

Preparation and Characterization of High Melt Strength Polypropylene with Long Chain Branched Structure by the Reactive Extrusion Process

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ABSTRACT: The reactive extrusion of maleic anhydride grafted polypropylene (PP-g-MAH) with ethylenediamine (EDA) as coupling agent is carried out in a corotating twin-screw extruder to produce long chain branched polypropylene (LCBPP). Part of PP-g-MAH is replaced by maleic anhydride grafted high-density polyethylene (HDPE-g-MAH) or linear low-density polyethylene (LLDPE-g-MAH) to obtain hybrid long chain branched (LCB) polyolefins. Compared with the PP-g-MAH, PE-g-MAH, and their blends, the LCB polyolefins exhibit excellent dynamic shear and transient extensional rheological characteristics such as increased dynamic modulus, higher low-frequency complex viscosity, broader relaxation spectra, significantly enhanced melt strength and strain-hardening behaviors. The LCB polyolefins also have higher tensile strength, tensile modulus, impact strength and lower elongation at

break than their blends. Furthermore, supercritical carbon dioxide (scCO₂) is constructively introduced in the reactive extrusion process. In the presence of scCO₂, the motor current of the twin extruder is decreased and LCB polyolefins with lower melt flow rate (MFR), higher complex viscosity and increased tensile strength and modulus can be obtained. This indicates that the application of scCO₂ can reduce the viscosity of melt in extruder, enhance the diffusion of reactive species, and then facilitate the long chain branching reaction between anhydride group and primary amine group. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3384–3392, 2011

Key words: polypropylene; polyethylene; long chain branched; high melt strength; reactive extrusion; supercritical carbon dioxide

INTRODUCTION

The melt strength and viscosity of commodity polypropylene (PP) decreases rapidly as the temperature rises over its melting point. High melt strength is very important for thermoforming, extrusion coating, blow molding, and foaming processes, etc. Grafting long chain branches onto PP backbone is a well-established technique to improve the melt strength of PP. Many methods have been developed to form the long chain branched (LCB) structure, including in-reactor homopolymerization and copolymerization with special catalysts and agents,^{1–3} and postreactor reaction, such as electron beam irradiation^{4–6} and peroxide curing.^{6–9} Recently, LCB polymers were prepared through chemical reactions between different functional groups on polymer chains.^{10–13} The lifetime of functional group is much longer than that of radicals generated in the electron beam irradiation and peroxide curing processes. In our previous work,¹⁴ PP with LCB structure was prepared by grafting PP, high density polyethylene (HDPE) or linear low density polyethylene (LLDPE) on its backbone in solution through intermolecular reaction between functional groups. The creation of LCB structure results in higher storage modulus at low frequency, higher zero shear viscosity, reduced phase angle, enhanced shear sensitivities, and longer relaxation time. However, reaction in solution has many problems, such as toxic solvent harmful to human and environment, long reaction time, and low efficiency. The reactive extrusion process is favorable due to its advantages like fast reaction, continuous process, and absence of solvent.¹⁰ To enhance the reaction, scCO₂ can be fed to the extruder during reactive extrusion processes. scCO₂ is a nontoxic, nonflammable, chemically inert and inexpensive fluid. scCO₂ can be used in the reactive

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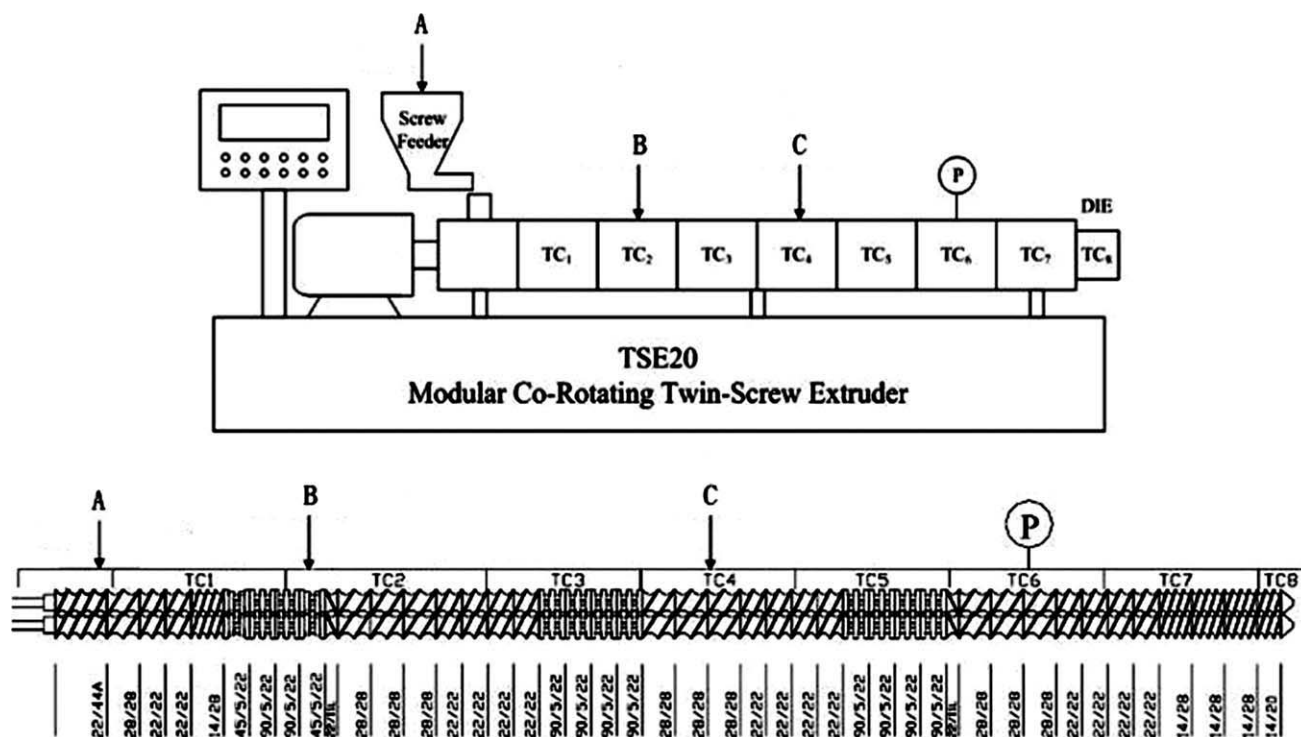


