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Chemical modification of poly(l-butene) resins through reactive processing

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Abstract

Controlled-rheology poly(1-butene) resins have been produced by chemical modification of commodity poly(1-butene) (PB-1) resins through reactive processing with an organic peroxide. Using various amounts of peroxide, samples have been produced and have been analyzed in terms of their molecular and rheological properties. Molecular weight distributions (MWD) as determined by gel permeation chromatography (GPC) indicate that polydispersity (PDI) remains approximately constant but weight-average molecular weight (Mw) decreases with increasing peroxide concentration. These trends are in agreement with predictions from a kinetic model previously developed for the production of controlled-rheology polypropylene. Linear viscoelastic measurements indicate that the modified samples are thermorheologically simple and that zero-shear viscosity decreases with increasing peroxide concentration while flow activation energy remains approximately constant. Finally, no significant variation in melting and crystallization properties was observed for the range of peroxide concentrations used. Based on these results, it is proposed that tailor-made controlled-rheology poly(1-butene) resins can be produced easily through reactive extrusion operations similar to those used for the production of controlled-rheology polypropylene (CRPP).

KEYWORDS: reactive processing, modification, polyolefins, rheology

1 | INTRODUCTION

Poly(1-butene) (PB-1) is a linear, highly isotactic, semicrystalline polymer which is produced during polymerization of 1-butene with a stereospecific catalyst. Commercially, polymerization of 1-butene can be carried out in solution, slurry, and gas phase processes [1] and currently, there are four producers of PB-1 resins, LyondellBasell, Mitsui Chemicals, Ylem Technology, and Shandong Hongye Chemical. LyondellBasell is the largest producer with an annual output of approximately 60 000 MT in 2016.[2]

Commodity PB-1 grades (extrusion, injection molding, and blow molding) are used widely in the industry in applications such as pipe/tubing manufacturing, peelable packaging, master-batching, and hot-melt adhesives. In particular, PB-1 resins find extensive use in applications requiring creep resistance even at elevated temperatures due to their exceptional combination of properties.[3] In certain applications, PB-1 is blended with polyethylene (PE) or polypropylene (PP) to improve mechanical properties. Compared to other polyolefins, PE and PP, PB-1 has remarkable creep

properties and chemical and environmental stress cracking resistance. Despite the importance of PB-1 resins, limited studies exist in the literature on the effect of their molecular weight distribution (MWD) on rheological properties and processability.[4-5]

Even though the market size of PB-1 is still lower than that of PE and PP, it is anticipated that it will increase significantly in the near future[2] and there will be a need of various PB-1 grades. Production of these grades can be achieved through controlled modification as in the case of PP.

Production of controlled-rheology polypropylene (CRPP) has been practiced widely in the industry[6] and it involves the controlled degradation of commodity resins by using various peroxides. Through peroxide-initiated β-scission reactions during reactive extrusion (REX), various CRPP grades can be produced having desired PDIs and Mw. The production of CRPP and their molecular and rheological properties have been studied extensively in the open literature.[7-43] The modification of the MWD of PB-1 resins by using peroxides has been addressed in the patent literature[44-45] for the production of very high melt flow rate (MFR) materials for film applications. However, the effect of peroxide concentration on MWD and rheological properties has not been presented in the open literature. Therefore, the objectives of this work were: (a) to perform chemical modification experiments for the production of controlled-rheology PB-1 (CRPB) from commodity PB-1 resins, and (b) to characterize the molecular and rheological properties of the commodity and modified resins and attempt to develop correlations between them.

2 | EXPERIMENTAL

2.1 | Materials

Two commercial homopolymer PB-1 resins from LyondellBasell were used in these experiments. The key properties of these resins are summarized in Table 1. The peroxide used in the modification reactions was 2,5-bis (tert-butylperoxy)-2, 5-dimethyl hexane which was purchased from SIGMA-ALDRICH with a trade name of Luperox101 (L101). The acetone used in this work was supplied by SIGMA-ALDRICH. All materials were used as received.

