

Structural and Rheological Properties of PP/EPR/PE Alloys

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Abstract Linear and non-linear rheological properties were examined for in-reactor alloy samples composed of isotactic polypropylene (*i*PP), ethylene-propylene rubber (EPR), and polyethylene (PE). The samples were prepared through two- or three-stage sequential polymerization, where *i*PP, as the majority, was synthesized in the first stage, and either EPR or PE, as the minority, was synthesized in the second or third stage. Above T_m of both PE and *i*PP, the linear viscoelasticity shows two relaxation processes, where the fast and slow processes are attributable to the relaxation of the *i*PP component and that of the EPR/PE domains, respectively. Both the damping behavior upon applying the step-strain measurements and the shear-thinning behavior under the shear-rate sweep measurements are strongly related to the different degrees of non-linearity of the two relaxation processes.

Keywords Polypropylene alloy; Structure; Nonlinear rheology

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INTRODUCTION

Polyethylene (PE) and isotactic polypropylene (*i*PP) are the two most abundantly produced plastics worldwide, they together constitute nearly two-thirds of the world's plastic production.^[1,2] Although *i*PP exhibits high performance in mechanical strength, chemical stability, and heat resistance, it usually exhibits low-temperature brittleness that restricts its application in broader occasions.^[3–8] To improve the toughness of *i*PP, two mostly explored pathways are (1) blending *i*PP with the softer components like rubber or elastomers, and (2) preparing the in-reactor alloys with another component, *e.g.*, PE, through sequential polymerization.^[9–15]

High impact polypropylene (HIPP) is one type of in-reactor alloy that is usually synthesized through two-stage polymerization using the Ziegler-Natta catalyst.^[16–18] The copolymer synthesized in the second-stage copolymerization, usually ethylene-propylene rubber (EPR), can significantly improve the impact resistance of the *i*PP synthesized in the first-stage polymerization.^[19–21] In a previous study by Ji and coworkers,^[22] the chain microstructure was examined for two commercial HIPP samples that exhibit a good balance between stiffness and toughness through a combination of the preparative temperature rising elution fractionation (TREF) and several additional techniques to characterize the chemical and condensed structures of each fraction, including high-tempera-

ture gel permeation chromatography (HT-GPC), Fourier transform infrared (FTIR) spectroscopy, ¹³C nuclear magnetic resonance (¹³C-NMR), and differential scanning calorimetry (DSC). For both samples, the major fractions other than *i*PP are EPRs occupying ~30 wt% of the whole sample. The EPRs having C2 contents of 57.4% and 43.7% are non-crystalline, which endow the samples with a high level of toughness.

It is well expected that a systematical increase in the C2 content in the second-stage reaction would lead to larger ethylene segments or even crystalline ethylene blocks, thereby reducing the compatibility between the components formed in the first- and second-step reactions. Nevertheless, a systematic investigation has yet to be attempted on the dependence of rheological properties on the sequence and content of the second-stage polymerization.

To this end, we conducted both two- or three-stage reactions, with the first stage for *i*PP and the second- or third-stage for EPR or PE using the Ziegler-Natta catalyst. Through systematically changing the ethylene content in the second- and third-stage reactions, we obtained a series of samples with systematically varied C2 content. We found that the increase of the C2 content led to a higher melting peak which was attributable to the PE crystals. Above T_m of both *i*PP and PE, these samples exhibited two relaxation processes, where the fast process was attributed to the relaxation of the *i*PP chains synthesized in the first stage, and the slow process to the EPR/PE domains synthesized in the second and third stages. Remarkably, we found that nonlinear rheological properties, including the damping and shear-thinning properties, were controlled by the different nonlinearity of the two relaxation processes manifested at the different time scales.

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MATERIALS AND METHODS

Materials

Ethylene and propylene, polymerization grade purity, were purchased from SHANGTE special gas Co., Ltd. (Changchun, China). MgCl_2 -supported Ziegler-Natta catalyst with DIBP as a donor (Ti mass fraction of 2.5%), triethyl aluminum (AlEt_3 , >98%), and diphenyl-dimethoxy silane (DDS, analytical grade) were kindly provided by LIAONING XIANGYANG chemicals group Co., Ltd. (Yingkou, China). *n*-Heptane, 1,3,5-trichlorobenzene, etc., were of analytical grade and treated according to standard procedures before use.

Preparation of Alloy Samples

The alloy samples were prepared through two- or three-stage sequential polymerization processes: AlEt_3 , DDS, and propylene were introduced into the reactor at constant pressure, and then the supported catalyst was added. The propylene bulk polymerization was carried out at 70 °C for 20 min to obtain enough PP particles to ensure the formation of a fluid bed in the gas polymerization process. The unreacted propylene was vented quickly and a certain feed ratio of ethylene/propylene mixture or ethylene was breathed into the reactor and reacted for 30 min at 80 °C, to obtain the *i*PP-E/P and *i*PP-E samples, respectively. Here, the hyphen “-” is used to connect feeding sequences during the synthesis, and the slash “/” separates feed gas compositions of the same feeding sequence. It should be mentioned that a certain amount of propylene monomer remained inevitably in either the reactor or the homo-PP particles even after the quick venting, which will join in the next-stage polymerization. To synthesize the *i*PP-E/P-E sample, remnants of ethylene and propylene monomers in the second-stage reaction were removed by vent, then ethylene was subsequently fed in the third stage and polymerized for 5 min. The products were poured into a large amount of ethanol containing 1% HCl solution and the granular samples were washed with plenty of ethanol, filtered, and dried in a vacuum oven at 60 °C for 8 h.

High-Pressure Liquid Chromatography (HPLC)

HPLC-SEC was performed using a Two-Dimensional Solvent Gradient Interaction Chromatography (SGIC-2D) instrument equipped with an IR detector from Polymer Char. The mobile phase consists of 1-decanol and 1,2,4-trichlorobenzene (TCB). The polymer samples were dissolved in TCB at a concentration of 2 mg/mL at a temperature of 140 °C; 200 μL of the sample solutions were injected and analyzed. The experiment performs an analytical fractionation of the polymer according to chemical composition by selective adsorption/desorption using an HPLC column, followed by a second separation according to molar mass using a GPC/SEC column. HPLC-SEC equipped IR detector

is a specialized instrument for characterizing the composition, molecular weight, and its distribution of polyolefins such as polyethylene and polypropylene. The basic principle of the IR detector for ethylene content is explained below.