Figure 1 Schematic diagram for the reactive extrusion system and its screw profile.

extrusion process to reduce the viscosity of molten polymer, enhance the diffusion of reactive species, and facilitate the reaction.¹⁵

In this paper, the LCBPPs are produced by the reaction between maleic anhydride grafted polyolefins and ethylenediamine (EDA) in a twin-screw extruder. The dynamic shear rheological properties, transient extensional rheological properties and mechanical properties of the obtained LCB polyolefins are compared with the raw materials and their blends. The effects of scCO_2 have also been investigated.

EXPERIMENTAL

Materials and preparation

Maleic anhydride grafted polypropylene (PP-g-MAH) is obtained from Ningbo Nengzhiguang New Material Co., Ltd, China (M_w : 130 kg/mol, M_n : 43 kg/mol, Grafting degree: 0.32%). Maleic anhydride grafted linear low-density polyethylene (LLDPE-g-MAH) is purchased from Nanjing Deba Chemical Co., Ltd, China (M_w : 79 kg/mol, M_n : 20.7 kg/mol, Grafting degree: 0.39%). Maleic anhydride grafted high-density polyethylene (HDPE-g-MAH) is provided by Dalian Haizhou Co., Ltd, China (M_w : 80 kg/mol, M_n : 11.5 kg/mol, Grafting degree: 0.19%). Ethylenediamine (EDA) is acquired from Hangzhou Changqing Chemical Reagent Co., Ltd, China. All materials are used directly without any purification.

Synthesis of long chain branched polyolefins

The reactive extrusion processes are performed in a specially designed corotating twin screw extruder (TSE) manufactured by the Ruiya Co. (Nanjing, China). The screw diameter is 20 mm and the ratio of length to diameter (L/D) is 48. The large L/D ratio leads to long resident time (about 3 min) and makes the TSE more suitable for reactive extrusion. The screw combination consists of four conveying sections and three kneading blocks alternatively. The extruder barrel is divided into eight sections plus the die. A pressure transducer is installed at section #6. There are three inlets for feeding raw materials along the extruder. A hopper equipped with a single-screw and two independent plunger pump side-injection systems are connected to the extruder barrel at section #0 (inlet A), 2 (inlet B) and 4 (inlet C). Maleic anhydride grafted polyolefins, EDA and scCO_2 are fed through inlet A, B, and C, respectively. Schematic diagram for the reactive extrusion system is shown in Figure 1.

The typical reactions occurred in the reactive extrusion process are shown in Figure 2. First, the MAH group on PP-g-MAH chain is reacted with NH_2 group of EDA to generate PP with NH_2 group (PP-g- NH_2). PP-g- NH_2 is further reacted with the residual PP-g-MAH to form LCBPP. Here, EDA acts as the bridge to link two polyolefin chains. When parts of PP-g-MAH are replaced with PE-g-MAH, the PP grafted with long PE chain is produced.

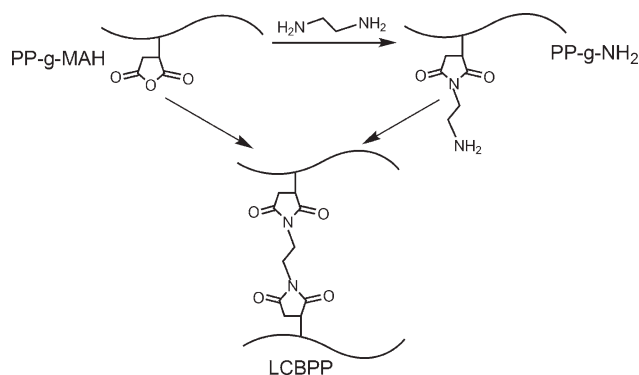


Figure 2 The typical functional group reactions in extrusion process to form long chain branched polyolefins.

Table I summarizes the formulation and process conditions in this work. Polyolefins are fed at a given rate (75 g/min) and the screw speed is constant (150 rpm). Both HDPE-g-MAH and LLDPE-g-MAH are also employed in this work. The weight ratio between PP and PE is 80 : 20 when PE is used. The temperature of the barrel section #1-7 and the die section #8 are set to 180°C. In Run 2, 4, 6, and 8, scCO₂ is fed to the TSE at 8MPa. The mass ratio between scCO₂ and polymers is controlled at 2%. The polymer stripe left the extruder is cooled in water and cut into pellets. The pellets are dried in room temperature.

