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Degree of branching of polypropylene measured from Fourier-transform rheology

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Abstract In this study, linear and branched polypropylenes (PP) were compared under medium strain amplitude oscillatory shear (usually strain amplitude range from 10 to 100%) with Fourier-transform rheology (FT rheology). On a log–log diagram, the third relative intensity (I_3/I_1), which is a parameter to represent nonlinearity, shows a linear relationship with the strain amplitude in the range of medium strain amplitude. The slope of I_3/I_1 of linear PP with various molecular weight and molecular weight distribution was 2 as most constitutive equations predict, while that of branched PP was 1.64, which is lower than that of linear PP. When the linear and branch PP were

blended, the slope of I_3/I_1 was proportional to the composition of the branch PP. Therefore, it is suggested that the degree of branching can be defined in terms of the slope of I_3/I_1 under medium amplitude oscillatory shear.

Keywords FT rheology · Medium amplitude oscillatory shear (MAOS) · The slope of I_3/I_1

Introduction

The rheological properties and therefore the processing properties of polymers are highly affected by the degree of long chain branches (LCBs) (Gabriel and Münstedt 2003; Gahleitner 2001; Wood-Adams et al. 2000). LCB affects viscosity and the onset of shear thinning and becomes the cause of strain-hardening behavior in elongation. It is well known that strain hardening is a determining factor in polymer processing such as film blowing, melt spinning, blow molding, foaming, and thermoforming where the extensional deformation is dominant (Wagner et al. 2004). As the strain-hardening behavior manifests a strong resistance against fast stretching of polymers, the processing becomes easier to control if the polymer melt shows strain-hardening behavior and the product can be produced in good quality. Theoretically, it was explained that under extensional deformation, the strain-hardening behavior is

caused by the restricted stretching of the backbone of the polymer between the branch points connecting to the side branches (Inkson et al. 1999). It is therefore very important to detect and to characterize LCB. While ^{13}C -NMR and solution techniques using light scattering combined with gel permeation chromatography were widely used for characterizing LCB, they have difficulty in detecting low levels of LCB, which are nevertheless able to drastically affect the rheological properties (Kratochvil 2000; Randall 1989). Thus, rheological methods were developed for detecting LCB because of its sensitivity to the presence of small levels of LCB. Rheology presents a big advantage in that it is not limited by the chemical composition of the characterized polymer (Fleury et al. 2004). Among rheological methods, Yan et al. (1999) have studied the steady shear viscosity as a function of shear rate of different branched polymers, which were characterized by ^{13}C -NMR as well. They showed significant effects of LCB densities

Table 1 Properties of PP and the slope of I_3/I_1

Sample	MFR (g/10 min)	Mn (g/mol)	Mw (g/mol)	MWD	Molecular structure	Slope I_3/I_1		
						Exp. 1	Exp. 2	Avg.
PP-A	0.5	106k	460k	4.3	Linear	1.999	1.995	1.997
PP-B	0.36	64k	480k	7.5	Linear	2.023	1.990	2.007
PP-C	5.2	48.6k	215k	4.4	Linear	1.995	1.989	1.992
PP-D	4.3	37k	270k	7.3	Linear	2.042	2.085	2.064
PP-E	4.6	50k	240k	4.8	Linear	2.012	1.937	1.975
PP-F	4.3	57k	230k	4	Linear	2.062	2.005	2.034
PP-G	4	76k	220k	3.9	Linear	2.187	2.066	2.127
PP-H	3.0	151k	1,640k	10.9	Branched	1.654	1.633	1.644