2.2 | Procedures

The modification experiments were carried out in a Haake Rheomix 3000 batch mixer. In each experiment, 200 g virgin resin was first melted in the batch mixer at 200° C and 80 rpm for about 3 minutes. Then, peroxide (solution of 20 wt% of L101 in acetone) was added directly to the melt in the batch mixer and reacted for another 3 minutes until the torque was stabilized. Experiments were carried out at peroxide concentrations of 0, 0.01, 0.02, 0.04, 0.06, and 0.08 wt%.

TABLE 1 Properties of commodity poly(1-butene) resins

Typical properties	Resin 1	Resin 2
Physical		
Melt Flow Rate (g/10 minutes)		
(190°C/2.16 kg)	4	0.4
(190°C/10.0 kg)	70	12
Density (g/cm^3)	0.915	0.914
Mechanical		
Flexural Modulus (MPa)	450	450
Tensile Strength at Break (MPa)	35	35
Tensile Elongation at Break (%)	300	300

Molten samples collected from the batch mixer were spread into a thin sheet and cooled down to room temperature. The solidified sample sheets were then ground using a laboratory-scale Wiley mill grinder. The ground sample material was either used as is for MFR measurements or pressed for oscillatory shear measurements. In the latter case, the ground sample was placed into a steel mold cavity (dimensions of 15 X 15 X 0.05 cm) and pressed into a sheet using a PHI hot press at 180°C and 90 kN for 5 minutes. The pressed sample was cooled down to room temperature under the same pressure to avoid warping of the sheet. Subsequently, a round sharpedged cutting die was used to punch out several 25 mm diameter disks that were used for oscillatory shear rheological measurements.

The melt flow rate (MFR) of all samples was measured using a Dynisco D4002 Melt Flow Indexer at 190° C and 2.16 kg according to ASTM D1238. Rheological properties were obtained using an ARES G2 (TA Instruments) parallel plate rheometer at 150°C, 170°C, and 190°C.

The MWD of each sample was measured by high-temperature GPC (HT-GPC, Polymer CHAR Spain), using 1,2,4 trichlorobenzene as the eluent solvent with 50 mg/L Irganox 1010 at 145°C.

The thermal properties were measured by a differential scanning calorimeter (DSC) (Q-2000, TA Instruments). A heat-cool-heat procedure was used for testing each sample. Specifically, each sample was heated up from 35°C to 150°C at a rate of 20°C per minute to remove thermal history. Subsequently, each sample was held isothermal at 150° C for 5 minutes and then cooled down to -30°C at the same rate for the cooling cycle. Finally, each sample was kept isothermal for another 5 minutes and then heated up to 150° C again at the same rate. In this process, the first cooling and second heating cycle data were used for analyzing the thermal crystallization and melting properties.

3 | RESULTS AND DISCUSSION

It is well known that the modification of PP with organic peroxides[7-10] involves two main reactions: (a) abstraction of tertiary hydrogen atoms from the PP backbone by radicals produced from peroxide decomposition and (b) β-scission of the polymer radicals resulting from the hydrogen abstraction. The modification of PB-1 is expected to involve similar reactions as illustrated in Figure 1. As a result of the p-scission reaction, it is expected that the average molecular weight will decrease. In addition, due to the fact that longer polymer chains contain more tertiary hydrogens, it is expected that cleavage of longer chains will be statistically more pronounced, thus leading to narrowing of the MWD. These changes in MWD are expected to affect rheological properties.