The range of response wavenumbers of IR detector is from 2800 cm^{-1} to 3000 cm^{-1} , in the case of polyolefins, the signals of C—H stretching vibration of $-\text{CH}_2-$ and $-\text{CH}_3$ appear at 2920 and 2960 cm^{-1} , respectively. Here, $-\text{CH}_3$ number per 1000 carbon atoms ($\text{CH}_3/1000\text{TC}$) is used as a factor to calculate the ethylene content in the ethylene/propylene copolymers, the theoretical value of $\text{CH}_3/1000\text{TC}$ is 0 and 333.3 for PE and *i*PP, respectively. In the actual measurements, a series of PE/PP blends with known ethylene concentration were used as the standards. Comparison of the signals detected by using the IR detector for the focused sample and for the standards enables calculation of the $\text{CH}_3/1000\text{TC}$ value and accordingly the content of ethylene as:

$$C_2 = (1000 - \text{CH}_3/1000\text{TC} \times 3)/1000 \quad (1)$$

where the value $\text{CH}_3/1000\text{TC}$ is multiplied by a factor of 3 to represent the number of carbon atoms per *i*PP monomer. The important parameters characterized by HPLC-SEC are summarized in Table 1.

Scanning Electron Microscopy (SEM) Measurements

SEM experiments were performed on four samples to characterize the morphology. The *i*PP and alloy samples were pressed into strips at 200 °C and the strips were microtomed into a trapezoid at -60 °C using a Leica CMFCS cryostat. The samples were stirred in the methylbenzene for 1 h to etch away the rubber phase at room temperature. Then the etched samples were sputtered with gold and examined on a field emission scanning electron microscope XL-30 ESEM (FEI, America).

Wide Angle X-ray Diffraction (WAXD)

The X-ray diffraction measurements were carried out using a Bruker D8 ADVANCE diffractometer equipped with Cu K α radiation, and the wavelength of the X-rays used was 0.154 nm. the electric current in the experiment was 40 mA and the voltage tested was 40 KV. The range of scattering angle 2θ was 5° – 25° . The test used a flickering counter with a step size of 0.05° and a velocity of 3 s.

Differential Scanning Calorimeter (DSC) Measurements

DSC experiments were carried out on a TA Instruments Q20 using sealed aluminum pans filled with specimens of weight of 6–8 mg. The DSC equipment was calibrated using indium and tin. All experiments were performed with nitrogen protection with a flow rate of 50 mL/min. For all DSC measurements, samples were firstly annealed at 250 °C for 10 min, higher than

Table 1 Results of HPLC-SEC of *i*PP and alloy samples.

Feed sequence	$M_w^a \times 10^4$ (g/mol)	M_w/M_n^b	C_2^c (%)	aPP ^d (%)	<i>i</i> PP ^e (%)	EP ^f (%)	PE ^g (%)	f_v^h (%)	$C_{2,v}^i$ (%)	$M_w^j \times 10^4$ (g/mol)	M_w/M_n^k
<i>i</i> PP	91.96	6.5	—	—	—	—	—	—	—	—	—
<i>i</i> PP-E/P	73.95	6.9	10.6	0.6	84.2	7.9	7.3	15.3	69.1	42.45	10.4
<i>i</i> PP-E/P-E	90.44	7.5	18.4	0.7	74.9	10.4	14.0	24.4	75.6	57.76	11.7
<i>i</i> PP-E	100.25	8.5	22.6	0.5	75.1	3.7	20.7	24.4	92.7	19.89	8.8

^{a–c} The weight average molecular weight, molecular weight distribution, and C_2 content of the whole sample; ^{d–g} contents of atactic PP, isotactic PP, ethylene propylene copolymer, and PE; ^h The content of fraction soluble in TCB at room temperature; ⁱ C_2 content in f_v ; ^{j,k} M_w and M_w/M_n of f_v .

the equilibrium melting temperature of homo *i*PP and PE, to remove the thermal and flow histories. After that, the samples were cooled down at 10 °C/min to −70 °C and equilibrated there for 3 min, and then heated up to 250 °C. Samples were subjected to two cooling-heating circles and the endothermic and exothermic curves were obtained in the second circle.

Rheological Measurements

Linear viscoelasticity (LVE) of all samples was conducted at a strain-controlled rheometer (ARES-G2 from TA Instruments) with 25 mm parallel plates in a nitrogen atmosphere. Frequency sweep measurements were conducted with a small strain within the linear regime. All measurements were conducted above the crystallization temperature.^[23] The samples were loaded on the rheometer at 250 °C and annealed there for 10 min, the same annealing procedure as the DSC measurements. After that, the temperature was decreased at 20 °C per step to the melting temperature. The frequency sweep measurements were conducted in a range of 150 °C ≤ *T* ≤ 250 °C for homo *i*PP, and the time-temperature superposition (tTs) principle was employed to construct the master curve. For the alloy samples, we found that the tTs did not hold, and thus we conducted the frequency sweep from 398 rad/s to 0.001 rad/s at 190 or 250 °C.

For the nonlinear rheological measurements, the 25 mm cone-and-plate geometries (0.0402 rad, truncation gap 0.0539 mm) were applied. Samples were loaded on the rheometer at 250 °C and annealed there for 10 min (the same as the frequency sweep measurements). After that, the temperature was held at 250 °C for the *i*PP-E sample or decreased to 190 °C for all other samples, a step strain from 0.05 to 20 was applied, and the stress relaxation process was recorded to examine the damping behavior. The start-up shear experiment was carried out at the same temperature with the shear rate changed from 0.001 s^{−1} to 100 s^{−1}. Considering the accumulative edge fracture effect during the step strain and start-up shear experiments, the frequency sweep measurement was conducted before each measurement to check the reproducibility at the high frequency (1–100 rad/s). When the edge fracture occurred, the sample near the edge was refilled (before the non-linear measurements) to ensure the filling of the sample.

RESULTS AND DISCUSSION

SEM Images

Fig. 1 compares the SEM images obtained for the microtomed *i*PP, *i*PP-E/P, *i*PP-E/P-E, and *i*PP-E samples after being dissolved in methylbenzene for etching away the EP rubber. The SEM image of *i*PP shows a flat surface while either *i*PP-E/P, *i*PP-E/P-E, or *i*PP-E shows the island-in-sea morphology. In particular, the fractions of the island domains seem to be in accordance with the content of EPR fraction shown in Table 1, i.e., 3.7 wt% for *i*PP-E < 7.9 wt% for *i*PP-E/P < 10.4 wt% for *i*PP-E/P-E. For all three samples, there is a fraction of the sample within the island domains remains after the etching, which could be the undissolved/ non-etched crystalline PE having an order of 7.3 wt% for *i*PP-E/P < 14.0 wt% for *i*PP-E/P-E < 20.0 wt% for *i*PP-E. This argument is supported by the observation that the etched part of *i*PP-E is shallower than either *i*PP-E/P or *i*PP-E/P-E. Another comment is on the shape of the domain that is not completely spherical, which is probably related to the

insufficient thermal equilibration after pressing into strips (at 200 °C) for microtoming.

Crystalline Form and Crystallinity

Fig. 2 compares the X-ray diffraction results obtained for the *i*PP and in-reactor alloy samples. The main scattering peaks, i.e., 110, 040, 130, 111, and 131 peaks, for all samples examined are predominately consistent with the isotropic α -phase, meaning that the EP and PE contents do not affect the crystalline form. Nevertheless, the crystallinity has changed greatly, as explained below.