MFR Melt flow rate, *Mn* number average molecular weight, *Mw* molecular weight, and *MWD* molecular weight distribution

on the shear-thinning effect. For the same molecular weight, higher LCB densities give higher viscosity at low shear rates and lower viscosity at high shear rates. However, shear viscosity seems to be less affected by LCB than extensional viscosity because the polymers, which are highly branched, are well known for their extreme strain-hardening behavior in extensional flows. Another way to characterize LCB should be nonlinear dynamical oscillatory rheology. Recently, Fleury et al. (2004), Schlatter et al. (2005), and Neidhöfer et al. (2004) reported that Fourier-transform rheology (FT rheology) can characterize the branched polymers. Fleury et al. (2004) investigated two rheological methodologies for assessing the differences between several branched polydisperse polymers: one is FT rheology and the second is studying the relaxation of polymers after strong nonlinear deformation. They concluded that FT rheology could be more sensitive to long branches. Neidhöfer et al. (2004) reported that linear and star-branched polystyrene solutions behaved similarly under linear oscillatory conditions. Furthermore, no difference occurred under nonlinear step-shear conditions, whereas significant differences could be monitored under nonlinear oscillatory conditions. Fleury et al. (2004) investigated the relative intensity of third harmonic [(third relative intensity (I_3/I_1))] as a function of strain amplitude of linear and branched polyethylene. Schlatter et al. (2005) investigated the relative intensity of third harmonic and the third phase shift of nine polyethylenes (two linear and seven densely and sparsely branched) in a wider range of frequency. They also compared theoretical models (Wagner–Stephenson integral model and differential multimode pom-pom model) with experimental results and reported that FT rheology is sensitive to the architecture of polymers regarding molecular weight and its distribution, number of branches, and their length. Neidhöfer et al. (2004) examined relative third intensity and phase angle as a function of frequency (Deborah number) with linear and star-branched polystyrene solutions. They reported that the third phase difference is better than intensity to detect the branched structure. FT rheology is certainly a good tool to distinguish linear from branched

polymers. However, in the previous papers, the third intensity and third phase angle gave an idea only for judging whether it is branched or not. Because we still lack the method for defining a parameter that characterizes the degree of branching, it will be challenging to probe the possibility

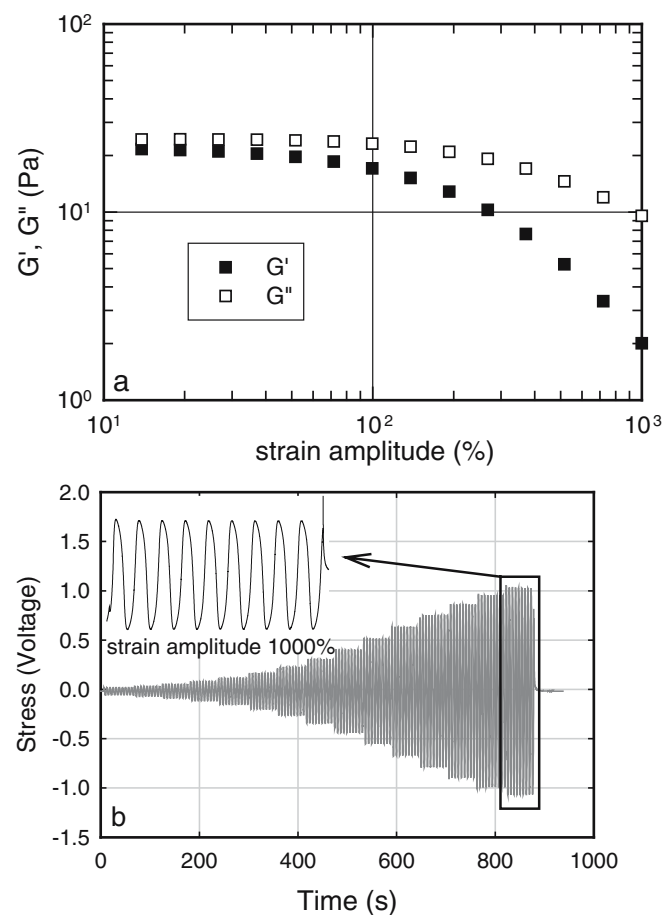


Fig. 1 **a** The G' and G'' of material as function of strain amplitude at frequency of 1 rad/s. **b** Stress data, which were obtained simultaneously by ADC card from rheometer under strain sweep test from strain amplitude 10 to 100%

whether the parameter in FT rheology can represent the degree of branching.