Figure 2 shows the torque profiles from the batch mixer experiments for both commodity PB-1 resins. In both cases, it can be seen that increasing the peroxide content leads to a lower final torque due to decreased molecular weight and viscosity as expected. Free radicals generated from the peroxide decomposition, abstract preferentially tertiary hydrogen atoms from the PB-1 backbone thus initiating p-scission reactions that lead to the production of shorter polymer chains. The final torque values for all samples and the corresponding MFR data are plotted against peroxide concentration in Figure 3. It can be seen that as peroxide concentration increases, final torque is reduced (indicating lower viscosity) and MFR increases. It can be seen that for Resin 1 (Figure 3A), MFR increases almost linearly and torque decreases exponentially with peroxide concentration. For Resin 2 (Figure 3B), torque decreases exponentially while MFR appears to be increasing nonlinearly (polynomial of power two) with peroxide concentration. The MWDs of the modified PB-1 samples are shown in Figure 4.
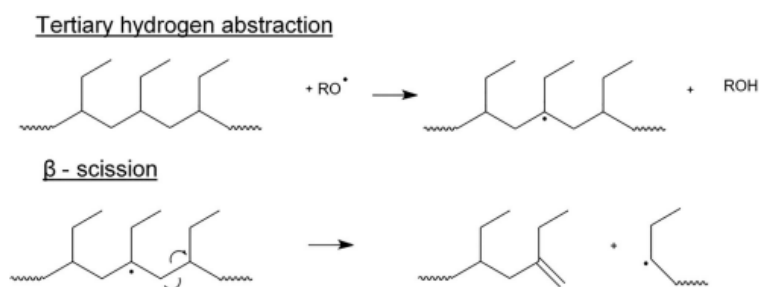
FIGURE 1 Tertiary hydrogen abstraction and p-scission reactions for PB-1

In this figure, "virgin" refers to the commodity resin while "0%" corresponds to the commodity resin processed without any peroxide. Comparing the starting Resins 1 and 2, it can be observed that Resin 2 has a broader MWD than Resin 1. In addition, it can be observed that as peroxide concentration increases, the distribution moves to the left (decreasing molecular weight) and its breadth appears to change slightly. Figure 5 shows the variation of Mw and PDI as a function of peroxide concentration for both resins. It can be seen that Mw decreases with increasing peroxide concentration while PDI seems to remain almost constant at peroxide concentrations above 0.02 wt %. These trends are similar to those observed in the production of CRPP from metallocene PP commodity resins.[37,42]

In this figure, the lines represent predictions from a kinetic degradation model previously developed for the peroxide modification of PP for the production of CRPP.[7,9] It can be observed, that even without any modification, this kinetic model can predict reasonably well the effect of peroxide concentration on Mw and PDI. To compare the effect of peroxide concentration on the extent of the scission of PB-1 compared to PP, we can use the degree of scission. This is a quantitative measure of the extent of degradation[24] and it is defined as $u = 1/r_N - 1/r^o_N$, where r_N and r^o_N are the number-average chain lengths of the modified and virgin materials. The degree of scission is plotted in Figure 6 as a function of peroxide concentration for CRPP produced from ZN-PP and for the CRPB produced in the present study. It can be observed that for both types of polymers, the degree of scission increases linearly with peroxide concentration. However, the rate of increase is much lower for CRPB resins regardless of the starting commodity resin.
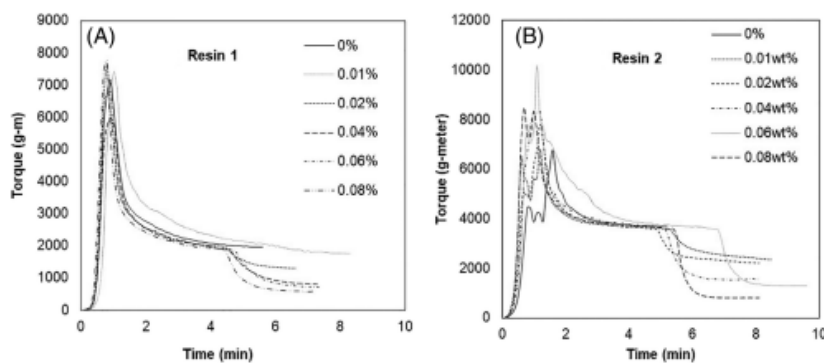