To investigate the difference in crystallinity, Fig. 3 compares the DSC traces of the *i*PP and in-reactor alloy samples. Fig. 3(a) compares the DSC traces obtained during the cooling process, where the peak at ~113 °C is attributed to the crystallization of homo *i*PP or long sequences of *i*PP segments, and the crystallization for the PE component is not clearly seen.

Fig. 3(b) compares the DSC traces during the following heating process, where two melting peaks are detected: the high-*T* peak at ~165 °C corresponds to the melting of *i*PP, and the low-*T* peak at ~121 °C is seen for all alloy samples except the neat *i*PP sample, indicating that this peak corresponds to the melting of PE. The order for the area of the low-*T* melting peak is *i*PP-E/P < *i*PP-E/P-E < *i*PP-E, which is in accordance with the content of PE revealed in HPLC-SEC in Table 1, lending

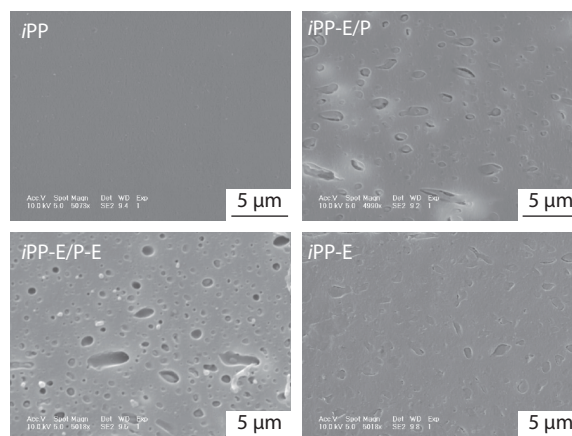


Fig. 1 SEM images of four samples etched away rubber phase.

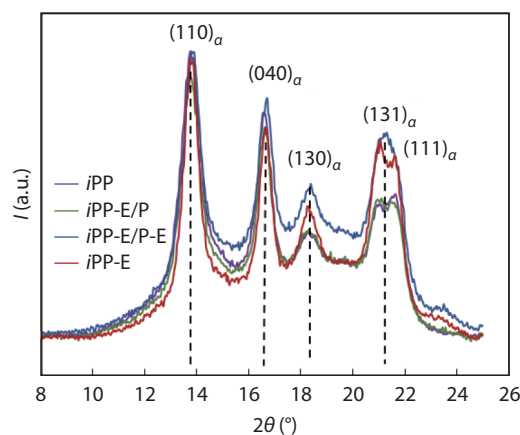


Fig. 2 Diffraction results of *i*PP and the alloy samples as indicated.

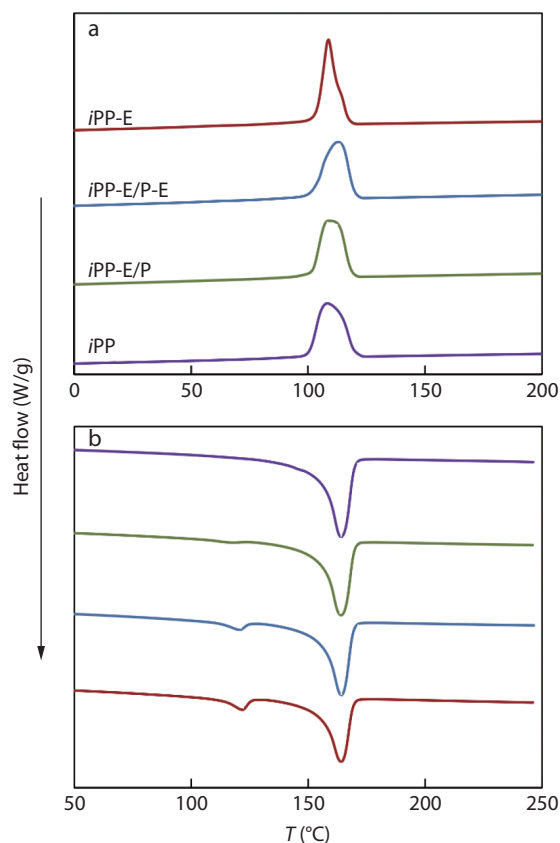


Fig. 3 DSC crystallization curves (a) and melting curves (b) of the homo *i*PP and alloy samples measured at a cooling/heating rate of 10 °C/min, after annealing at 250 °C for 10 min.

support to the assignment of this exothermal peak. In principle, the exotherm peaks during the heating process should be in accordance with the endotherm peaks during the cooling process if the crystal is not formed by the cold crystallization. Nevertheless, the crystallization of PE is not clearly seen during either the cooling (down to −50 °C) or the following heating process. We believe this feature is owing to that the crystallization of the PE chains occurs in confined domains, and the readily crystallized *i*PP chains strengthen the spatial confinement. Then, the PE chains exhibit the asynchronous crystallization process, *i.e.*, crystallization occurring over a wide *T* range, thereby making the crystallization process non-detectable in either the heating or cooling process.

In principle, the contents of PP and PE can be obtained by integrating the areas of the corresponding melting peaks. Nevertheless, both melting peaks are broad and there is a broad *T* range where the two peaks merge, which makes the resolution of the two peaks a challenging task. To this end, we assume that the shape of the melting peak is the same for neat *i*PP and the *i*PP component in the alloy samples. This assumption has been partly justified through comparing directly the shape of the peaks in Fig. 4(a), where the *i*PP peaks are properly normalized *via* multiplying the peak of *i*PP-E/P, *i*PP-E/P-E and *i*PP-E by an intensity parameter so that the main *i*PP peak agree with that of *i*PP.

The area of the crystallization peak of PE A_{PE} can be obtained by subtracting the area of neat *i*PP from the area of the

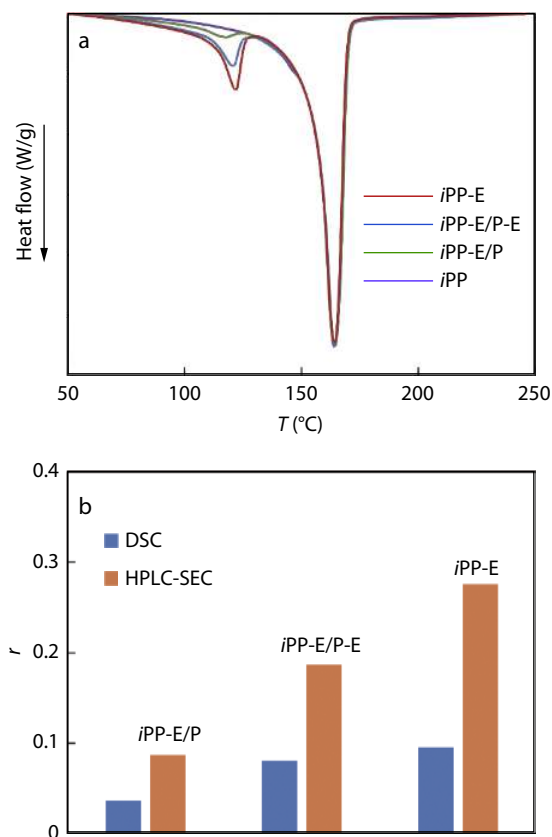


Fig. 4 (a) Melting curves of all alloy samples after normalizing the *i*PP melting peaks (b) a ratio of PE and *i*PP determined by DSC and HPLC-SEC.