Characterization

FTIR spectra of samples are obtained under a dry nitrogen atmosphere in an IR spectrometer (Nicolet 5700) with Omnic software for data collection and analysis. Samples for FTIR measurement are pressed to 8- μ m-thick films under the conditions of 180°C and 100 kgf/cm².

The shear rheological behavior is measured using an ARES Rheometrics (TA, Rheometrics) with parallel plates of 25 mm in diameter and a gap of 1.5 mm. Cylindrical samples of a thickness of 2 mm and a diameter of 25 mm are prepared by compression-molding at 180°C. Dynamic frequency sweep

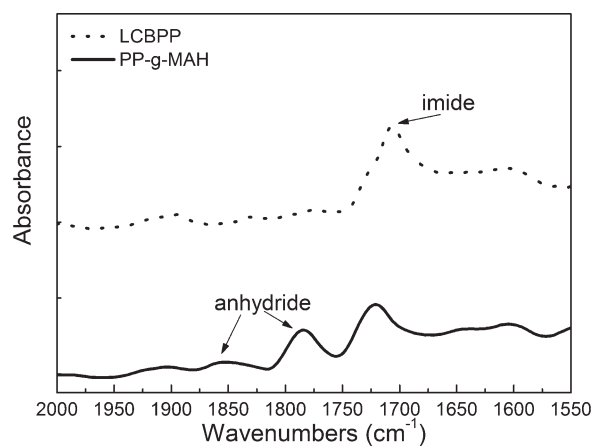


Figure 3 The FTIR spectra of the raw material (PP-g-MAH) and the product of the Run 2 (LCBPP).

measurements are carried out at 180°C with fixed shear strain (1%). The frequency range is varied from 0.1 to 100 rad/s.

Transient extensional rheology is measured on an ARES Rheometrics with extensional clamps. Quadrate samples with a dimension of 2 × 10 × 17 mm³ are prepared by compression-molding at 180°C. Measurements are conducted at 180°C with various elongation rate.

Using a CEAST melt flow indexer, the melt flow rate (MFR) of all samples are measured at 230°C according to ASTM D1238 with a load of 2.16 kg.

The tensile and impact properties are measured according to ASTM D638 and D5420-96 using a Zwick Z020 universal tensile machine. The samples used for testing are prepared through injection molding. At least six replicates are conducted for each property. The values within a standard deviation of <10% are used to calculate the mechanical properties.

RESULTS AND DISCUSSION

The FTIR spectra of the raw material (PP-g-MAH) and the product of the Run 2 (LCBPP) are compared in Figure 3. The absorption bands at 1784 cm⁻¹ and

TABLE I
Formulation and Process Conditions of the Reactive Extrusion

Run	PP-g-MAH wt %	HDPE-g-MAH wt %	LLDPE-g-MAH wt %	R ^a	Temperature °C	Assisted scCO ₂
1	100	–	–	1	180	No
2	100	–	–	1	180	Yes
3	80	20	–	0	180	No
4	80	20	–	1	180	Yes
5	80	20	–	1	180	No
6	80	–	20	0	180	Yes
7	80	–	20	1	180	No
8	80	–	20	1	180	Yes

^a R: the molar ratio between anhydride group and primary amine group.

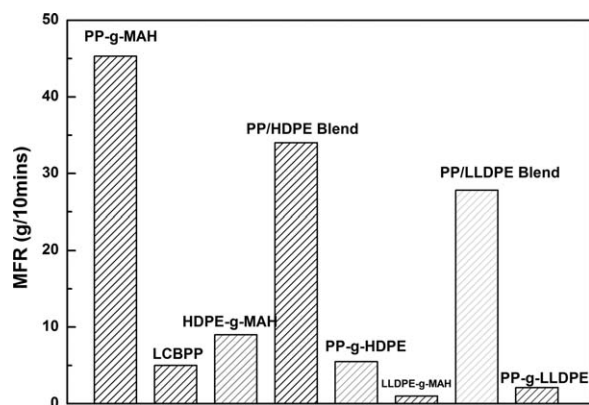


Figure 4 The MFR data of various samples.

1862 cm^{-1} (small) are assigned to the cyclic anhydride in the PP-g-MAH. The intensities of these absorption bands at 1784 cm^{-1} and 1862 cm^{-1} are negligible in the spectra for LCBPP. A new absorption band at 1707 \sim 1708 cm^{-1} appeared due to the formation of imide. This indicates that the reaction shown in Figure 2 has occurred.

Figure 4 compares the MFR of raw materials, their blends and products of reactive extrusion. It can be seen that the product of reactive extrusion between PP-g-MAH and EDA has significantly lower MFR than the starting polymer, PP-g-MAH. This further suggests that PP with LCB structure has been generated. The MFR of the blend of PP-g-MAH and HDPE-g-MAH is lower than the MFR of PP-g-MAH and higher than that of HDPE-g-MAH. The product with PP-g-HDPE of the reactive extrusion between PP-g-MAH, HDPE-g-MAH, and EDA has a MFR lower than that of both PP-g-MAH and HDPE-g-MAH. On the other hand, MFR of the product with PP-g-LLDPE of reactive extrusion between PP-g-

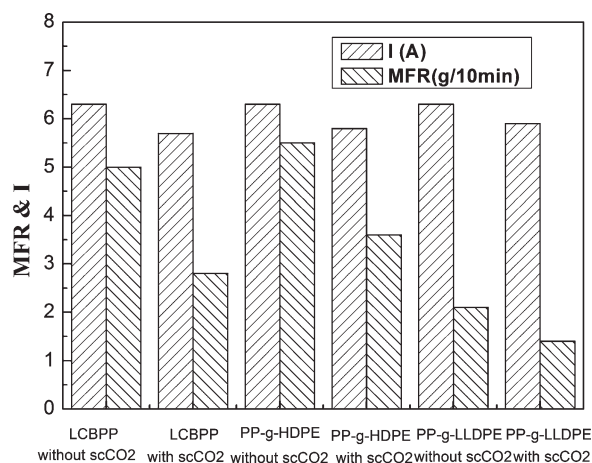


Figure 5 Effect of scCO_2 on the MFR and motor current of TSE.

