Dynamic Shear Rheological Behavior of PP/EPR In-Reactor Alloys Synthesized by Multi-Stage Sequential Polymerization Process

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ABSTRACT: The rheological behavior, morphology, and mechanical properties of in-reactor alloy of polypropylene (PP)/ethylene propylene rubber (EPR) synthesized by multi-stage sequential polymerization process are studied in this article. The relationship between polymerization parameters, morphology, and rheological properties are evaluated by scanning electron microscopy (SEM) and small amplitude oscillation rheometry in the linear viscoelastic region. The electron microscopy of samples is showed that by increasing switching frequency in polymerization time, the size of EPR particles decrease. By increasing switching frequency, the curves of complex viscosity against angular frequency of samples are shifted to higher values at low range of shear rates with no significant change at higher frequencies in Power-law region. The modified Cole-Cole plots revealed the enhanced melt elasticity by increasing switching frequency up to 230°C. The plot of phase angle versus absolute value of complex modulus G^* is used for the evaluation of matrix-droplets interaction at various temperatures. It is observed two different behaviors before and after 230°C which is the evidence of the change in relaxation mechanism of the blend components because of coarsening the rubber particles in the phase separation process. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3635–3641, 2011

Key words: in-reactor alloys; polymerization; rheology; PP/EPR blend

INTRODUCTION

Polypropylene (PP) is a high melting point polyolefin with excellent chemical resistance and acceptable range of mechanical properties. There are various grades of PP available in the market to cover wide range of applications.[1] For engineering applications, PP shows limited toughness, especially at room and low temperatures. Toughening of polypropylene homopolymer (iPP) via addition of ethylene-propylene copolymer or ethylene-propylene rubber (EPR), in-reactor,[2–6] or post reactor,[7–9] processes has been a subject of interest. Mechanical blending of PP and EPR or EPDM (ethylene propylene diene monomer) generally use to enhance the impact strength. In the mechanical blending, a general correlation can be established between the mode and state of dispersion of the rubbery domains (EPR/EPDM) and melt rheological properties of the single components. The dependency of the size of the dispersed particles upon the viscosity ratio of the melt of phases has found by Mighri and coworkers,[7] and demonstrated that a general correlation can also be established between the toughness of iPP/EPR blends and the dispersion state of EPR copolymers.

Heterophasic ethylene-propylene copolymers (HECO) were developed by *in situ* sequential homopolymerization of propylene monomer and copolymerization of propylene and ethylene monomers to improve low temperature impact resistance of polypropylene homopolymers. The versatility of polymerization processes made possible the production of blends *in situ* directly in the reactor.[10,11] The understanding of the relationship between structure, morphology, and deformation phenomena is necessary to develop polymeric systems with good mechanical properties.[12]

It has been proposed a new method to improve the particle size of dispersed phase in (PP) reactor alloys without any change in the catalyst system. In this method, a multistage sequential polymerization process was used to improve the morphology and mechanical properties of PP/EPR in-reactor alloys.[13] To the best of our knowledge, many reports on the rheological behavior of in-reactor alloys are not available.

In this work, the PP/EPR in-reactor alloys were prepared by multi-stage sequential gas-phase homopolymerization of propylene and gas-phase copolymerization of

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TABLE I
The Polymerization Time and Switching Sequence of Samples

Code	Homopolymerization time (min)	Copolymerization time (min)	Switching frequency number
EP20	60	20	1
EP10	30	10	2
EP5	15	5	4

ethylene propylene in a circular mode. The effects of polymerization condition on morphology, dynamic shear rheology, and mechanical properties of the alloys are studied, and the interfacial interaction between PP homopolymer and EPR phases were determined.

EXPERIMENTAL

Synthesis of the PP/EPR in-reactor alloy

The PP/EPR in-reactor alloys were synthesized through a multi-stage sequential polymerization process. In the first prepolymerization stage, the slurry polymerization of propylene was done at 0.1 MPa and 50°C, for 30 min in n-heptan as solvent. After this stage, propylene was added to the reactor at 0.6 MPa and homopolymerization is started. Propylene was homopolymerized for 60 min at 60°C. At the end of this stage, the solvent and propylene were evacuated at 5 mmHg during 3 min, and circular process in gas-phase mode started. The ethylene and propylene monomers mixture in a fixed ratio were fed to the reactor at constant pressure of 0.4 MPa at 60°C.