In this study, we investigate the slope of I_3/I_1 for the FT parameter not only of linear polypropylene (PP-D) with diverse molecular weight and molecular weight distribution (MWD) but also of branched PP (PP-H). Secondly, we investigate the effect of branched chain on the slope of I_3/I_1 as blending PP-D with PP-H and therefore suggest a new parameter that characterizes the degree of branching.

Experimental part

Materials and sample preparation

A wide variety of PP was used. The samples were eight types of PP (seven linear and one branch PP). The characteristics of the materials are shown in Table 1. The PP-H is a propylene homopolymer treated with electron beam irradiation at postreactor that contains LCBs as will be proved by its extensional viscosity. More detailed information on the preparation and characterization of the branched polymer we have used can be found elsewhere (Sugimoto et al. 2006). We blended linear PP with PP-H using twin kneading screws machine (Lab. Plast Mill, Toyo Seiki Seisaku-Sho, Japan). Mixing time was 5 min and the temperature was 190°C.

Experimental methods

Rheological measurements were carried out on a strain-controlled rheometer (ARES, TA Instruments) using a 25-

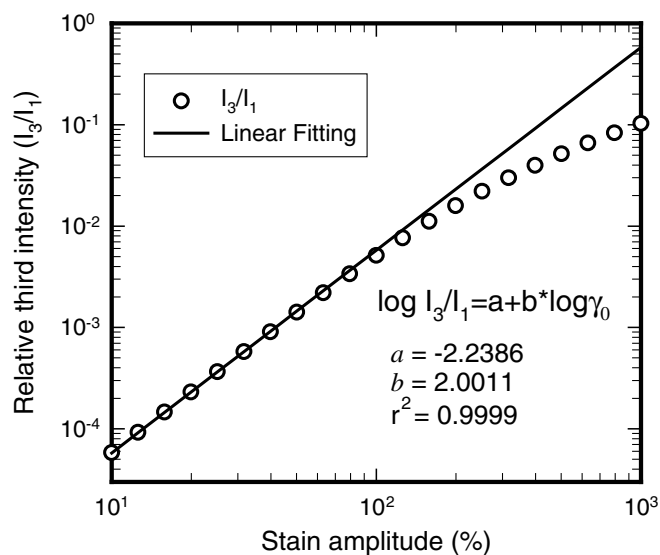


Fig. 2 The relative third intensity (I_3/I_1) as a function of strain amplitude for the Giesekus model ($G=1$, $\lambda=1$, $\alpha=0.3$, and frequency=1 Hz) and the I_3/I_1 is fitted by Eq. 1 in the medium strain amplitude range. The slope of I_3/I_1 is two

mm parallel plate fixture. Strain sweep test was carried out at a fixed frequency (1 rad/s). For the raw data acquisition, a 16-bit analog-to-digital converter (ADC) card (PCMCIA-6036E; National Instruments, Austin, USA) with a sampling rate up to 200 kHz was used. This ADC card was plugged into a Laptop computer equipped with a lab written LabView software (National Instruments). Strain sweep test was carried out at a fixed frequency (1 rad/s). The stress data were obtained simultaneously by ADC card. Figure 1a shows rheological properties and raw stress data obtained from strain sweep test at a frequency of 1 rad/s. To obtain steady stress data, nine cycles were passed and only the data from the last four cycles were used