MAH, LLDPE-g-MAH, and EDA is lower than MFR of PP-g-MAH but higher than that of LLDPE-g-MAH.

The effect of scCO_2 is shown in Figure 5. It can be found MFR of the LCB polyolefins obtained with scCO_2 are significantly lower than that of the LCB polyolefins obtained without scCO_2 . Moreover, the

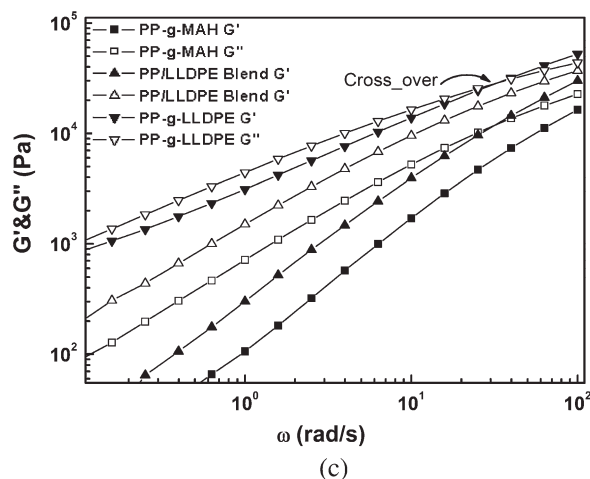
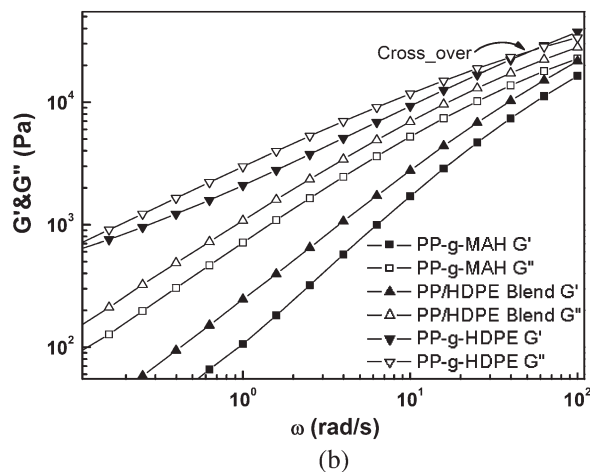
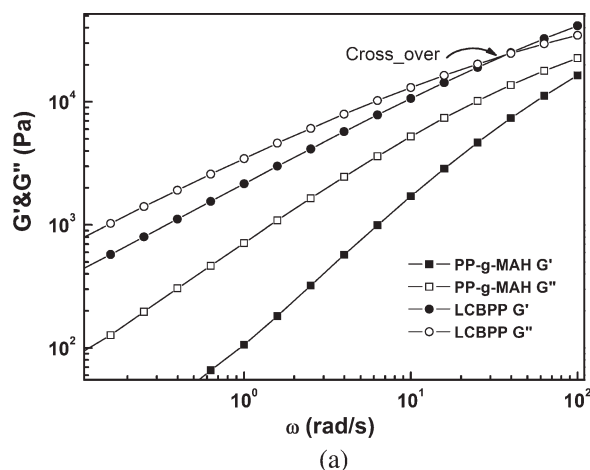


Figure 6 The storage modulus and loss modulus of various samples.

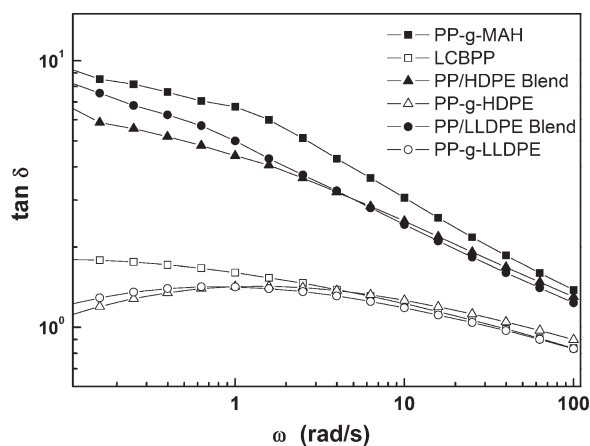


Figure 7 The loss angle of various samples.

motor current of TSE is decreased when scCO_2 is introduced. This proves that using scCO_2 can reduce the melt viscosity in TSE, enhance the mobility of EDA and segment of polymer chain, and facilitate the reaction in the extrusion process.