After copolymerization of ethylene and propylene for a designated time (Table I), the ethylene propylene mixture was removed by evacuation to 5 mmHg for 3 min, and propylene monomer at a constant pressure of 0.6 MPa was continuously supplied to the reactor at 60°C. After propylene homopolymerization, ethylene-propylene copolymerization and subsequently propylene homo polymerization were performed at the same conditions as above. Finally, the circular reaction mode was carried out for 80 min.

As is seen in Table I, the sample EP20 was synthesized by ethylene-propylene copolymerization for 20 min and then propylene homopolymerization for 60 min, namely, the switching number of this sample is 1. The sample EP10 was synthesized by ethylene-propylene copolymerization for 10 min and then propylene homopolymerization for 30 min, namely, the switching number of this sample is 2, in other words, this process was repeated twice and in this case total copolymerization time was 80 min. Ana-

logically, the switching number of EP5 was 4, respectively.

EPR content of samples

To achieve a uniform separation of EPR, samples were extracted in boiling n-heptan in a Kumagawa extractor for 12 h. The extract solution was concentrated and precipitated by ethanol, and the extracted substance was washed and subsequently dried in vacuum. The weight percentage of the fraction was used as the content of EPR in the blends (Table II).

Oscillation rheometry

The rheological properties of the materials were evaluated by a Rheometric Scientific ARES Rheometer-902-30004. The 25-mm circular samples with 1.4 mm thickness were prepared by compression molding process. The responses of melts in the linear viscoelastic range of oscillatory deformation at 180, 210, 230, and 250°C under nitrogen atmosphere were evaluated in the angular frequency range of 0.01–100 rad/sec with 1 mm gap.

Scanning electron microscopy

The morphology and dispersion state of EPR phase in the PP matrix were investigated using a JSM-T20 scanning electron microscope. The samples compression molded at 14.5 MPa and 180°C for 5 min were fractured in liquid nitrogen. The fractured surfaces were dipped into xylene and etched under ultrasonic for 5 min, at room temperature. The fractured surface of samples after etching was gold coated before scanning electron microscopy (SEM) test.

Measurement of molecular weight

The molecular weights of samples were measured by PL-220 gel permeation chromatography (GPC). Analyses were performed at 150°C using trichlorobenzene as solvent with concentration 0.2–0.3 w/v% and 1.0 mL/min flow rate.

TABLE II
The GPC Test Result of Samples

Sample	Fraction part (wt %)	M_n	M_w	M_w/M_n
EP5-PP	83.7	74,700	294,000	3.9
EP5-EPR	16.3	54,700	129,100	2.3
EP10-PP	83.5	75,400	287,000	3.8
EP10-EPR	16.5	53,300	124,200	2.3
EP20-PP	83.9	78,200	304,400	3.8
EP20-EPR	16.1	59,800	132,700	2.2

Measurement of mechanical properties

The notched Charpy impact strength of the compression molded sample was measured on a Ceast impact strength tester, according to ASTM D256. The flexural modulus of samples was measured according to ASTM D790 on a Shimadzu AG-500A electronic tester. Five parallel measurements were made and the average values were reported.

RESULTS AND DISCUSSION

Morphology of copolymers

Figure 1 shows SEM images of fractured surface of EP5, EP10, and EP20 samples. As seen, EP20 has many large cavities with non-uniform distribution. EP10 with an average droplet size of about 1 μm, shows more uniform distribution, smaller than EP20. The EPR droplets in EP5 samples have the smallest size, more uniform in distribution than other two samples. The rough nonspherical morphology of particles and the effect of block copolymer which also produces during copolymerization process[13] may lead to improved matrix-rubber domains interconnection. It is believed that at higher switching frequency, the interconnected surface area between rubber droplets and iPP matrix resin increased because of rough, nonspherical morphology as well as size of rubber particles.

