HMS PP, PF (Basell, PF814), was introduced into the study to compare with FPP and EPS.

Experiment

Materials

Three types of polypropylene were used in this study. Their characteristics and brand name were listed in Table 1. EPS (EPS30R, Qilu Petrochemical Co.) is a commercial linear PP, while PF (Profax PF814, Basell (Montell)) and FPP (modified PP) are branching polypropylene. PF has higher molecular weight and its MWD is distinctly wider than that of EPS and FPP. After modification, the molecular weight of FPP is still similar with that of EPS; however the MWD increased slightly. The melt flow index (MFI) of the three polymers is not very different from one another. Therefore, the large difference of melt strength between PF and FPP may be caused by both MWD and branching structures.

The modified PP, i.e. FPP, was obtained by grafting ULP onto the backbone of linear PP, i.e. EPS [19]. The number average molecular weight of the ULP ranged from 1,700 to 2,500. This preparation method of HMS PP has been discussed previously [20]. The branching EPS, i.e. FPP, and the general structures of the ULP were shown in Schemes 1 and 2 respectively.

 Table 1
 PP grades used as the precursor for the modification and referential commercial HMS PP. The second polymer is modified PP by melt grafting

Code	Commercial name	M_w	M_w/M_n	M _b (g/mol)	Melt strength (N)	MFI (g/10 min)
EPS	EPS30R	398,000	4.1	Linear	0.30	2.7
FPP	Branched EPS	419,000	4.8	283,663	0.39	2.1
PF	Profax PF814	629,000	9.3	$-^{a}$	0.64	2.3

^a $M_{\rm b}$ for PF could not be obtained due to the unavailability of its original PP for us



Scheme 2 The general structure of a ULP chain

Where, x and y are the degree of polymerization of two parts in the ULP respectively. Thereof, y is the degree of polymerization of saturated polyester which was polymerized by esterification using hexane diacid and butanediol. And x is the degree of polymerization of unsaturated part in which the double bond was provided by fumaric acid. In the ULP chain, the amount of saturated polyester which is used as the soft parts is much higher than that of x for the purpose of melt grafting.

Preparation of sample

The PP pellets, mixed with ULP, styrene, diisopropylbenzene hydroperoxide, and antioxidant agent 1,010, were fed into the Haake Rheomin 600p mixer at 180 °C, and 60 rpm for 5 min. The transient torque curve was recorded by the specified software during the reaction.

Characterization

Melt flow properties of PP samples were measured using a SRSY-1 capillary rheometer. MFI of all samples was measured at 230 °C using a load of 2.16 kg according to the ASTM D-1238-86T. Extrusion swell and melt sag of these samples were measured under a similar condition. The values of extrusion swell were determined by calculating the ratio of the initial diameter (mm) of the samples when it just exits the die of the capillary to the diameter of the die of the capillary (2.095 mm). For the test of the melt sag of theses polymers, the length from the capillary die to the end of the melt strip was used as the value of melt sag.

The melt strengths of all PP samples were measured using a Gottfert rheotens melt strength tester consisting of a pair of rollers rotating in opposite directions. Samples strand extruded vertically downwards from a capillary die is drawn by the rotating rollers whose velocity increases at the constant acceleration rate of 20 mm/ s^2 . The tensile force in the strand measured by the balance beam is called the melt strength when the polymer melt breaks.

The modified sample was cut into small pieces and packed with filter paper, respectively, and then was Soxhlet extracted in boiling xylene for 24 h. No gel was observed for the modified sample.

The number average molecular weight \overline{M}_n , the weight average molecular weight \overline{M}_w and the MWD $(\overline{M}_w/\overline{M}_n)$ were determined via a high temperature size exclusion chromatography at 150 °C (Waters 150C gel permeation chromatography, PS gel columns). The polypropylene (0.1 g) was dissolved in 100 mL of ortho-dichlorobenzene containing 0.1 wt% butyl hydroxyl toluene. Their molecular weight was calculated in a standard procedure based on universal calculation of PP.