Figure 6 compares storage modulus (G') and loss modulus (G'') of the all samples. The reactive extrusion process has significantly changed G' over entire frequency range. The remarkable higher G' at low shear rate indicates the higher level of elasticity induced by the formation of LCB structure. The crossover between G' and G'' is found for all samples with LCB structure, which is similar to the previously reported results.¹⁵

Loss angle (δ), defined as $\tan \delta = G''/G'$, is another parameter of melt elasticity: the higher elastic is, the lower loss angle would be. The loss angle of PP-g-MAH, their blends and LCB polyolefins are plot as a function of frequency in Figure 7. The LCBPP, PP-g-HDPE, and PP-g-LLDPE demonstrate lower loss angle than PP-g-MAH and PP-g-MAH/PE-g-MAH blends, respectively. This is another indication of the presence of LCB structure in the resulting products.

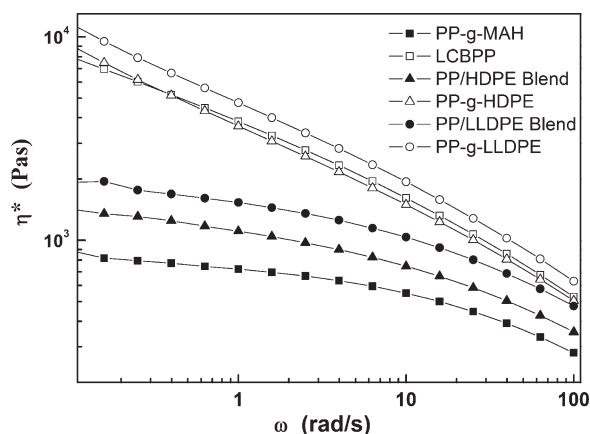


Figure 8 The complex viscosity of various samples.

The complex viscosities of PP-g-MAH, PP-g-MAH/PE-g-MAH blends, and LCB polyolefins are presented in Figure 8. PP-g-MAH/PE-g-MAH blends have higher complex viscosities than PP-g-MAH over the entire frequency range studied. In the

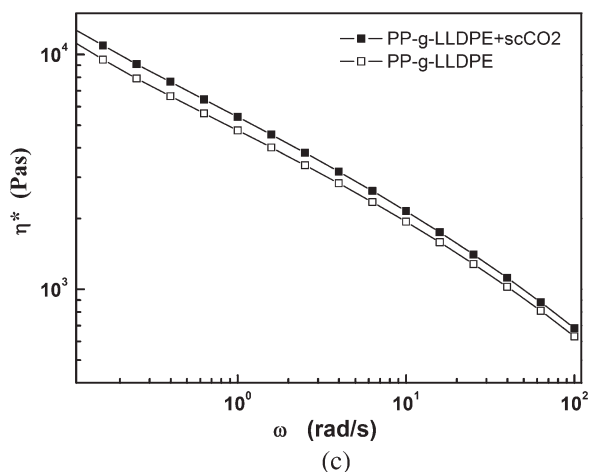
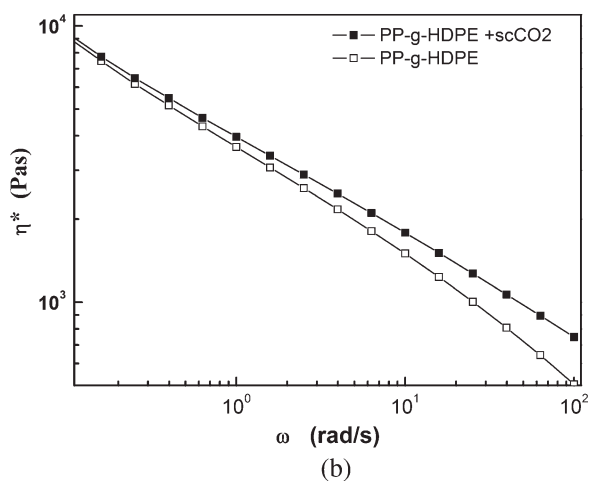
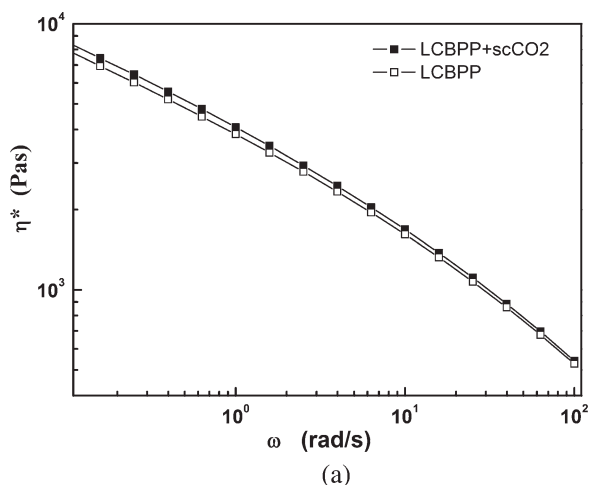
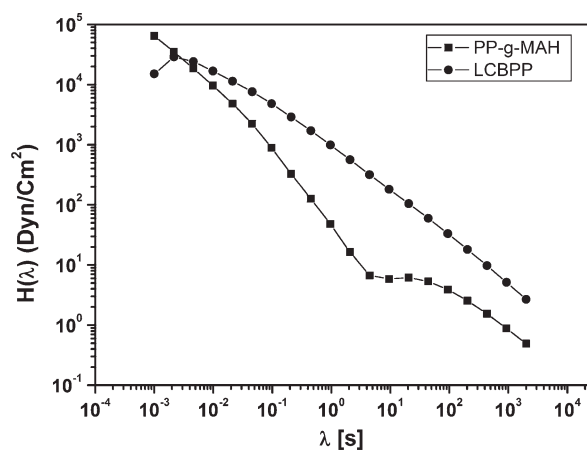
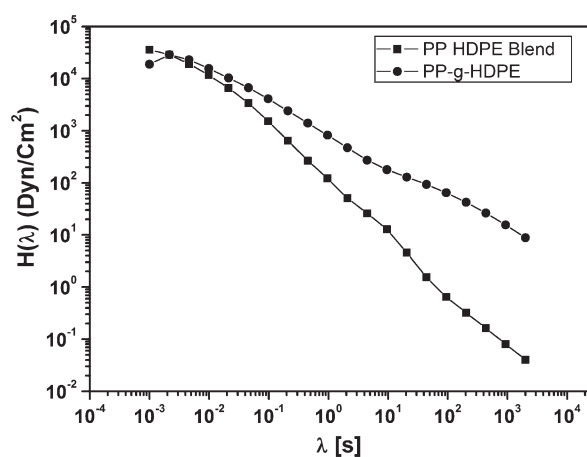