Rheology of samples

Effect of switching frequency on complex viscosity and storage modulus

The complex viscosities (η^*) curve of samples against angular frequency (ω), at 180°C is shown in Figure 2(a). It can be seen that by increasing the switching frequency, the viscosity curves shifted to higher values at low range of shear rates with no significant change at higher angular frequencies in power-law region. The power-law exponents (n) of EP5, EP10, and EP20 samples are nearly the same in the range of 0.36, 0.42, and 0.44 at 180°C, 210°C, and 230°C, respectively. This is the evidence of similarity in the rheological behavior at high shear rates. The measurements showed that the molecular weight characteristics and also the rubber content of samples are not big different to each other as is shown in Table II. Therefore, the increase in complex viscosity by increasing the switching frequency can be attributed to the number, size, and morphology of EPR particles which is evident in the SEM images.

The storage modulus (G') of samples as a function of angular frequency is shown in Figure 2(b). The storage modulus of samples increased by increasing the switching frequency at low range of frequencies
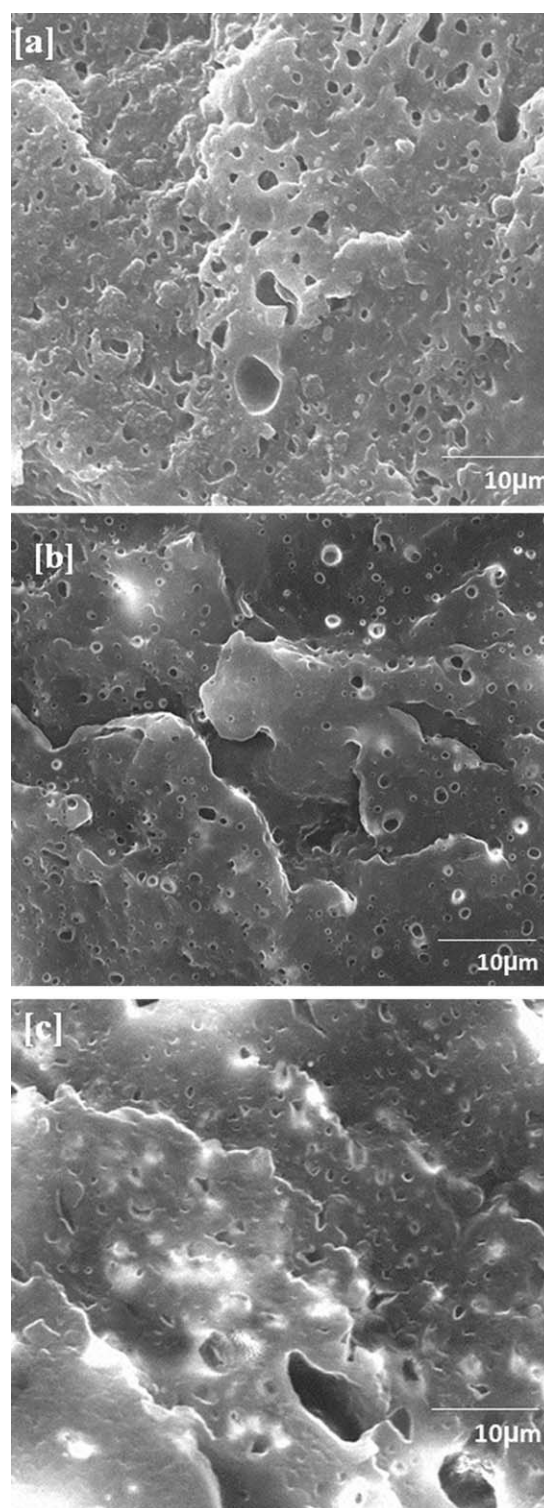

Figure 1 SEM images of the impact fractured surface of (a) EP20, (b) EP10, and (c) EP5.