two peaks as a whole ensemble. The ratio between PE and *i*PP is thus evaluated as:

$$r = \frac{PE}{iPP} = \frac{A_{PE}/\Delta H_{PE}}{A_{iPP}/\Delta H_{iPP}} \quad (2)$$

where A_{PE} and A_{iPP} are the areas of the PE and *i*PP melting peaks, respectively, determined by this analysis. ΔH_{PE} and ΔH_{iPP} are the melting enthalpies of ideal crystals of *i*PP and PE, of which the values are 207.9 and 293.0 J/g,^[24,25] respectively. *r* determined by Eq. (2) is compared with that determined by HPLC-SEC in Fig. 4(b), where *r* determined by DSC is smaller than that by HPLC-SEC, meaning that PE detected by HPLC-SEC is not all crystallizable, probably because there is a fraction of EPR having low *i*PP content has been assigned as PE in the HPLC-SEC measurements. In other words, the actual content of PE could be lower and the actual content of EPR could higher than those determined by HPLC-SEC.

Linear Viscoelasticity

Fig. 5 compares the linear viscoelastic storage and loss moduli, G' and G'' obtained for the *i*PP and alloy samples. G' and G'' are plotted against the angular frequency ω . The master curve for the homo *i*PP sample is constructed using the time-temperature superposition (tTs) rule and reduced to 190 °C. In comparison, the failure of tTs has been noted for the *i*PP-E/P-E and *i*PP-E samples, therefore we conduct the frequency sweep measurements at 190 °C with ω from 398 rad/s to 0.001 rad/s, the maximum ω range allowed by the rheometer in this study.

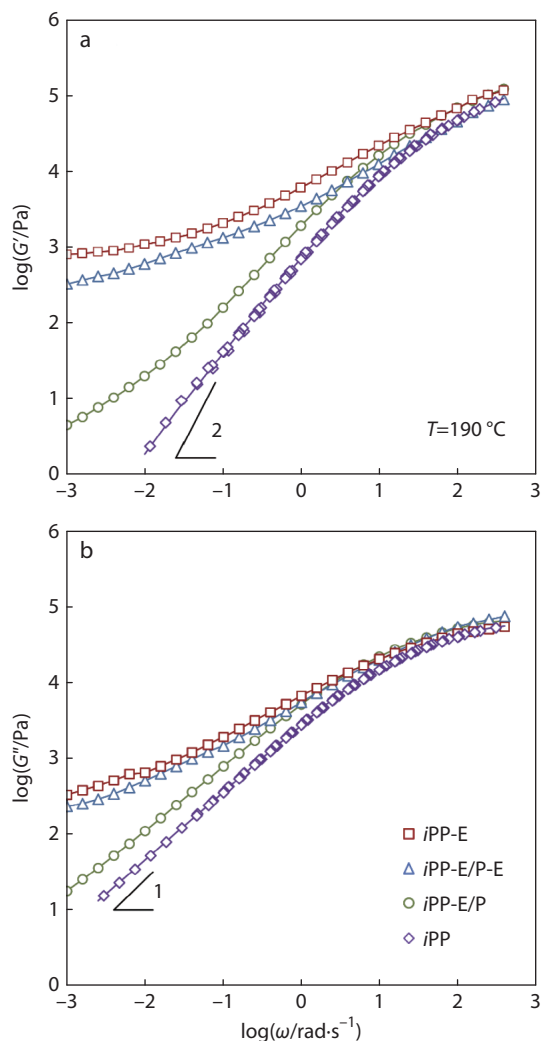


Fig. 5 Comparison of LVE storage and loss moduli, G' and G'' , measured as functions of angular frequency ω . For the three *iPP* alloy samples, frequency sweep was carried out at 190 °C from 398 rad/s to 0.001 rad/s. For the homo *iPP* sample, the master curve was obtained through the tTs and reduced at the reference temperature 190 °C.

In Fig. 5, the four samples show a similar amplitude of the modulus at the highest ω , but a different amplitude of modulus at the low ω . The amplitude of the low- ω modulus follows the order $iPP < iPP-E/P < iPP-E/P-E < iPP-E$, agreeing with the order of the PE content revealed in the HPLC-SEC and DSC measurements. This agreement suggests that the low- ω modulus stems from the relaxation of the PE-rich domains. EPR could either form their own domains or locate at the interface of the *iPP*-rich and PE-rich domains, serving as the compatibilizer.

The *iPP-E/P* sample exhibits LVE not strongly deviated from *iPP*, where a slow process manifests at $\omega < 0.01 \text{ s}^{-1}$, which is attributable to the existence of the EPR phase formed during the second-stage reaction. The rheological behavior is akin to that seen for the poly(styrene-*co*-acrylonitrile) (SAN) filled with rubber particles.^[26,27] The dispersion of the rubber particles was tuned through grafting SAN chains. When the particles are well dispersed, the rheological behavior is char-

acterized by a slow process that is attributed to the graft SAN chains being retarded because they are tethered to the rubber domain. For the *iPP-E/P* sample here, GPC reveals the EPR content of 7.9 wt% and PE content of 7.3 wt% (the actual EPR content could be even higher as suggested by DSC), respectively. The interface of the domains rich in EPR and PE could be those EPR chains having a higher content of *iPP*. The relaxation of these tethered chains is expected to be more delayed than that of *iPP* chains in the matrix. The interfacial relaxation after the deformation could be another source of the modulus at the low frequency.

The amplitude of modulus at low ω increases with increasing the content of PE chains formed in the third-stage reaction for *iPP-E/P-E*. These PE chains are enthalpically not in favor in contact with the *iPP* chains, thereby strengthening the phase segregation, which is seen through comparing the SEM images of *iPP-E/P* and *iPP-E/P-E* in Fig. 1. This feature is again reminiscent of the behavior of SAN filled with rubber particles grafted with SAN chains, where the modulus increases and a plateau-like region manifests when the miscibility is lowered between the SAN chains in the matrix and those grafted on the rubber particles. In the present case, the amplitude of the slow process further increases if the pure ethylene is directly introduced in the second-stage reaction for *iPP-E*, which lowers the miscibility between the *iPP* and EPR/PE-rich phases. For either *iPP-E/P-E* or *iPP-E*, both G' and G'' decay weakly with decreasing ω (much weaker than those expected for the terminal tails) even the lowest $\omega = 0.001 \text{ rad/s}$, meaning the relaxation time is much longer than 1000 s. The weak decay may reflect a wide distribution of the domain sizes, and the lowest ω plateau region may reflect the agglomeration of the EPR/PE-rich phases that sustained the elastic force.