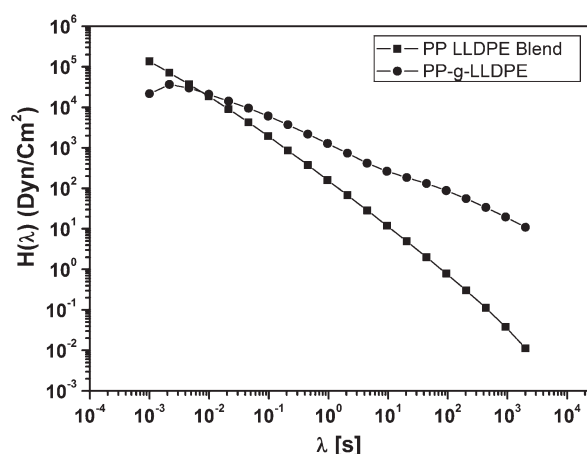
Figure 9 Effect of scCO_2 on the melt rheology of LCB polyolefins.



(a)



(b)



(c)

Figure 10 Comparison of relaxation spectrum of the melts for the blends and LCB samples.

low frequency range, the complex viscosities of LCB polyolefins are significantly higher than that of PP-g-MAH and PP-g-MAH/PE-g-MAH blends. Differences of the complex viscosities are narrowed in the high frequency range.

Effect of scCO_2 on the complex viscosity of LCB polyolefins is shown in Figure 9. It can be seen that

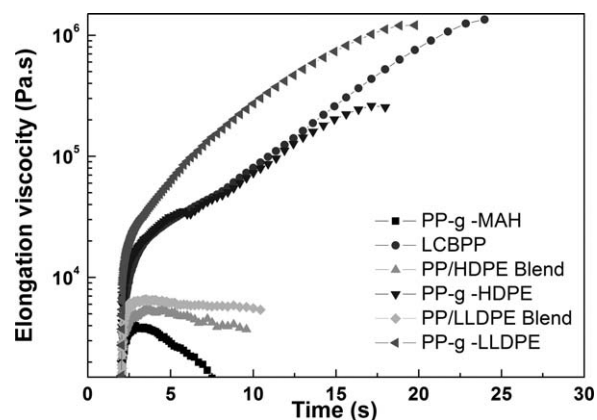


Figure 11 The melt elongation viscosity of various samples.

the complex viscosities of LCB polyolefins obtained with scCO_2 are higher than those of polymers obtained without scCO_2 in the all frequency range. The complex viscosity of LCB polyolefins is believed to be increased with the increase in the density of LCB. Therefore, the application of scCO_2 results in higher reaction degree and higher LCB density.

The relaxation spectra of polyolefins with various structures have been evaluated from the dynamic modulus as shown in Figure 10. Following the trends of the dynamic modulus, $H(\lambda)$ increases at high relaxation times after grafting reaction. At short relaxation times, the change in $H(\lambda)$ is less significant. Therefore, the spectra of polyolefins with LCB structure are broader. This is another indication of the increases of elasticity for LCB polyolefins.

The results of transient extensional rheology test are shown in Figures 11 and 12. The extensional viscosity of PP-g-MAH is very low and decreases with the increase in strain time, which is termed as strain-softening phenomena. Blending PP-g-MAH with PE-g-MAH can improve the extensional

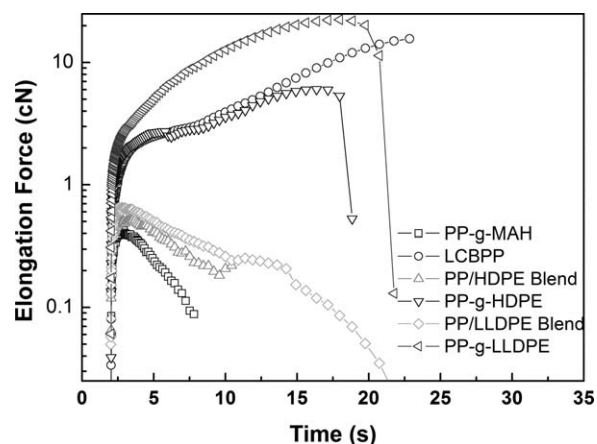


Figure 12 Melt elongation force of various samples.