The crystal status of EPS and FPP were studied from -50 to 450 °C using a LV100POL optical rheology microscope (Nikon Corporation) with a Cryo-CSS450 heating and cooling system (Linkam Scientific Instruments Ltd). EPS and FPP were heated to 200 °C at 20 °C/min and kept for 5 min at 200 °C to eliminate the thermal history. They were then crystallized non-isothermally from 200 to 25 °C, decreasing 20 °C/min.

Shear dynamic measurement was carried out with a rotational rheometer (Rheostress600, Haake Co). A parallel plate with a diameter of 25 mm and a gap height of 2 mm was used for frequencies sweeps. The test specimen was cut from a sheet prepared by compression molding at 180 °C. The frequency sweeps ranged from 0.001 to 100 rad/s, while the maximum strain was fixed at 5%. These conditions were confirmed to be within the linear viscoelastic region because the linear viscosity range of conventional PP [14] is within ~10%. The shear dynamic measurement was carried out at a constant temperature of 180 °C. During the measurement dry nitrogen was maintained to remove oxygen and eliminate oxidative degradation of the polymers. The values of storage modulus G' and loss modulus G'' against the frequencies were obtained from the results.

Results and discussion

Characterization of ULP Branching Chains

LCB structure increases the possibility for entanglements in the polymeric melt, and, thus its elasticity. A similar effect, however, could result also from a broadening of the MWD [21]. Gathering information about the presence of LCB in modified PP from some characterizations is necessary for illuminating the effect of LCB structure to the rheological properties of modified PP.

As shown in Scheme 1, EPS was grafted by ULP to form branching macromolecules, FPP. The changes in structure could lead to an increase in the viscosity of the reaction system during the preparation of HMS PP. Figure 1 showed the transient torque traces of modified PP and EPS during the reaction. For the EPS sample, the torque curve kept nearly horizontal after complete melting. However, for the torque curve of FPP, a new peak appeared at about 1.4 min besides the melting peak, implying that a grafting reaction took place in the system. In fact, no gel was detected in the FPP sample. Therefore, the increase of torque, corresponding to the increase of viscosity, can be attributed to the grafting reaction of PP macromolecules chains.

The crystallization process and crystal status of PP and FPP can be clearly observed by optical rheology microscope. Figure 2 showed the micrographs of



Fig. 1 Transient torque curves of virgin PP and modified PP

linear PP and modified PP which was non-isothermal crystallized from 200 to 25 °C, decreasing 20 °C/min. It can be seen from Fig. 2 that the crystallization of EPS and FPP is significantly different. The initial global crystals of EPS were clearer and larger initially, and at the end of the crystallization the interface between crystals and the phenomenon of maltese-cross extinction were clear (Fig. 2a). Compared to EPS, for FPP, an excess of irregular crystals were formed initially, and finally the interfaces and maltese-cross extinction of crystals disappeared (Fig. 2b). The differences implied that the branching chains on the FPP performed the function of heterogeneous nucleation. By observing the process of non-isothermal crystallization of two samples, it could be found that most of the crystal nuclei of FPP were formed instantaneously, implying that the introduced branching structures speeded up the nucleation of the FPP. However, the growth rate of its crystals decreased because the chains transfer from the PP melt to the crystallization interface was restrained by the branching chains. On the other hand, the crystal nuclei of EPS were formed slowly and irregularly in comparison with FPP, which indicated that the formation of global crystals for EPS is due to homogeneous nucleation, however for FPP, heterogeneous nucleation and homogeneous nucleation worked jointly to generate more irregular crystals.

Linear viscoelastic properties

Rheology has proved to be a reliable method for the verification of the existence of long branches on polymeric chain and it is easier to implement [5]. Rheological properties of branched polypropylene can be characterized via several methods, such as elongational rheology and shear rheology. Of all the measurements, elongational flow test is a better method to characterize the melt strength of



Fig. 2 The final status of crystals of EPS and FPP. **a** The formed crystal of EPS. **b** The formed crystal of FPP

branched polypropylene; the strain-hardening behavior that was not revealed in conventional PP by elongational flow represents the enhancement of the melt strength of long chain branched PP. However, shear dynamic measurement is a more appropriate and feasible method for characterizing the viscoelastic behaviors of HMS-PP, especially its long chains branching structures.