One may think it is possible to apply the constitutive model applicable for the strongly immiscible polymer blends having the island-in-matrix morphology and the sharp interface for the *iPP-E/P-E* and *iPP-E* system, e.g., the models of Palierno,^[28] Maffettone and Minale^[29] and Yu and Bosmina.^[30] However, based on the linear relaxation behavior of these two samples, we think the current system is quite different from the strongly immiscible polymer blends. The terminal relaxation is hardly achieved even if we extend the measurement to 3000 s (shown later in the stress relaxation measurements), indicating the significant role of the EPR fraction serving as the compatibilizer that strongly stabilized the deformed interface, making the LVE behavior of these alloy samples quite different from those of the strongly immiscible polymer blends with a sharp interface.

Non-linear Rheological Properties

Damping behavior

Fig. 6 compares the stress relaxation modulus $G(t, \gamma)$ as a function of strain amplitude γ (as indicated) and time t for the *iPP* and alloy samples, where $G(t, \gamma)$ is plotted against t . For the *iPP*, *iPP-E/P* and *iPP-E/P-E* samples (Panels a, b, and c), the measurements were conducted at 190 °C, the same T for conducting the LVE measurements. Nevertheless, we found that the *iPP-E* sample cannot be easily pressed using the 25 mm cone and plate at 190 °C, so a higher testing temperature of 250 °C was chosen, at which the measurements can be well conducted.

For the *iPP* sample (Panel a), the relaxation modulus $G(t, \gamma)$

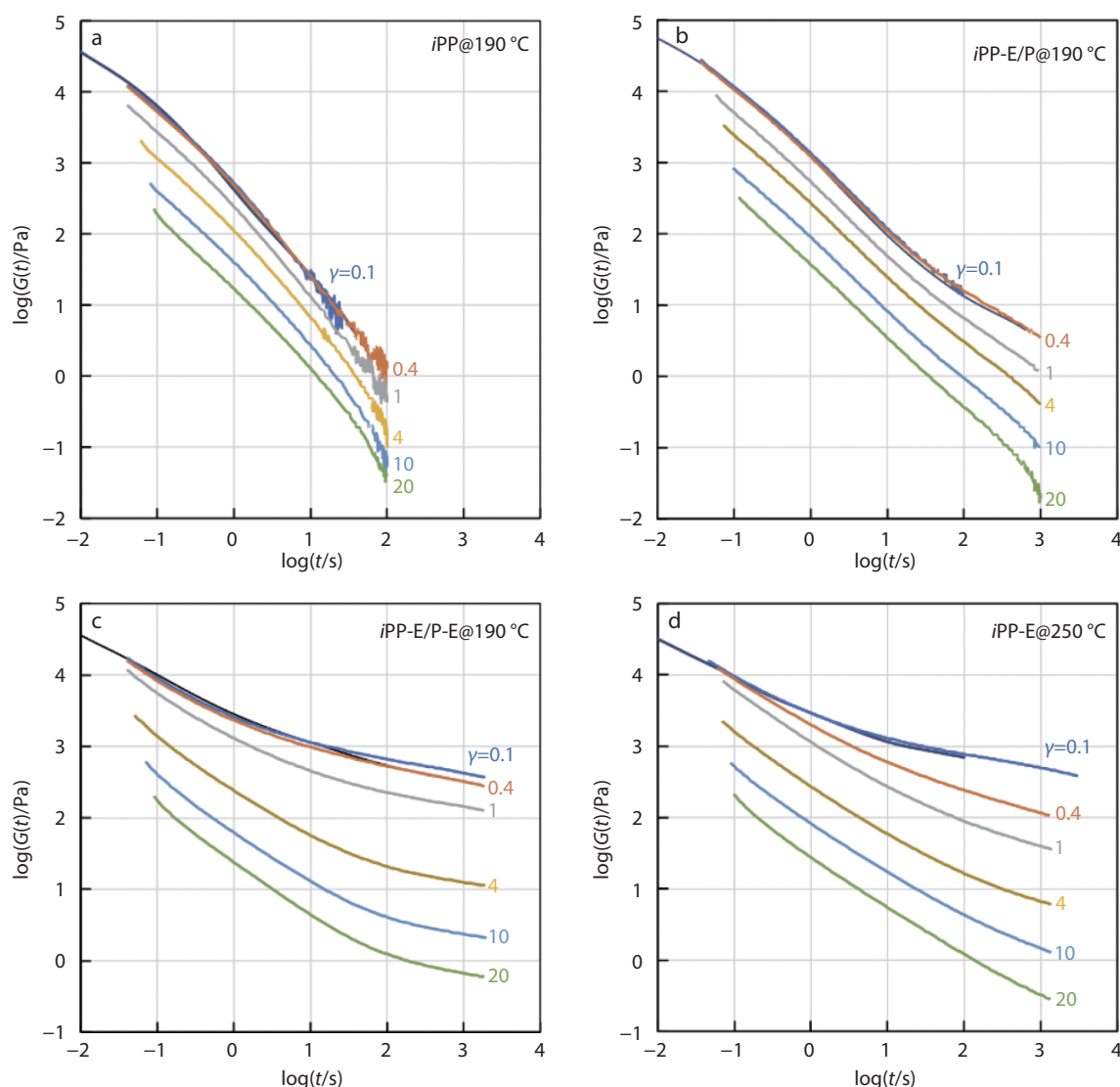


Fig. 6 Comparison of nonlinear relaxation modulus $G(t, \gamma)$ of homo *iPP* and alloy samples at $T=190$ or 250 °C as indicated.

shows one-step relaxation. In particular, $G(t, \gamma)$ at $\gamma=0.1$ and 0.4 agrees with that calculated from the linear viscoelasticity (solid black curve), meaning that this measurement is obtained in the linear regime. Increasing the strain amplitude to $\gamma \geq 1$ leads to moderate damping behavior. From LVE we estimate the terminal relaxation time as $\tau_d = [G' / \omega G''] = 4$ s. Therefore, the relaxation behavior at $t > 10$ s should represent the terminal relaxation of *iPP*. Considering that the molar mass of *iPP* is similar in all the *iPP* and alloy samples (cf. Table 1), we may consider the *iPP* chains to be relaxed at $t > 10$ s.

For all alloy samples, two-step relaxation behavior is seen (Panels b, c, and d). For *iPP-E/P*, the reduction of the modulus with increasing the applied strain is stronger on the long- t side than on the short- t side, leading to the more widely separated curves at the longer time ($t > 10$ s) where the *iPP* chains have relaxed. The stronger damping at the long- t side is attributed unequivocally to the higher nonlinearity for the relaxation of chains tethered at the interface as well as that of the deformed interface. Both *iPP-E/P-E* and *iPP-E* show qualitatively similar nonlinearity at the long- t side (~ 2000 s) that is

even higher than that of *iPP-P/E*, because of the twofold effects: (1) increase of a ratio between PE and EPR, from 0.92 for *iPP-E/P*, to 1.34 for *iPP-P/E-E* and 5.59 for *iPP-E*, and (2) a sum the PE and EPR that form the domains, from 15.2 for *iPP-E/P* to 24.4 for both *iPP-P/E-E* and *iPP-E*. The increase in PE/EPR ratio should reduce the miscibility, and accordingly the stronger tendency for agglomeration of the PE/EPR-rich phases, while the increase of the sum fraction of PE and EPR would lead to more deformable domains. The degree of damping is equally strong for *iPP-E/P-E* and *iPP-E* at high $\gamma > 100\%$, but stronger for *iPP-E* at low $\gamma \leq 100\%$, meaning that the E/EPR-rich domains in *iPP-E* are more easily deformed or destructed at the lower γ , probably owing to the less compatibilizer therein.