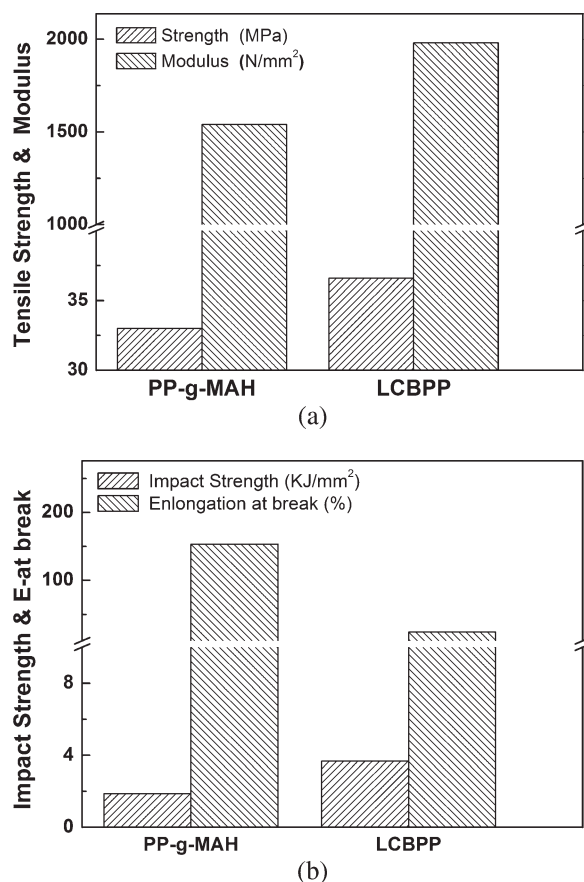


Figure 13 Tensile and impact properties of PP-g-MAH and LCBPP.

viscosity but can not change their strain-softening behaviors. On the other hand, all samples with LCB structure show very high extensional viscosity and strain-hardening behaviors.

Melt strength can be defined as the largest elongation force before the polymer melt breaks.¹⁶ Figure 12 shows the time evolution of elongation force during the transient extensional rheology tests for various samples. The melt strength of starting PP-g-MAH is very low (0.45 cN). The melt strength of LCBPP reaches 15.7 cN, which is more than 30 times higher than the melt strength of PP-g-MAH. Blending PP-g-MAH with PE-g-MAH can improve the melt strength slightly (0.52 cN for PP/HDPE blend and 0.66 cN for PP/LLDPE). Grafting LLDPE onto PP can improve the melt strength by over 30 times while grafting HDPE onto PP can improve the melt strength by over 10 times.

Figure 13 compares tensile and impact properties of PP-g-MAH and LCBPP. After LCB modification, tensile strength is more than 38MPa and increased by more than 10% over the starting PP-g-MAH. The tensile modulus of LCBPP is close to 2000 N/mm², which is a 25% increase over the PP-g-MAH. The

notched impact strength of LCBPP, which reaches 3.7 kJ/m², is increased by 96% over that of the PP-g-MAH. However, the elongation at-break of LCBPP is lower than that of the PP-g-MAH.

Mechanical properties of PP-g-MAH, PE-g-MAH, their blends and hybrid LCB polyolefins are shown in Figures 14 and 15, respectively. Compared with the PP, the PEs have lower tensile strength and modulus but higher impact strength and elongation at break. The tensile strength and modulus of the PP/PE blends are higher than that of the PE and lower than that of the PP. The hybrid LCB polyolefins (PP-g-HDPE and PP-g-LLDPE) have higher tensile strength and modulus than the corresponding PP/PE blends. The impact strength and elongation at break of the PP/PE blends are lower than that of the PE and higher than that of the PP. The PP-g-HDPE and PP-g-LLDPE have higher impact strength but lower elongation at break than the PP/PE blends.

Figure 16 shows the effect of scCO₂ on the mechanical properties. It can be seen that the tensile strength and modulus of the LCB polyolefins obtained with scCO₂ are significantly higher than

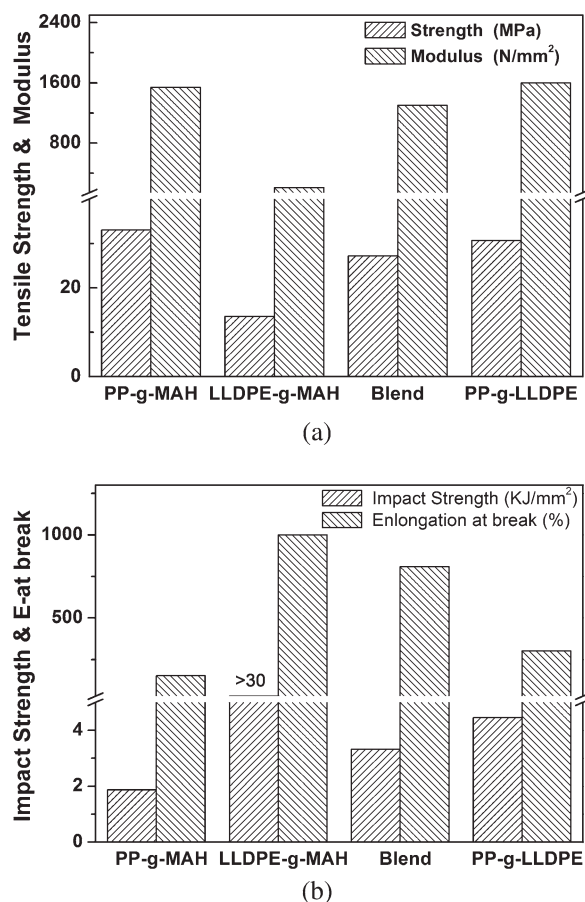


Figure 14 Tensile and impact properties of PP-g-MAH, LLDPE-g-MAH, the blend and hybrid LCBPP.

those of the polymers obtained without scCO_2 . The LCB polyolefins obtained with scCO_2 has higher density of long chain branch as the result of enhanced reaction.