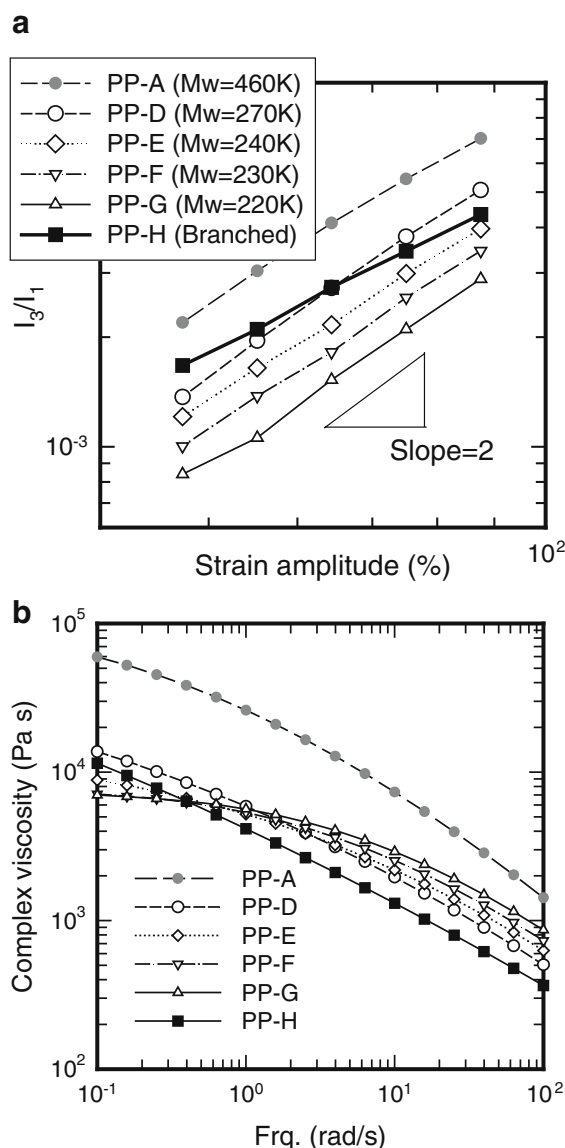


Fig. 3 a The I_3/I_1 of linear/branch PP as a function of strain amplitude at 1 rad/s and 180°C. b The complex viscosity as a function of frequency in the linear regime at 180°C

for data processing at each strain amplitude (Fig. 1b). For elongational viscosity measurements, a Meissner-type extensional rheometer (RME, TA Instruments) was used. The samples were prepared by compression molding at 200°C into the sheet shape of 1~2-mm thickness. The test specimens were cut into a width of 10 mm and a length of 56 mm. The sample width was recorded during the tests to confirm the uniform elongation and to calculate the actual strain rates. The measurements were carried out at constant strain rates of 0.05~1 s⁻¹.

Results and discussion

When the strain amplitude is large in the oscillatory shear flow, the stress becomes no longer sinusoidal and has higher harmonic contributions (Hyun et al. 2003). Recently, to analyze higher harmonic contributions, “high sensitivity Fourier transform rheology” method was introduced (Wilhelm et al. 1999; Wilhelm 2002). FT rheology decomposes stress data in time domain into frequency-dependent spectrum. Among these contributions, the I_3/I_1 is the most important parameter to represent nonlinearity or distortion of the stress curve. In the linear regime, I_3/I_1 is trivial because there is no stress distortion. In the nonlinear regime, I_3/I_1 becomes significant and its intensity increases as the strain amplitude increases. On a log–log diagram, I_3/I_1 shows a linear relationship with strain amplitude at intermediate or medium strain amplitude (Neidhöfer et al. 2003).

$$\log(I_3/I_1) = a + b \log \gamma_0. \quad (1)$$

On a log–log diagram, Eq. 1 predicts a linear relationship between I_3/I_1 and strain amplitude with intercept a and slope b . Earlier theoretical predictions (Pearson and Rochefort 1982; Helfand and Pearson 1982) showed that slope b equals 2. We also obtained

the slope of 2 with various constitutive equations including Giesekus, Phan–Thien Tanner (PTT), finite extensible nonlinear elastic-Perterlin (FENE-P) model, and more. For example, with the Giesekus model of the following form:

$$\nabla \cdot \sigma + \frac{1}{\lambda} \sigma + \alpha \frac{1}{\lambda G} \sigma \cdot \sigma = 2GD, \quad (2)$$