The argument above about the damping behavior is in accordance with the microstructure revealed earlier in Fig. 1. The etched domains are deeper and more condensed for *iPP-E/P-E* than for either *iPP-E/P* or *iPP-E*. The deeper etched domains for *iPP-E/P-E* indicate that the domains are mainly the PE stabilized by EPR at the interface. Then, the whole domain

can be etched away by the solvent. The shallower and less condensed etched domains for *i*PP-E/P are attributed to the lower EP+PE content (of 15.2 wt%). Nevertheless, the shallower and less condensed domain for *i*PP-E is not attributable to the lower EP+PE content, because its *i*PP-E/P-E content (of 24.4 wt%) is the same as *i*PP-E/P-E. We suspect that the PE is not well compatibilized by the EPR in *i*PP-E, because the crystalline PE can hardly be etched away if not fully surrounded by EPR. Probably, the *i*PP-E sample contains domains having a wide distribution of the EPR/PE ratios, and the etched domains are those with sufficiently high EPR/PE ratios.

In Fig. 7, we test the damping behavior through shifting $G(t, \gamma)$ obtained at high γ upward, by a factor of $h(\gamma)^{-1}$, to be superposed to that obtained at low γ . For *i*PP (Panel a), reasonably good superposition has been achieved particularly at long $t > 10$ s where the terminal relaxation has been achieved, indicating the time-strain separability.^[31] For the alloy samples (Panels b, c, d), we superpose the short- t side of $G(t, \gamma)$, which enables a better comparison of the intensified damping at the long- t side. For comparison, we also add the relaxation behavior of *i*PP at the same T in the dashed curve. The superposition can only be achieved in a region where the modulus is close to that of *i*PP, which rationalized that the su-

perposition mainly reflects the damping of the PP matrix.

The deviation of the modulus at the long- t side enables us to compare quantitatively the damping behavior of the EPR- and PE-rich domains. The similar damping behavior for *i*PP-E/P-E and *i*PP-E suggests that the damping is mainly attributed to the deformation or even breakup of the domains rich in PE. If we take a close look at the long t sides of $G(t)$ for *i*PP-E/P-E and *i*PP-E, we find that the gradient of $G(t)$ with t does not change too much with γ for the *i*PP-E/P-E sample, while the gradient decreases with increasing γ for the *i*PP-E sample. This difference is again attributable to the better compatibilizing effect for the *i*PP-E/P-E sample with the higher EPR content. The EPR stabilizes the PE/EPR rich domains of *i*PP-E/P-E against the high step strain.

The damping function $h(\gamma)$ obtained in Fig. 7 is compared in Fig. 8, where we find the degree of damping is similar for *i*PP and the fast relaxation process of *i*PP-E/P, *i*PP-E/P-E, and *i*PP-E. This similarity again justifies our assignment of the fast process to the relaxation of the *i*PP matrix. The solid line shows the prediction of $h(\gamma) = 1/(1 + 0.27\gamma^2)$,^[32] which is indistinguishable from the well-known Doi-Edwards damping function for $\gamma \leq 10$ (numerically calculated without the independent alignment approximation).^[33] The damping behavior of

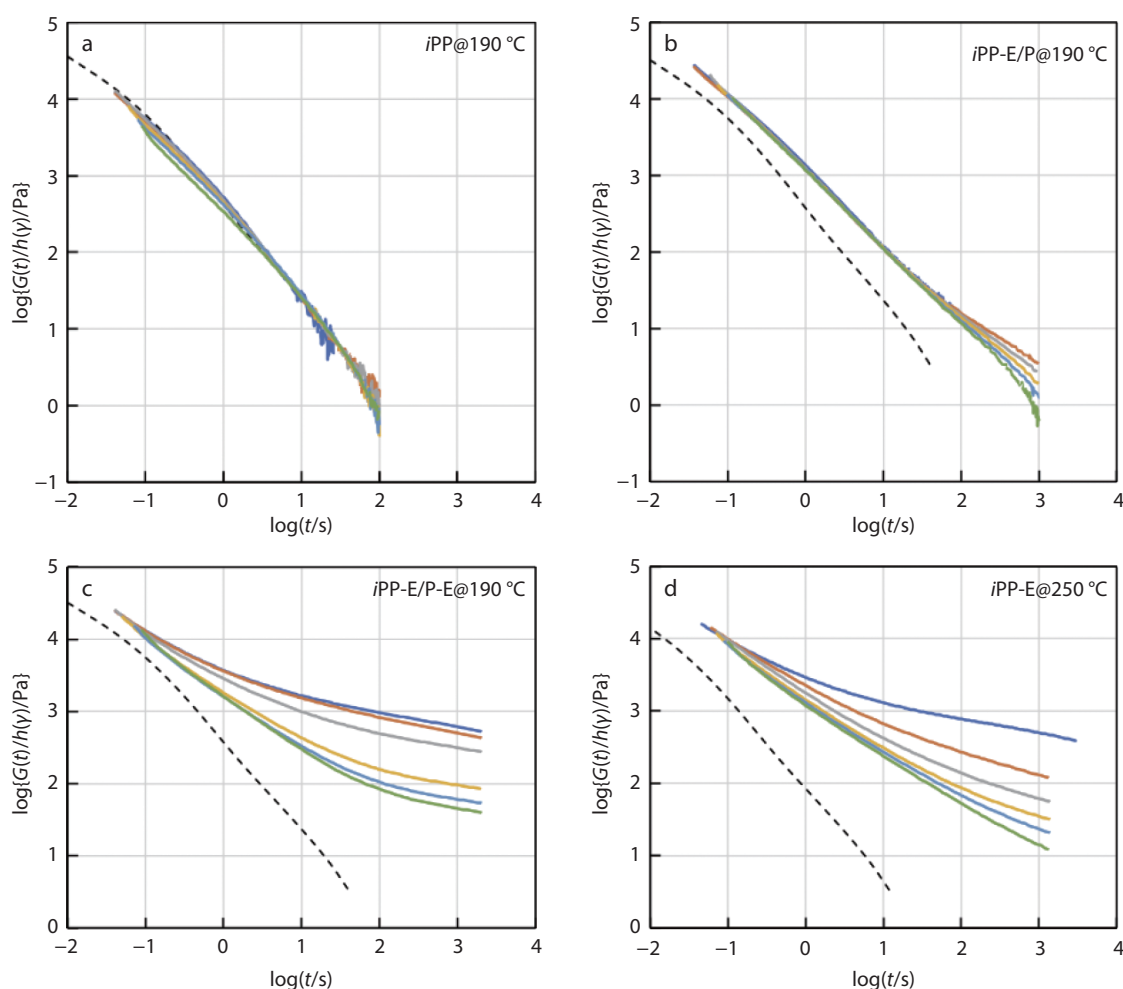


Fig. 7 Comparison of the *i*PP and alloy samples through superposition under the guidance of the fast relaxation process, the relaxation behavior of *i*PP at the same T is indicated in the dashed curve.