The elasticity of polypropylene, namely the first normal stress difference, is so high that it may detach the parallel plate to splatter the melt PP when measured by rotational rheometer in steady shear mode at higher shear rate (normally, $<10 \text{ s}^{-1}$). However, the range of shear rate in normal extrusion process is $\sim 10-10^3 \text{ s}^{-1}$, so it is not compatible to carry out the shear quiescent measurement in the shear rate region of extrusion. Therefore, shear dynamic measurement with frequency sweep was introduced in this study. The values of the shear viscosity in the high shear rate were calculated by Cox-Merz [22] law.

$$\eta(\dot{\gamma})\big|_{\dot{\gamma}=w} = \frac{\sqrt{G'^2 + G''^2}}{w} \tag{1}$$

where G' and G'' are storage modulus and loss modulus, and w is angular frequency. G', G'' and w were obtained from the results of frequency sweep.

Figure 3 shows the shear viscosity plots of three kinds of PP at 180 °C. The shear viscosity of all samples decrease with the increasing of frequency, indicating the shear thinning behavior of PP, that is, a decrease in shear viscosity. With the increase of frequencies, the shear viscosity of PF is always lower than that of EPS and FPP, meanwhile, the shear viscosity of FPP is lower than that of EPS at the same frequency.

FPP sample was HMS PP that was modified by melt grafting with ULP. The space of macromolecular chains of PP is increased by the branching chains on the backbone of FPP, which reduced the molecular forces among macromolecules. Therefore, the shear viscosity of FPP is lower than that of EPS at the same frequency. However, it is not obvious because FPP contains sparse branching chains of ULP on the backbone. This corresponds with the low graft yield of FPP described in detail previously [19]. PF, as a commercial HMS PP for foaming, contains more long branching chains, and its shear viscosity is the lowest at the same frequency in all samples.



Fig. 3 Variation of shear viscosity of different PP with angular frequency

Storage modulus

The polypropylene samples were stable at 180 °C, as the values of G' did not change throughout the measurement. Figure 4 exhibits G' plotted as the function of frequencies for polypropylene samples. The storage modulus of PF is significantly high at lower frequencies in comparison with that of FPP and EPS and distinctly lower at relatively high frequencies. The shoulder peaks of PF and FPP at lower frequencies were not observed within the frequency region examined. In addition, the storage modulus of FPP is higher at lower frequencies and lower at high frequencies than that of EPS, implying that there is a longer relaxation mechanism, which can be ascribed to the long chain branches formed by the melt grafting. Storage modulus is an important parameter to characterize polymer viscoelastic properties. At lower frequencies, the higher value of G' curve, the higher elasticity of polymer [23]. Figure 4 indicates that the elasticity of PF is apparently higher than those of FPP and EPS; the elasticity of FPP is slightly higher than that of EPS due to the presence of sparse branching chains.

Busse [24] reported that there was a dependent relationship between melt strength and melt elasticity, i.e. the higher melt elasticity of the polymer, the higher melt strength. The relationship was confirmed through numerous studies [2, 25]. Wang et al. [3] characterized melt strength by melt elasticity; therefore, it can be confirmed by Fig. 3 that PF, a kind of long chain branching PP, has the highest melt elasticity, which indicates it has the highest melt strength. This result is in agreement with the fact that PF is commercial available HMS PP for foaming. FPP has higher melt elasticity than EPS because it also has branching structures. EPS could not be foamed by an extruder in the studies, due to its low melt strength. These indicate that the properties of foaming for polypropylene are determined by melt strength or melt elasticity.



Fig. 4 Variation of storage modulus of different PP with angular frequency

Steady state compliance

Steady state compliance (J_e^0) is an important value characterizing the elastic energy stored in PP melt and can also be applied to characterize the value of the melt elasticity of PP [4]. Steady state compliance can be calculated by Eq. 2 as follows [26]:

$$J_e^0 = \lim_{w \to 0} \frac{G'(w)}{\left[G''(w)\right]^2}$$
(2)

where G' and G'' were obtained from the shear dynamic measurement.