we obtained the stress data as a function of time and I_3/I_1 as a function of strain amplitude ($G=1$, $\lambda=1$, $\alpha=0.3$, and frequency=1 Hz). The I_3/I_1 is plotted in Fig. 2. At medium strain amplitude, the I_3/I_1 as a function of strain amplitude shows a linear relationship and the slope is 2 on a log–log diagram. The higher harmonics were not significant at medium strain amplitude and we focused only on the slope of I_3/I_1 , which gives information on the microstructure of the material in the transition zone from linear to nonlinear regime. Frequency-dependence on the slope of I_3/I_1 was not observed in this set of experiments.

The slope of I_3/I_1 of linear and branch PP

The I_3/I_1 as a function of strain amplitude is plotted in Fig. 3a for various linear PP with different molecular weight and MWDs and PP-H. The I_3/I_1 is fitted by Eq. 1 and the results are given in Table 1. From the figure, the I_3/I_1 becomes larger as the molecular weight and the zero complex viscosity increase (Fig. 3b). However, all linear PP show the same slope $b=2$, which corresponds to the theoretical predictions. Of course, there is a little deviation at low strain amplitude, which is caused by experimental error (there exists mechanical noise due to low torque value at low strain amplitude on the contrary to simulation results). All linear PP show the same slope $b=2$, however, the slope of PP-H is lower than that of linear PP. Neidhöfer et al. (2003) reported that the slope of I_3/I_1 of polystyrene

Table 2 The slope of I_3/I_1 of PP-D/PP-H blends

Sample	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Avg.±SD
PP-A (linear)	1.999	1.995	1.984	1.994	2.021	1.999±0.014
PP-A 90/PP-H 10	1.881	1.895	1.882	1.872	1.857	1.877±0.014
PP-A 70/PP-H 30	1.810	1.819	1.827	1.806	1.847	1.822±0.016
PP-A 30/PP-H 70	1.689	1.721	1.735	1.694	1.718	1.711±0.019
PP-B (linear)	2.023	1.991	1.990	2.039	2.062	2.021±0.031
PP-B 90/PP-H 10	1.89	1.929	1.959			1.926±0.034
PP-B 30/PP-H 70	1.722	1.721	1.722	1.724	1.755	1.729±0.014
PP-E (linear)	1.950	1.995	1.978	1.989	1.960	1.974±0.019
PP-E 90/PP-H 10	1.922	1.877	1.921	1.881	1.861	1.892±0.027
PP-E 70/PP-H 30	1.874	1.834	1.845	1.815	1.809	1.836±0.026
PP-E 30/PP-H 70	1.687	1.723	1.745		1.670	1.709±0.034
PP-H (branched)	1.628	1.654	1.650	1.633	1.664	1.646±0.015