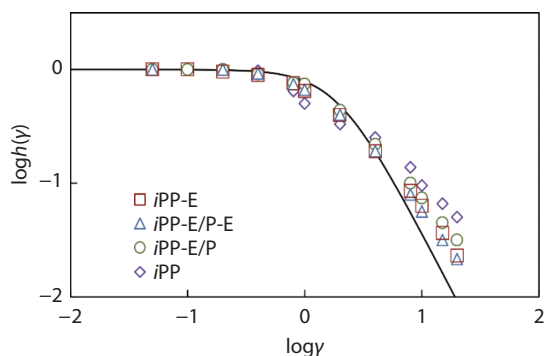


Fig. 8 Damping function $h(\gamma)$ for the fast process of homo *iPP* and alloy polymers. The thin solid curve indicates prediction of the Doi-Edward damping function.

all samples in this study is not well deviated from the prediction, lending further support to the argument that the fast relaxation process detected in the time range of our measurement arises from the disentanglement relaxation of the *iPP* chains. The deviation at $\gamma \geq 4$ ($\log \gamma \geq 0.6$), where the damping is weaker than that expected by the Doi-Edward model, is probably due to the high polydispersity of the current samples (cf. Table 1).^[34–36]

Steady shear

Fig. 9 compares the time evolution of transient viscosity $\eta^+(t, \dot{\gamma})$ obtained over a wide shear rate range from 0.001 s^{-1} to 100 s^{-1} for *iPP*, *iPP-E/P* and *iPP-E/P-E* at 190°C and for *iPP-E* at 250°C : $\eta^+(t, \dot{\gamma})$ as a function of shear rate $\dot{\gamma}$ (as indicated) and time t obtained from the start-up shear measurements is plotted against t .

The *iPP* sample (Panel a) exhibits similar $\eta^+(t, \dot{\gamma})$ at $\dot{\gamma} = 0.001$ and 0.003 s^{-1} , indicating the linear regime therein. Further increasing the shear rate leads to the shear thinning behavior. The steady state has been achieved for the low shear rate $\dot{\gamma} \leq 3 \text{ s}^{-1}$, but not for the high shear rate $\dot{\gamma} \geq 10 \text{ s}^{-1}$, where the shear stress decays continuously with t after the highest transient viscosity has been achieved. This decay is attributed to the edge fracture that becomes serious when the flow rate is too high. For the *iPP* sample having $M_w = 310 \text{ kg/mol}$ and $M_e = 5.3 \text{ kg/mol}$,^[37–39] we estimate an average number of entanglements per chain to be ~ 60 .

From the terminal relaxation time $\tau_d = 4 \text{ s}$, we estimate an average Rouse time of $\tau_R = \tau_d (M/M_e)^{-1.4} = 0.04 \text{ s}$. Therefore, the majority of chains would be oriented if the shear rate is higher than $1/\tau_d = 0.25 \text{ s}^{-1}$, and be stretched if the shear rate is higher than $1/\tau_R = 25 \text{ s}^{-1}$. The edge fracture is observed at $\dot{\gamma} \geq 10 \text{ s}^{-1}$, suggesting that it arises from the flow instability caused by the chain stretch at the high shear rate.

For the alloy samples, we observed the stress responses of the slow processes at $\dot{\gamma} < 0.1 \text{ s}^{-1}$, where the shear rate is slower than the relaxation rate of the *iPP* chains. The η^+ higher than that of *iPP* ($\sim 10^4 \text{ Pa}\cdot\text{s}$) is likely attributed to the stress responses of the deformed PE/EPR-rich domains. The transient viscosity obtained at $\dot{\gamma} < 0.1 \text{ s}^{-1}$ shows a clear overshoot for all alloy samples, and η^+ decreases continuously after the overshoot and no steady state has been achieved for *iPP-E/P-E* and *iPP-E*. This behavior should be attributed to the continuous deformation or even breakup of the PE/EPR-rich domains during the shear flow. Since we conduct the steady-shear

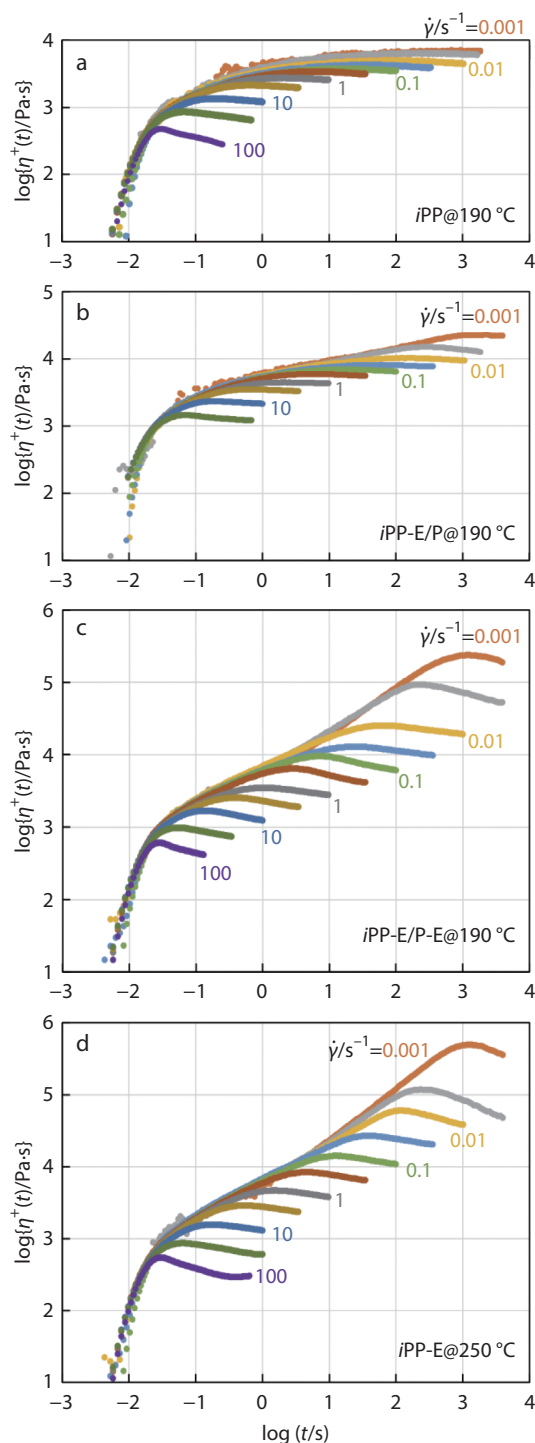


Fig. 9 Evolution of the transient viscosity $\eta^+(t, \dot{\gamma})$ with time t for *iPP*, *iPP-E/P*, and *iPP-E/P-E* at 190°C and for *iPP-E* at 250°C . The numbers associated to the curves indicate the shear rate. The shear rates are 0.001, 0.003, 0.01, 0.03, 0.1, 0.3, 1, 3, 10, 30, 100 s^{-1} from top to the bottom.

measurements from the low shear rate to the high shear rate, the structural changes are accumulative during the measurements.