which is because of enhanced hydrodynamic effect of increased number of EPR particles. The storage modulus of immiscible polymer blends may depend on the domain size, interfacial tension, and concentrations of the dispersed phase. It is found that the concentration of dispersed phase is nearly the same
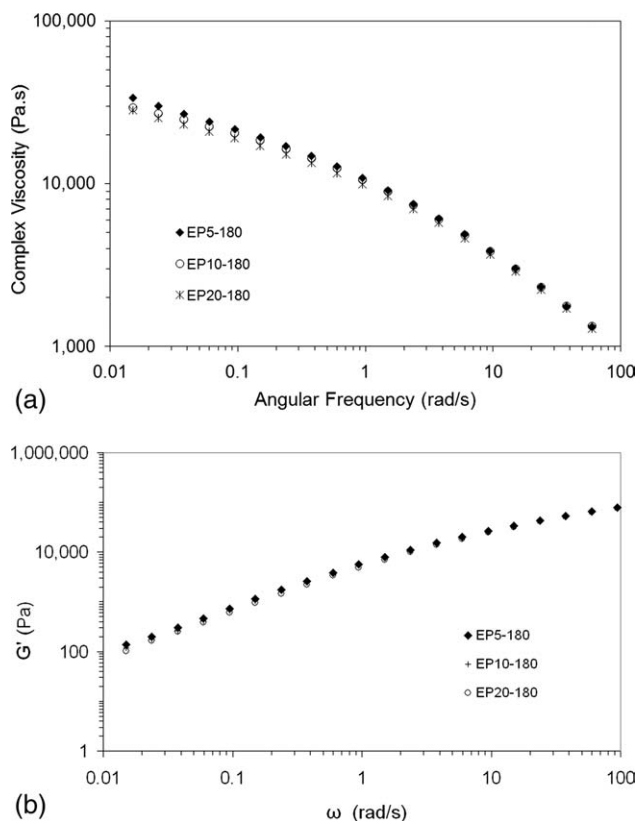
Figure 2 (a) Complex viscosities and (b) storage modulus, against angular frequency at 180°C.

network can be also deduced from the damping behavior at various temperatures. It can be seen in Figure 5 that at higher temperature than 230°C, the damping behavior of EP10 sample is decreased and at 250°C fell down the reference line of tan δ = 1 in all range of angular frequency.

Effect of temperature on the storage modulus

The storage modulus of samples at 180°C was shown in Figure 2(b) and at 210 and 230°C are shown in Figure 6(a,b). It can be seen that the order of G'–ω curves of samples at 180°C is changed at 210 and 230°C. The storage modulus of EP20 sample in terminal zone is increased at higher temperature and moved toward the EP5 curve. At 180°C, no definitive secondary plateau is observed in the G'–ω curves. At higher temperatures, a small shoulder is distinguished in all samples, can be attributed to coarsening of EPR particles. A part of matrix resin confine within the cluster of rubber particles and leads to apparently increase in concentration of rubber phase. The effect of concentration of dispersed phase on the secondary plateau has been studied also by Graebling[15] and Souza and Demarquette.[16] They
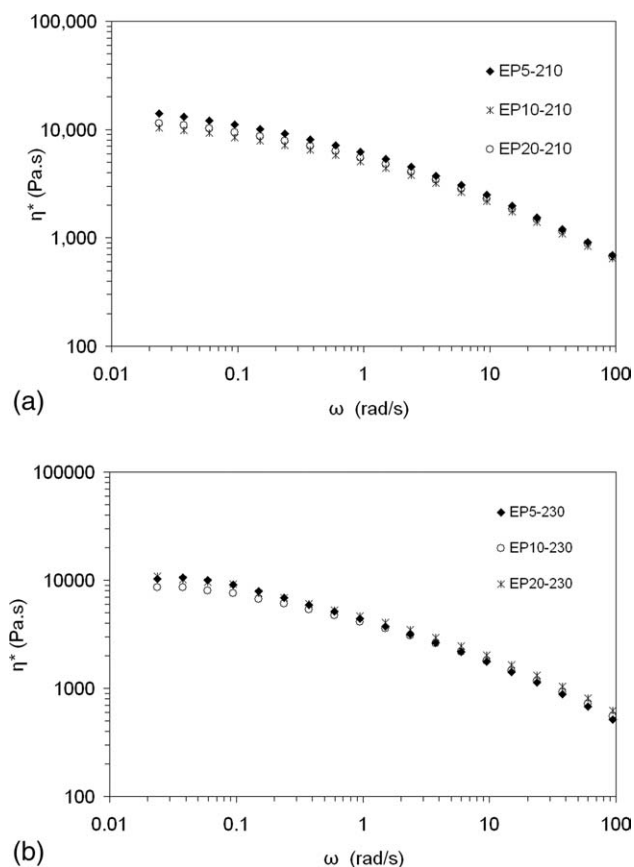
in all samples, while the SEM images show that the EPR domain size decreases at higher switching frequencies. The increased number of rubber particles and improved interfacial interaction between iPP and EPR particles lead to enhanced melt elasticity.