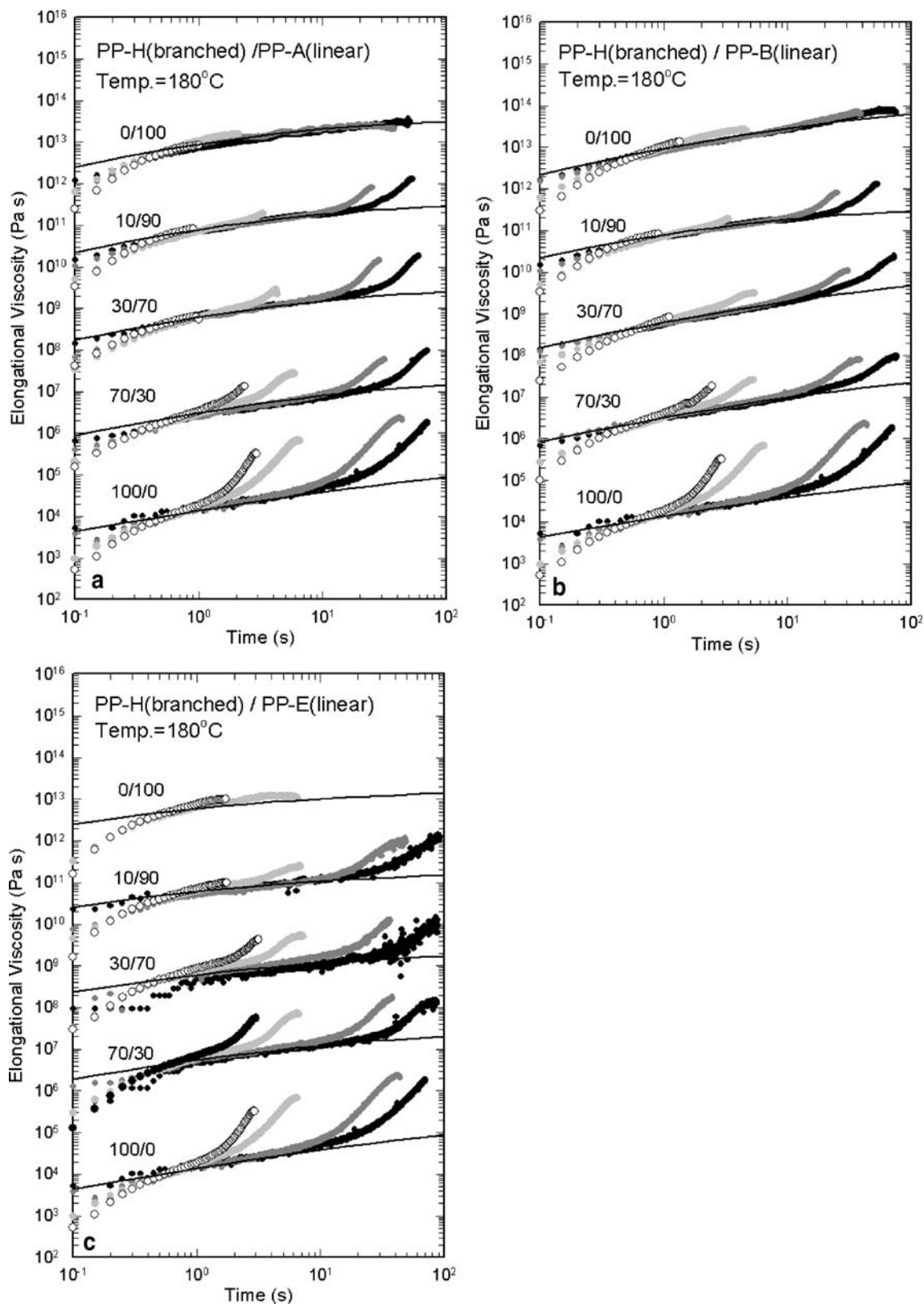


Fig. 4 The extensional viscosity of **a** PP-A (linear)/PP-H (branched), **b** PP-B (linear)/PP-H (branched), and **c** PP-E (linear)/PP-H (branched) blended samples under constant strain rates at 180°C. *Solid lines* represent three times shear viscosity

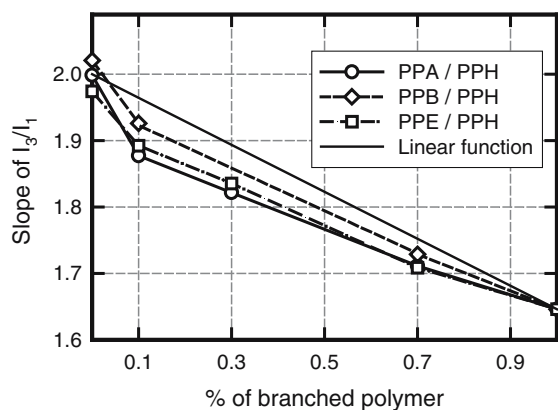


Fig. 5 The slope of I_3/I_1 of PP-D/PP-H blended samples from oscillatory shear test at a fixed frequency of 1 rad/s as a function of the amount of PP-H