In Fig. 10, we attempt to compare the complex viscosity η^* ($= [G'^2 + G''^2]^{1/2}/\omega$) plotted against the angular frequency ω

(thick solid curves), and the plots of the (pseudo-) steady viscosity η plotted against shear rate $\dot{\gamma}$ (symbols) to test the Cox-Merz rule.^[40,41] For comparison, the dashed curves show η^* against ω for *i*PP at the respective temperature to be compared with the results of *i*PP-E/P, *i*PP-E/P-E and *i*PP-E. For clarity, the results related to the *i*PP-E/P, *i*PP-E/P-E and *i*PP-E are shifted upward by a factor K ($= 1, 2, 3$) as indicated.

For the *i*PP and *i*PP-E/P samples, the steady state is achieved at $\dot{\gamma} \leq 3 \text{ s}^{-1}$ but not at $\dot{\gamma} \geq 10 \text{ s}^{-1}$. For the *i*PP-E and *i*PP-E/P-E samples, the steady state is not achieved in the whole $\dot{\gamma}$ range. However, we find that the position of the overshoot is consistently around a strain of $\gamma \sim 1$, so we choose the transient viscosity at $\gamma \sim 2$ as the pseudo-steady viscosity, also denoted as η , when no steady state has been achieved.

The (pseudo-) steady viscosity η thus-obtained for *i*PP and *i*PP-E/P agrees well with the solid curves, indicating the validity of the Cox-Merz rule. The slight deviation seen at the high shear rate $\dot{\gamma} \geq 10 \text{ s}^{-1}$ should be attributed to the edge fracture that manifests during the steady shear, which lowers the (pseudo-) steady viscosity. Although the shear thinning at the low- $\dot{\gamma}$ side is stronger for *i*PP-E/P (than for *i*PP), the Cox-Merz rule is still valid there, probably because the PE/EPR rich domain is stable against the steady shear, owing to the high fraction of EPR that serves as the compatibilizer, and thus the shear does not induce a significant change of the domain structure.

In comparison, the *i*PP-E/P-E and *i*PP-E samples clearly show two-step shear thinning and failure of the Cox-Merz rule, where the first step shear thinning at the low $\dot{\gamma}$ side is much stronger than that of *i*PP-E/P. In addition, η obtained at the lowest shear rate $\dot{\gamma} = 10^{-3} \text{ s}^{-1}$ is closer to η^* than those obtained at the higher $10^{-3} \text{ s}^{-1} < \dot{\gamma} \leq 0.1 \text{ s}^{-1}$ for *i*PP-E/P-E, probably due to the accumulative change of the domain structure during the continuous start-up shear measurements from low to high $\dot{\gamma}$. The destruction of the agglomerated domains and

the breakup of the domains could be the two major sources of this strong nonlinearity.

The second-step shear thinning at the high- $\dot{\gamma}$ side is in accordance with the shear thinning behavior of the *i*PP chains (dashed curves), indicating that the nonlinearity is mainly attributed to the flow-facilitated disentanglement, through mechanisms like the convective constraint release (CCR) mechanism.^[42] At the sufficiently high viscosity, all alloy samples exhibit viscosity that becomes very similar to that of *i*PP, suggesting that these alloy samples, though solid-like at low shear, can be liquid-like and thus processable upon applying sufficiently high shear rate.

CONCLUSIONS

In this study, we synthesized in-reactor alloy samples containing isotactic polypropylene (*i*PP), ethylene-propylene rubber (EPR), and polyethylene (PE). The C_2 content in EPR was varied from ~60% to ~90% in EPR/PE, which was higher than that of the usual commercial HIPP (~50%). We studied both the linear and nonlinear rheology behavior of these alloy samples and detected two relaxation processes in the LVE and stress relaxation measurements. A combination of LVE and the damping behavior enabled us to attribute unequivocally the fast and slow relaxation processes to the stress response of the *i*PP and those of the tethered chains at the PE/EPR domains as well as the deformed PE/EPR domains. The behavior of the steady shear flow showed that the structure of the PE/EPR domains was more stable for the *i*PP-E/P sample than for the *i*PP-E/P-E and *i*PP-E samples. The structure evolved continuously for the *i*PP-E/P-E and *i*PP-E samples during the steady shear, making the steady state unachievable at the low shear rates (lower than $0.1 \text{ s}^{-1} \sim$ the inverse of the terminal relaxation time of the *i*PP chains). Although the viscosity at the low shear rates increased consistently with increasing the C_2 content in PE/EPR, the viscosity at the high shear rates was governed by that of the *i*PP matrix. These features should play a significant role in affecting the melt processability of the alloy samples under different processing routes, which is considered as an interesting subject for future study.

NOTES

The authors declare no competing financial interest.

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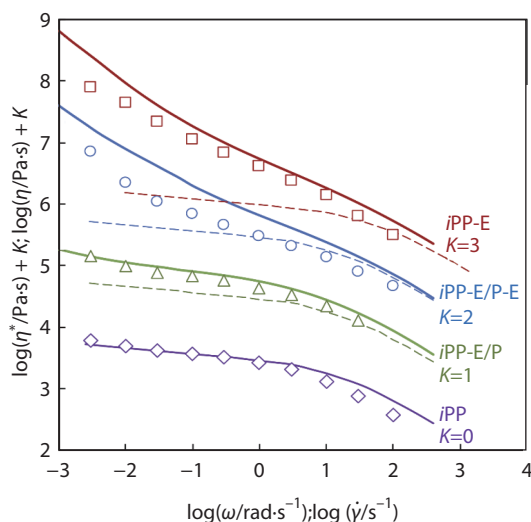


Fig. 10 Test of the Cox-Merz rule through the comparison of η^* plotted against ω (solid curve) and (pseudo-) steady viscosity η plotted against $\dot{\gamma}$ for *i*PP, *i*PP-E/P and *i*PP-E/P-E at 190°C and *i*PP-E at 250 °C. η^* plotted against ω for *i*PP at the respective T are also added in dashed curve to be compared directly with η^* and η of the alloy samples. For clarity, the results related to the *i*PP-E/P, *i*PP-E/P-E and *i*PP-E are shifted upward by a factor K ($= 1, 2, 3$) as indicated.

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