FIGURE 2 Batch mixer torque profiles for controlled-rheology PB-1 samples produced from: A, Resin 1 and, B, Resin 2
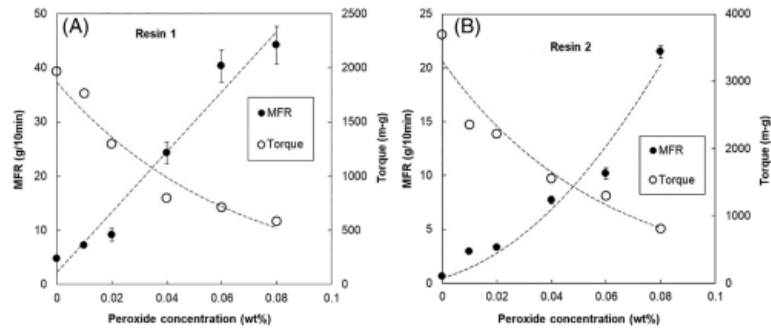
FIGURE 3 Effect of peroxide concentration on MFR and final batch mixer torque for: A, Resin 1 and, B, Resin 2
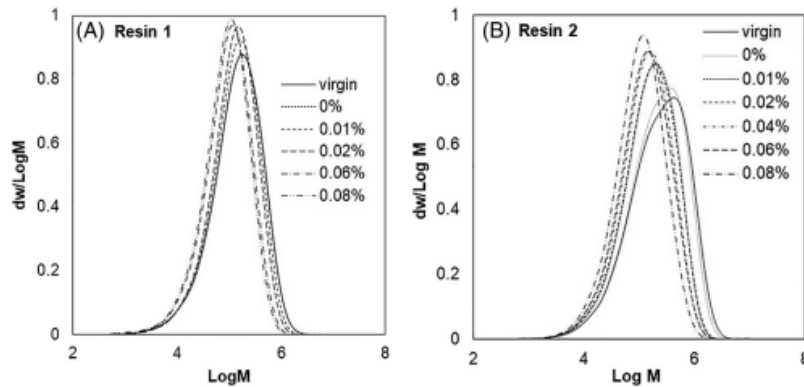

FIGURE 4 MWDofCRPB produced from: A, Resin 1 and, B, Resin 2. MWD, molecular weight distributions; CRPB, controlled-rheology PB-1

As molecular weight decreases with peroxide concentration, the melting and crystallization properties may be affected. These properties were measured by DSC for both resins and the results are listed in Table 2. It can be seen that the melting temperature of both resins decreases slightly with peroxide concentration. This is expected because of the reduction of MW as shorter chains require less energy for phase change transi-tions.[46] In terms of crystallization temperature, it appears that peroxide concentration does not have a significant effect and we can only observe a slight increase in the crystallization temperature for Resin 2 at high peroxide concentrations. No trends can be seen in terms of the effect of peroxide concentration on the heats of melting and crystallization.
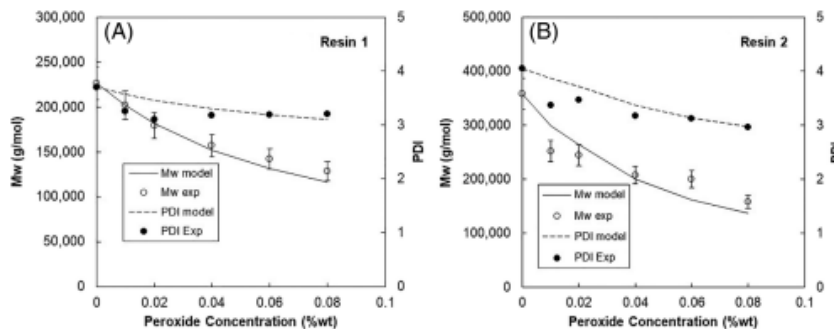

FIGURE 5 Effect of peroxide concentration on weight-average molecular and polydispersity of CRPB produced from: A, Resin 1 and, B, Resin 2. CRPB, controlled-rheology PB-1
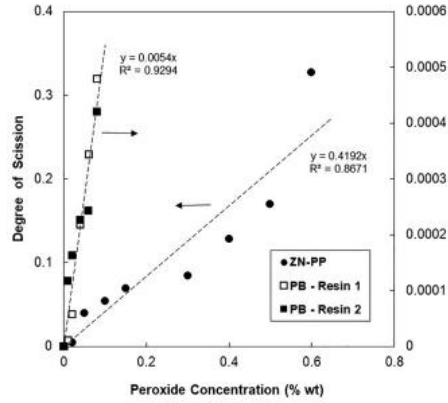
FIGURE 6 Degree of scission as a function of peroxide concentration

These results are in general agreement with previous general studies, in which polymer crystallization temperature was not found to change with molecular weights.[46] Overall, the results suggest that no significant changes in crystallization should be expected due to the chain scission reaction initiated by the peroxide radicals. In the future, additional experiments at very high levels of peroxide should be performed to see if this is still the case at much lower molecular weights.