Effect of temperature on complex viscosity

The η*–ω curves of samples at 210°C and 230°C are shown in Figure 3(a,b). At 180°C, the complex viscosity increased by increasing switching frequency at low frequencies. This is more significant for EP20 samples with bigger rubber particles.

The η*–ω curves of EP10 and EP20 at various temperatures are shown in Figure 4(a,b). The change in rheological behavior at low angular frequencies can be obtained by finding the minimum in the η*-temperature behavior. By increasing temperature, a network-like structure may form because of expansion of EPR particles and leads to an increase in complex viscosity at low range of shear rates. This is the typical behavior in polymer phase separation process.[14]

The hydrodynamic effect of expanded rubber droplets and the network structure hinder the molecular mobility of matrix resin at low frequencies. The effect of expanded rubber droplets and the

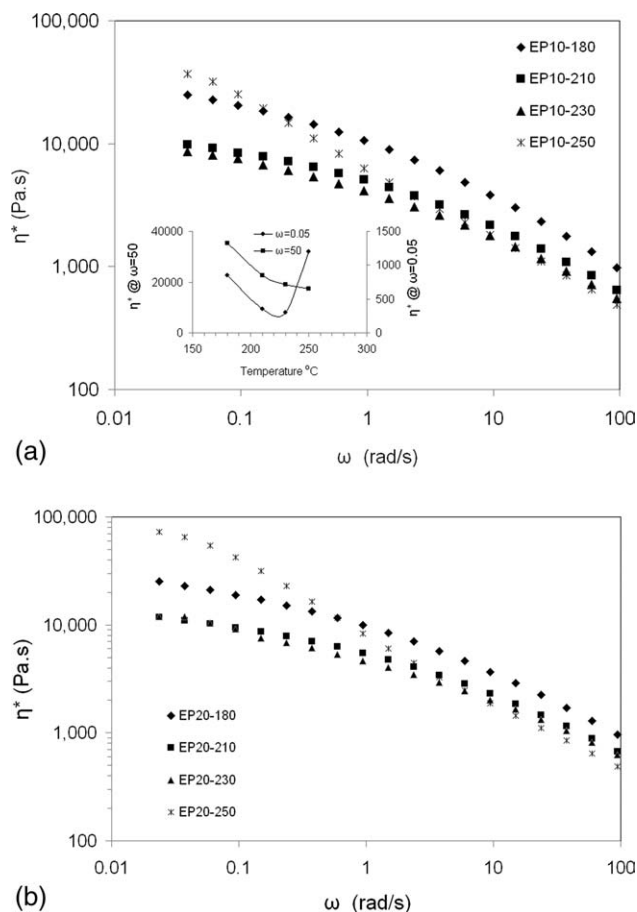Figure 3 Complex viscosities of samples (a) at 210°C and (b) at 230°C.

Figure 4 The η^*–ω curves of (a) EP10 and (b) EP20 samples at various temperature.

have been observed that storage modulus increase at higher concentration of dispersed phase, with extended secondary plateau.

Cole-Cole plot and its modified form[17,18] frequently used to investigate the viscoelastic properties of two-phase systems such as polymer blends and filled plastics. The plots of G''–G' of samples at various temperatures are shown in Figure 7. As is seen, the elasticity of melt increase by increasing switching frequency up
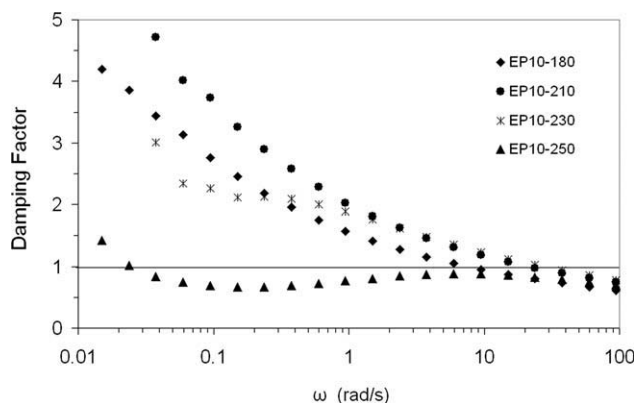