According to G' and G'', the curve of G'(w)/G''(w) plotted as the function of frequencies for PP can be obtained in the range of frequencies measured. However, in order to obtain the value of J_e^0 , the curve needs to be integrated by polynomial fitting curve using ORIGIN at lower frequencies beyond the range of measured. The constant obtained from the polynomial is the value of J_e^0 . The values of J_e^0 obtained by the polynomial fitting were listed in Table 2. The results show that the value of J_e^0 of PF is significantly high in comparison with the other two samples, even three times that of FPP and four times that of EPS. It can also be observed in Table 2 that the value of J_e^0 of FPP is higher than that of EPS, which is attributed to the branching structure of FPP. The values of J_e^0 in Table 2 also indicate that the elasticity of PF is

Samples	Steady state compliance $(\times 10^{-6} \text{ Pa}^{-1})$	Ratio of extrusion swell (<i>B</i>)	Melt sag (mm)	Zero shear viscosity $(\times 10^4 \text{ Pa.s})$		
PF	1624.5	2.4	90	1.23		
FPP	549.3	1.4	196	1.18		
EPS	387.6	1.2	250	1.12		

 Table 2
 Steady state compliance of various PP

the highest among three samples. Due to the branching modification of EPS, the value of J_e^0 for PF is also higher than that of EPS.

Extrusion swell

Extrusion swell of PP is a phenomenon closely related to its elasticity. It can reflect the magnitude of the elasticity of the polymer. Therefore it is one of the important characteristics of non-Newtonian viscoelastic fluid. Figure 5 is a representation of extrusion swell phenomenon.

Extrusion swell of all samples was measured using a SRSY-1 capillary rheometer, and the values are obtained by Eq. 3 as follows:

$$B = \frac{D_1}{D_0} \tag{3}$$

where D_0 is the internal diameter of the capillary (2.095 mm), and D_1 is the diameter of the strand when it just exits the die of the capillary. B, the ratio between D_1 and D_0 , is the value of extrusion swell.

The extrusion swell (B) of three PP samples are summarized in Table 2. The table shows that B of PF is distinctly greater than those of FPP and EPS, which represents the melt elasticity of PF, namely melt strength, is the highest in all PP samples. The extrusion swell of FPP is greater than that of EPS, which demonstrates that the branching chains on the backbone of FPP increase the melt elasticity and melt strength. The results of extrusion swell measurement are similar to the storage modulus measurement.

Melt sag

The value of melt sag is related to the melt strength of materials, and melt strength is related to the branching structure of HMS PP; therefore, melt sag can characterize the structures of long chain branching PP. The saggy length from the die of the capillary to the end of the strand of PP sample is the value of the melt sag. The shorter the melt sag is, the higher the melt strength of PP is.

As shown in Table 2, the length of the melt sag of EPS is the longest and PF has the shortest length of melt sag among all samples. The results indicate that the melt strength of PF is the highest in all samples and FPP has a higher melt strength than that of EPS which was contributed to the introduction of branching chains on the backbone of FPP. Also the results correspond with the conclusions obtained previously and demonstrate that FPP is an applicable HMS PP due to its higher melt strength. Therefore, it can be confirmed that the melt strength of conventional PP can be increased effectively by melt graft reaction with ULP.



Estimation of the extent of branching chains

Zero shear viscosity (η_0) will be increased by the introduction of long branching chains onto the backbones of conventional PP. The values of η_0 of all PP samples can be represented by Eq. 4 as follows [2]:

$$\eta_0 = \lim_{w \to 0} \frac{G''(w)}{w} \tag{4}$$

where G'' and w can be obtained from the results of shear dynamic measurement.