The reduction of molecular weight due to chain scission from the peroxide radicals leads to the reduction of viscosity. The complex viscosity of all samples was measured and results obtained at 170° C are shown in Figure 7. Increasing peroxide concentration leads to reduced zero-shear viscosity, however, the shear-thinning behavior at high shear rates appears to remain approximately constant. This agrees with previous observations of the shear-thinning properties of PB-1.[4] In addition, it can be seen that the effect of peroxide concentration on viscosity reduction depends on the type of the starting commodity resin, in agreement with findings from photo-degradation experiments of PB-1.[47]

TABLE 2 Variation of melting and crystallization properties with peroxide concentration

	Peroxide (wt %)	Melting temperature T_m (°C)	Heat of melting ΔH_m (J/g)	Crystallization temperature T_c (°C)	Crystallization onset temperature $T_{c,\ onset}$ (°C)	Heat of crystallization ΔH_c (J/g)
Resin 1	0.00	117.3	35.3	72.2	85.4	39.9
	0.01	116.3	33.2	72.0	85.6	37.8
	0.02	115.2	31.7	72.1	85.3	37.6
	0.04	112.9	33.8	72.3	87.6	38.2
	0.06	111.8	34.5	71.6	85.2	37.9
	0.08	112.2	33.6	71.6	84.8	37.6
Resin 2	0.00	117.7	34.4	70.5	85.4	36.2
	0.01	114.0	40.6	70.1	86.1	36.8
	0.02	114.1	35.8	72.2	87.1	38.2
	0.04	113.0	30.3	71.6	88.2	34.6
	0.06	112.9	35.7	71.2	84.5	37.2
	0.08	111.9	34.8	72.5	84.6	35.0

The complex viscosity data obtained at three temperatures (150°C, 170°C, and 190°C) were fitted by the Carreau-Yasuda model to estimate the zero-shear viscosity (η_0), power-law index (n) and average relaxation time constant (λ) values for all samples. The estimated values for all samples are summarized in the online supporting information.

It was observed that the power-law index values did not change substantially with peroxide concentration and they ranged from 0.4 to 0.5 thus indicating that the shear-thinning behavior remains approximately unchanged. This was expected since the PDI of all CRPB did not change substantially with peroxide concentration.

Using the estimated zero-shear viscosity data at various temperatures and peroxide concentrations, the flow activation energy was obtained from an Arrhenius plot (η_0 vs $1/T$) and it was found to be approximately equal to 47.5 kJ/mol for all samples.

The relationship between zero-shear viscosity and the weight-average molecular weight is shown in Figure 8. It can be seen that the expected power-law relationship is holding with the power-law exponent being similar for all samples and in general agreement with entangled polymer melt theory. It can be observed that the values of the exponent are slightly higher than the 3.4 value typically observed for linear materials. This could potentially indicate some deviation from linear architecture due to branching or crosslinking which may be taking place along with the peroxide-induced scission reactions. Spectroscopic studies on chemical modification of polyolefins through irradiation[48] have shown that the yield of vinyl-idenes in PB-1 is lower than that in PP. This suggests the presence of more stable backbone radicals which can potentially lead to chain coupling and formation of branching. However, no indication of observable branching was evident from the GPC measurements in the present study. Therefore, the slightly higher exponent values are attributed to fitting errors both in this figure as in the estimation of zero-shear viscosities.
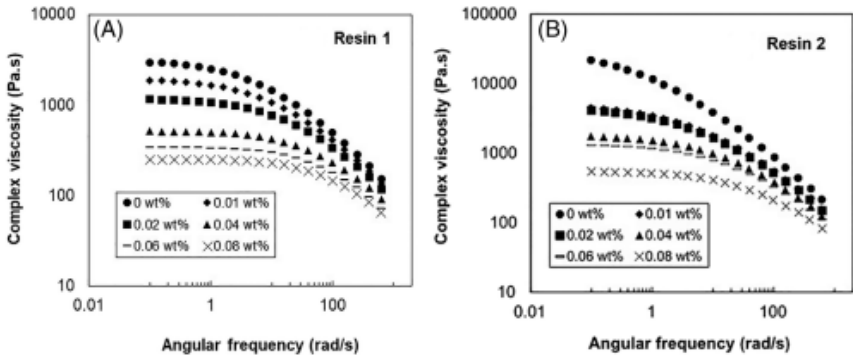