Figure 5 Damping factor of EP10 sample at various temperature.

to 230°C and this trend reverse at 250°C. This behavior reveals two different mechanisms at various ranges of temperatures. The G''–G' curve of EP5 sample is closer to reference line of $G' = G''$ at 230°C, which is the evidence of higher number of rubber particles and also improved interfacial interaction. The smaller EPR particles and higher interfacial adhesion by increasing switching frequency affect the phase separation process and can visibly be traced by modified Cole-Cole plot at higher temperatures. The network formed by coalescence of rubber droplets leads to higher melt elasticity of EP20 sample.

The δ–G^* curves of samples at various temperatures are plotted in Figure 8(a–c). It can be seen that up to 210°C, all samples showed nearly the same trend while it is changed at higher temperature. This can be due to difference in matrix-droplet interfacial stress and frictional interaction which may affect dynamics of blend components by changing the temperature.[19] Coarsening the rubber particles in the phase separation process leads to change in relaxation mechanism and temperature sensitivity of the samples.[20]

Determination of interfacial interaction of blend composition

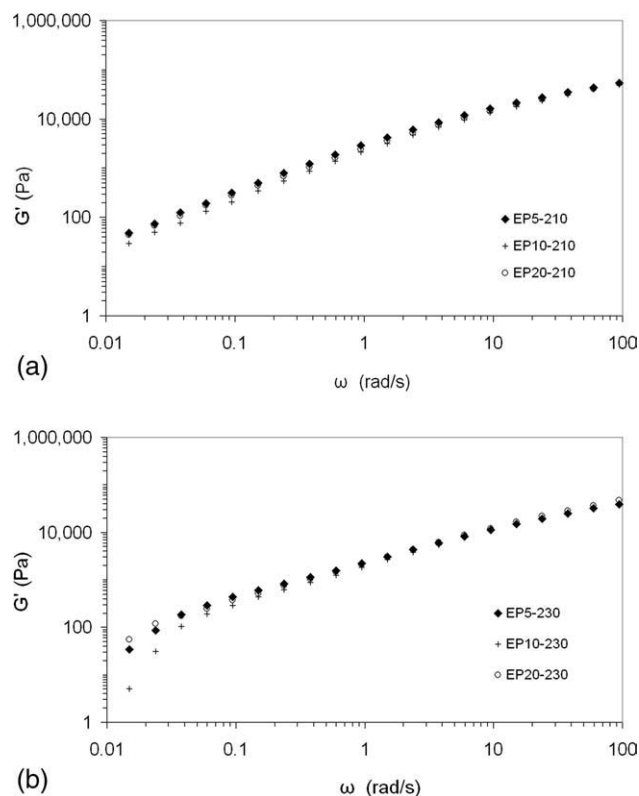The interfacial tension between two polymers in the blends can be determined by several methods[21–23] as