CONCLUSIONS

The LCB polyolefins are obtained by the group reaction between maleic anhydride grafted PP, HDPE, or LLDPE and ethylenediamine in a twin-screw extruder. It has been found that the products of reactive extrusion have significantly lower MFR than the raw materials and their blends. The shear and transient extensional rheological properties have been examined. Compared with the PP-g-MAH, PE-g-MAH, and their blends, the LCB polyolefins possess enhanced dynamic modulus, increased low-frequency complex viscosity, broader relaxation spectra, and significantly higher melt strength. The LCB polyolefins also exhibit strain-hardening behaviors instead of the strain-softening behaviors of the raw materials and their blends. The tensile strength and modulus of LCBPP are considerably higher than the PP-g-MAH. The notched impact strength of LCBPP

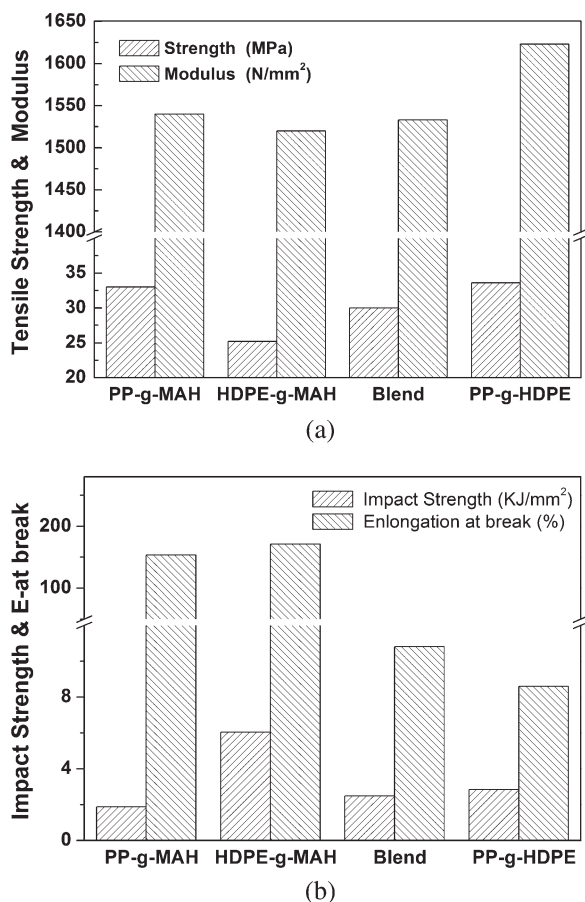


Figure 15 Tensile and impact properties of PP-g-MAH, HDPE-g-MAH, the blend and hybrid LCBPP.

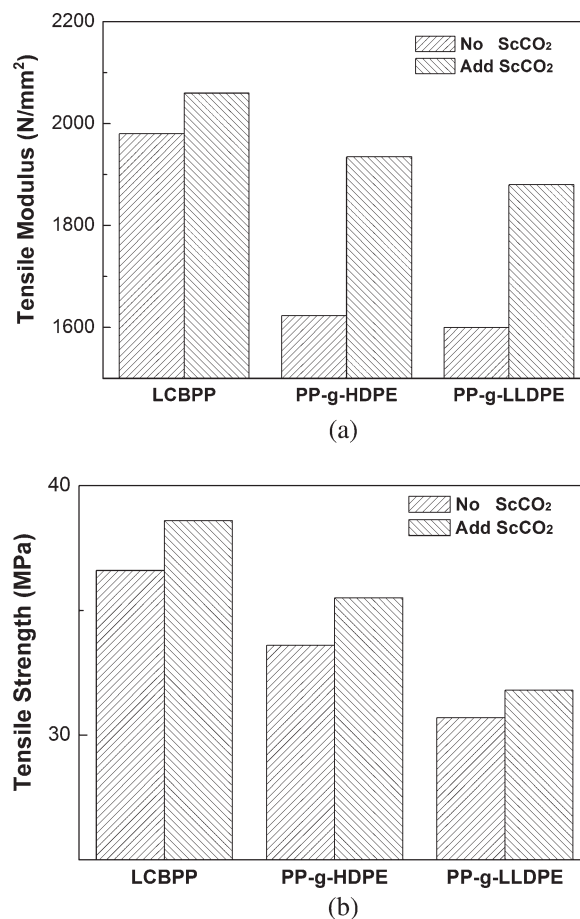


Figure 16 Effect of scCO_2 on tensile strength and modulus of obtained LCB polyolefins.

reaches 3.7 kJ/m^2 , which is a 96% increase over the PP-g-MAH. The elongation at-break of LCBPP is lower than PP-g-MAH. PP-g-HDPE and PP-g-LLDPE have higher tensile strength, tensile modulus impact strength and lower elongation at break than blends of PP and PE. It has been found that introducing scCO_2 can facilitate the reaction between the functional group grafted on polymer chains and resulted in lower MFR, higher complex viscosity, and increased tensile strength and modulus.

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