FIGURE 7 Effect of peroxide concentration on the complex viscosity (T = 170° C) for CRPB produced from: A, Resin 1 and, B, Resin 2. CRPB, controlled-rheology PB-1
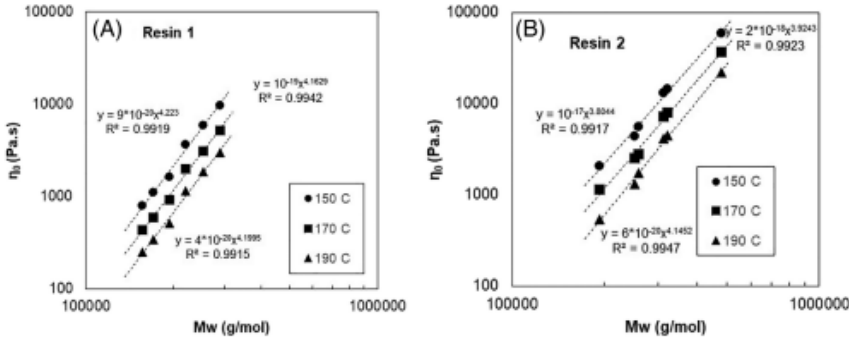

FIGURE 8 Correlation between zero-shear viscosity and weight-average molecular weight at different temperatures for CRPB produced from: A, Resin 1 and, B, Resin 2. CRPB, controlled-rheology PB-1

Figure 9 shows the effect of peroxide concentration on storage moduli data obtained from oscillatory shear measurements at 170° C. Similar trends were observed at all temperatures. It can be seen that increased peroxide concentration results in reduced elasticity due to the elimination of large polymer chains as expected based on the MWD results. The storage and loss moduli data were used to determine the crossover modulus (GC) and crossover frequency (raC) for all samples and the results are listed in Table 3. These results indicate that the crossover modulus value somehow does not depend on temperature. However, the crossover frequency value increases both with temperature and peroxide concentration. In addition, both crossover modulus and frequency increase with peroxide concentration for both resins, however, the effect of peroxide concentration is more pronounced on the crossover frequency.
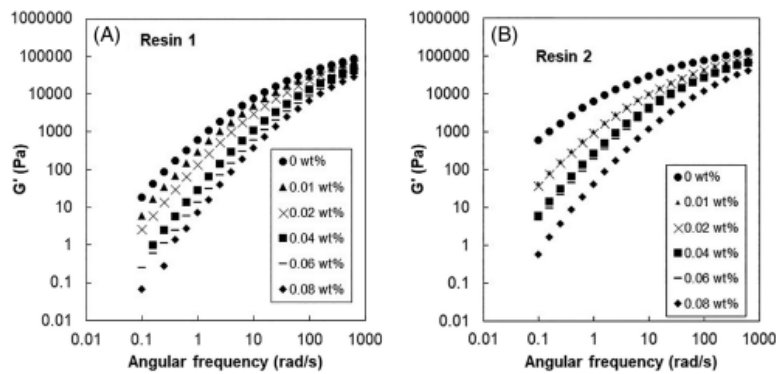