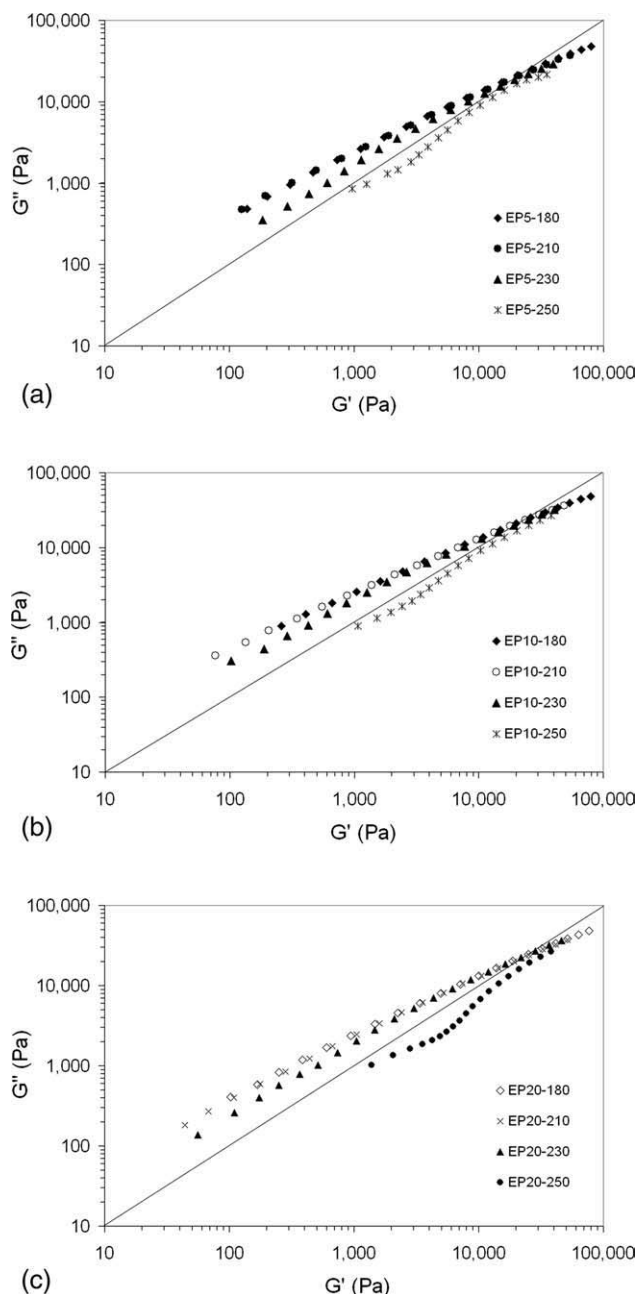**Figure 6** The storage modulus of samples at (a) 210°C and (b) 230°C.

Figure 7 The plots of G''–G' of samples at various temperatures: (a) EP5, (b) EP10, and (c) EP20.

Figure 8 Phase angle versus G^* (Pa) of samples at (a) EP5, (b) EP10, and (c) EP20.

well as oscillation rheometry.[24,25] It is assumed that the small amplitude in the oscillation rheometry does not affect morphology and the interfacial tension can be evaluated by rheological parameters. Using Palierne emulsion model,[26] complex shear modulus (G^*) of a blend can be correlated to the morphology, interfacial tension, and complex modulus of each phase.[15,27]

The interfacial interaction between two phases in polymer blends can be evaluated by using linear viscoelastic behavior of blends based on the work of Choi and Schowalter.[28] A constitutive equation is
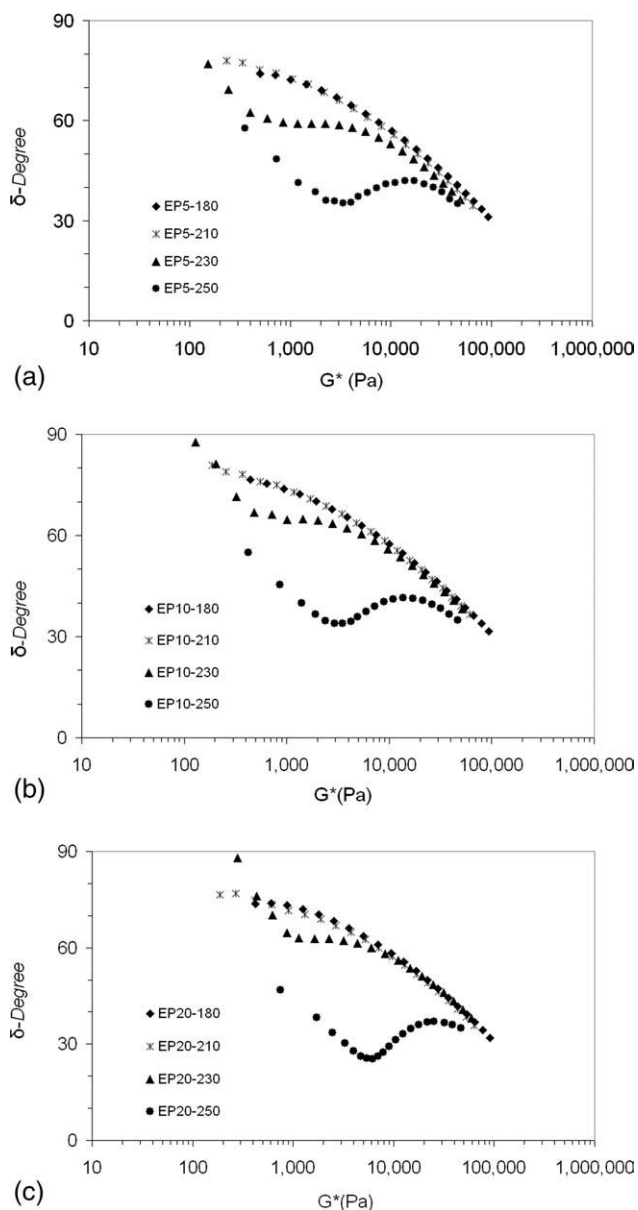
proposed for emulsions by Gramespacher and Meissner,[29] according to linear mixing rule.[16,30]