According to w and G'', the curve G''(w)/w plotted as the function of frequencies for PP can be obtained in the range of frequencies measured. In order to obtain the value of η_0 , Eq. 4 was fitted using ORIGIN at lower frequencies. The constant obtained from the polynomial is the value of η_0 . The values of zero shear viscosity of all PP samples obtained by polynomial fitting were summarized in Table 2. It should be noticed that the zero shear viscosity of FPP was distinctly higher than that of EPS. In consideration of the similar molecular weight of FPP and EPS, it indicates that the rheological properties of FPP were enhanced after modification by melt grafting. Zero shear viscosity is very sensitive to the topological structure of macromolecules. The presence of very low amounts of LCB chains can change the zero shear viscosity and the degree of shear thinning, as compared to the linear polymer with similar molecular weight [27]. Therefore, the enhancement of zero shear viscosity can be attributed to the introduction of branching chains. However, for PF it is very difficult to compare the LCB structure with EPS and FPP using the obtained values of zero shear viscosity due to its significant different molecular weight, linear original polymer and modification reaction.

A detailed method to estimate branching chains by comparing the zero shear viscosity of the linear and branched polymer has been proposed by Janzen and Colby [28]. An average molecular weight between branches, $M_{\rm b}$, was introduced to characterize LCB and the zero shear viscosity was related to $M_{\rm w}$ and $M_{\rm b}$.

$$\eta_0 = AM_b \left[1 + \left(\frac{M_b}{M_c}\right)^{2.4} \right] \left(\frac{M_w}{M_c}\right)^{s/\gamma}$$
(5)

$$s/\gamma = \max\left[1, \frac{3}{2} + \frac{9}{8}B\ln\left(\frac{M_{\rm b}}{90M_{\rm Kuhn}}\right)\right] \tag{6}$$

$$\eta_0 = AM_w \left[1 + \left(\frac{M_w}{M_c} \right)^{2.4} \right] \tag{7}$$

where, A is a parameter that can be evaluated if η_0 and M_w of the linear polymer are known. B is a constant taken from [29] (B = 6). The Kuhn length, M_{Kuhn} , for polypropylene is 187.8 g/mol [29]. M_c is a critical molecular weight for entanglement of random branches, $M_c = 2M_e = 13,640$ g/mol.

Utilizing the measured zero shear viscosity and weight average molecular weight of HMS PP, the M_b of FPP could be obtained from Eqs. 5 and 6. Table 1 contains

the result for M_b of FPP. The calculated M_b slightly decreases in comparison with M_w , suggesting sparse branching on the backbone of FPP. The value of M_b for PF can not be obtained because its original linear PP was not available for us.

Conclusions

The present work showed that it is possible to produce branching chains on the backbone of conventional PP by melt grafting with ULP. This represents, to our knowledge, a first attempt in this direction. The grafting of ULP and the branching of PP could occur when PP was modified with ULP in the Haake mixer, which has been verified by the torque curves. The formation of branching structure was confirmed by optical rheology microscope. Shear dynamic measurement was used to investigate the rheological properties of linear PP, modified PP and commercial HMS PP.

- (1) It is an effective method for the shear dynamic measurement to characterize the melt elasticity and melt strength of PP. The measurements of melt flow properties including MFI, extrusion swell and melt sag are also effective methods to characterize the melt elasticity and melt strength of branching polypropylene.
- (2) According to the results of rheological and melt flow measurements, it is confirmed that the melt elasticity and melt strength of PF is distinctly greater than that of FPP and EPS. Meanwhile the melt elasticity and melt strength of FPP containing sparse branching chains is higher than that of EPS.
- (3) The rheological and melt flow properties of HMS PP, such as lower shear viscosity throughout all frequencies, higher G' at low frequencies, higher values of steady state compliance and extrusion swell and lower melt sag are related to different relaxation mechanism from linear PP.
- (4) In order to estimate the branching extent of modified PP, M_b of FPP was obtained by a detailed method using zero shear viscosity. The result shows that the level of branching chains is approximately $M_b/M_w = 0.677$. This indicates that the backbone of FPP contains sparse branching chains. Nevertheless, the melt strength of PF was increased and it could be foamed in practice. However, EPS can not be foamed due to its linear structure. PF has better properties in extrusion foam which is attributed to longer branching chains and a wider MWD.

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