solutions is lower than theoretical predictions (slope $b=2$) in experiments. However, for the first time, we find that the slope of I_3/I_1 of linear PP melts is the same as the theoretical predictions, which is confirmed using various constitutive equations (Giesekus, PTT, and FENE-P), and the slope of all linear PP is the same regardless of molecular weight and MWD. And, in the case of PP-H, the slope is 1.64, which is lower than that of linear PP and theoretical predictions. We also compared linear and branch PP with linear dynamic oscillatory shear test. The complex viscosity of PP-H looks similar to PP-D though a little bit lower than PP-D (Fig. 3b). However, at the beginning of nonlinear region, the I_3/I_1 of PP-H is larger than PP-D. This means that nonlinearity (I_3/I_1) of PP-H is larger than PP-D due to the branched chain. However, as the strain amplitude increases, the I_3/I_1 of PP-H increase slowly than PP-D and the I_3/I_1 crosses at intermediate strain amplitude. Finally, at strain amplitude of 100%, the I_3/I_1 of PP-H is lower than that of PP-D. Due to the branched chains, the slope of I_3/I_1 of PP-H is lower than PP-D. And it was found that the slope of I_3/I_1 as a function of strain amplitude of PP-D is 2 and the slope of PP-H is 1.64, which is lower than 2. From these results, it is inferred that the slope of I_3/I_1 is a good parameter to distinguish linear from branched polymers.

The slope of I_3/I_1 of linear PP blends

We controlled the amount of branched chain by blending linear and branch PP to investigate the effect of the degree of branching on the slope of I_3/I_1 . Linear PP with various molecular weight and MWD (PP-A, B, and E) were blended with PP-H. The blend ratios of PP-H to PP-A, B,

and E were 0, 10, 30, 70, and 100wt%. The extensional viscosity of linear/branched polymer blend was measured. In Fig. 4a, the extensional viscosities of the blend of PP-H (branched) and PP-A (linear) at different extension rates are plotted. In the figure, as the contribution of PP-H increases, the extent of strain hardening increases. And the other blends (PP-H/PP-B and PP-H/PP-E) also show the similar strain-hardening behavior (Fig. 4b,c). To obtain the exact slope of I_3/I_1 , the strain sweep experiments are carried out five times with new samples at each test. The slopes of linear/branch PP blends are listed in Table 2. From these results, it can be confirmed that the slope of I_3/I_1 of linear PP is 2. As the contribution of branched polymer (PP-H) increases, the slope of I_3/I_1 becomes lower than 2. In Fig. 5, the averaged slope of linear/branch PP blends is plotted. The blends with the same composition show a similar slope with I_3/I_1 independent of different linear PP (PP-A, B, and E; see Table 1). In summary, it is observed that the slope of I_3/I_1 is sensitive to the amount of branched chains than the characteristics of linear chains such as molecular weight or MWD. It is concluded that the slope of I_3/I_1 under medium amplitude oscillatory shear (MAOS) can be used to distinguish linear and branch PP and also can be used as a parameter to define the degree of branching. Currently, this work is being extended with various well-defined linear and branched polymers.

Conclusions

We compared linear and branch PP melts in the medium strain amplitude region (usually strain amplitude range from 10 to 100%) with FT rheology. On a log-log diagram, the I_3/I_1 shows a linear relationship with the strain amplitude in the range of medium strain amplitude. From simulation results with various constitutive equations, the slope of I_3/I_1 equals 2. And from careful experiments, it was found that the slope of I_3/I_1 of linear PP was also 2 regardless of molecular weight and MWD, however, the slope of I_3/I_1 of branch PP was 1.64, which is lower than that of linear PP. The slope of I_3/I_1 of linear/branch PP blends decreases as the amount of PP-H increases. Therefore, it is suggested that the degree of branched chains can be distinguishable in terms of the slope of I_3/I_1 under MAOS and the slope of I_3/I_1 can be used as a parameter to define the degree of branching.

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