$$G^* = G_m^* + G_d^* + G_{interface}^* \qquad (1)$$

$$G^* = (1 - \varphi)G_m^* + \varphi G_d^* + G_{interface}^* \qquad (2)$$

TABLE III
Comparison Between Calculated and Experimental Value of Complex Modulus

Sample	$G_{calculated}^*$	$G_{experimental}^*$	$G_{interface}^*$
EP5	320	1010	690
EP10	601	935	334
EP20	759	870	108

$G_{calculated}^*$ = calculated by mixture rule.

TABLE IV
The Influence of Switching Frequency on
Mechanical Properties of Samples

Sample	Switch frequency	Impact strength (KJ/m^2)	Flexural modulus (MPa)
EP20	1	4.3 ± 0.2	680 ± 40
EP10	2	10.8 ± 0.3	840 ± 50
EP5	4	11.4 ± 0.2	850 ± 50

where G^*, G_m^*, and G_d^* are complex shear modulus of the blend, matrix, and dispersed phase, respectively, and ϕ is the volume fraction of dispersed phase. In this equation, the complex modulus of a blend is a function of the contribution of complex modules of the matrix and dispersed phased plus the share of their interfacial interaction.

The $G_{interface}^*$ of samples calculated according to eq. (2) are tabulated in Table III. The calculation is made at angular frequency of 0.03 (1/s). The share of complex modulus of interface for EP5 sample is considerably higher than $G_{interface}^*$ of EP10 and EP20, which approve the improved interfacial interaction at higher switching frequency.

Mechanical properties

The mechanical properties of samples are summarized in Table IV. The impact strength of EP5 is much higher than that of EP20. The impact strength of the copolymers synthesized at higher switching frequency was greatly improved because of enhanced interfacial strength of iPP and EPR. Flexural modulus of samples increased simultaneously with impact strength by increasing switching frequency.

CONCLUSIONS

In this article, the influence of switching frequency in feeding of monomers in the copolymerization of ethylene and propylene, on the rheological behavior, morphology, and mechanical properties of in-reactor alloy of iPP/EPR synthesized by multi-stage sequential polymerization process is studied. According to the experimental work, the following conclusions can be drawn:

- The morphology study of reactor blends revealed that by increasing switching frequency, the size of EPR droplets in the iPP matrix decrease. The increased interconnected surface area due to smaller rubber particles leads to increased interfacial adhesion forces, which is approved by enhanced value of $G_{interface}^*$ for EP5 sample.

- The complex viscosity of samples at low range of frequencies increases by increasing switching frequency which is due to the number, size, and morphology of EPR droplets.
- The $G'-\omega$ curves are declared that the increased number of rubber particles affect the hydrodynamic of melt and enhance melt elasticity.
- The rheological behavior of the samples at various temperatures revealed a different trend at higher temperature than 230°C. The change in rheological behavior at various temperatures is the evidence of the change in relaxation mechanism and temperature sensitivity of the blend components due to coarsening the rubber particles in the phase separation process.

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