FIGURE 9 Effect of peroxide concentration on storage moduli data (170°C) for CRPB produced from: A, Resin 1 and, B, Resin 2. CRPB, controlled-rheology PB-1

TABLE 3 Cross-over moduli (G_c, Pa) and frequencies (ω_c, rad/s) for all CRPB samples

| Peroxide (wt %)	Temperature (°C) 150 G_c	ω_c	170 G_c	ω_c	190 G_c	ω_c
Resin 1						
0.00	23 233	13	21 747	21	24 925	48
0.01	24 717	22	24 880	44	25 237	75
0.02	26 685	39	27 746	78	27 811	138
0.04	29 361	96	29 739	170	29 841	303
0.06	30 011	144	29 893	270	28 313	456
0.08	29 315	196	30 127	377	27 072	588
Resin 2						
0.00	17 043	1.1	17 705	2.2	18 122	4.3
0.01	21 108	7.8	22 192	16.5	23 332	21
0.02	21 639	8.9	22 520	18	22 699	35
0.04	24 260	24	25 336	52	24 878	89
0.06	25 076	35	24 251	60	25 167	124
0.08	26 711	78	26 554	140	26 630	305
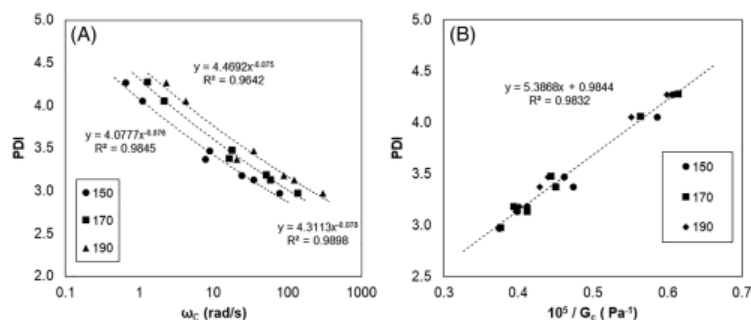
FIGURE 10 Correlation between polydispersity and: A, crossover frequency and, B, cross-over modulus of CRPB produced from Resin 2. CRPB, controlled-rheology PB-1

Finally, an attempt was made to correlate polydisper-sity (PDI) data with the crossover modulus and crossover frequency. Such correlations for these CRPBs produced from Resin 2 are shown in Figure 10. The correlation between PDI and crossover frequency (Figure 10A) seems to be following a power-law model which is temperature-dependent while the correlation between PDI and inverse crossover modulus (Figure 10B) is found to be linear. This correlation is similar to one proposed for polypropylene resins[49] and it seems to be temperature independent at low PDI values but slightly temperature-dependent at high PDI values. Similar correlations could not be obtained for CRPB produced from Resin 1 and this attributed to the fact that PDI values of these resins do not vary significantly.

4 | CONCLUSIONS

CRPB materials were produced by reactive processing in a batch mixer. This was accomplished by using two commodity PB-1 resins and various amounts of organic peroxide to induce p-scission reactions that reduce molecular weight and narrow the MWD of the starting polymer. It was found that average molecular weights decrease mono-tonically as a function of peroxide concentration while the PDI of the starting MWD does not change significantly. Predictions from a kinetic model previously developed for CRPP, agree reasonably well with the experimental observations on the effect of peroxide concentration on Mw and PDI for the current CRPB materials. As a result of these molecular weight changes in the produced CRPB, it was found that increased peroxide concentration leads to reduced viscosity while the shear thinning behavior remains almost constant. The zero-shear viscosity of all CRPB produced was found to correlate well with weight-average molecular weight. In addition, the linear viscoelastic properties decreased as a function of peroxide concentration and it was observed that peroxide concentration had a more pronounced effect on the storage modulus. Correlations between PDI and the crossover modulus and cross-over frequency were developed and those can be used in future work to quickly assess changes in MWD of controlled-rheology PB-1 materials. In conclusion, it was demonstrated that the well-known peroxide-induced chain scission reactions, used industrially for modifying polypropylene resins, can be successfully applied in the case of poly(1-butene) to produce resins of targeted controlled-rheology.

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