Melt Rheological Properties of Polypropylene–Maleated Polypropylene Blends. I. Steady Flow by Capillary

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ABSTRACT: Melt rheological properties of blends of polypropylene (PP) and PP grafted with maleic anhydride (PP-*g*-MA) are studied using a capillary rheometer. A pseudoplastic flow behavior is observed. The pseudoplasticity of the melt reduces with an increase of PP-*g*-MA content and/or temperature. The PP-*g*-MA component in the blend acts as decreasing melt viscosity, especially in the lower shear rate region, while the addition of PP-*g*-MA to PP does not cause obvious increase of die swell ratio. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1641–1648, 1999

Key words: polypropylene; polypropylene grafted with maleic anhydride; melt rheology; blend

INTRODUCTION

Blends of polypropylene (PP) for improving properties suited to some specific application were extensively studied with a large number of polymers, including polyethylene,[1–5] polycarbonate,[6] polyamide,[7–10] polystyrene,[11,12] acrylonitrile-butadiene-styrene (ABS),[13] ethylene-vinyl acetate (EVA),[14] elastomers.[15–18] However, the blends of PP and PP grafted with maleic anhydride (PP-*g*-MA) seem to have been scantily studied.[19,20] Our previous article[21] had reported the role of the PP-*g*-MA with low molecular weight. Addition of PP-*g*-MA to PP not only improves adhesiveness of PP with polar polymers but also mechanical properties. To choose optimum processing parameters, in this article, melt rheological properties of PP–PP-*g*-MA blends are studied using two kinds of PP, namely, homopolypropylene and ethylene–propylene copolymer, by means of a capillary rheometer. The effect of component structure, blending ratio, shearing, and temperature on melt viscosity and melt elasticity have been discussed. It was well known from the literature, as mentioned above, that, in the past, much of research activity on the rheological behavior of two-phase polymer blends had dealt mainly with the polymer blend systems, with no large difference in melt viscosity between the two components. While the PP-*g*-MA used in the study has very low melt viscosity, the article also presented some characteristics of melt rheological properties of the PP–PP-*g*-MA blends with a large difference in melt viscosity between the two components.

EXPERIMENTAL

Materials

In this study, the PP used was PP VC20 82C (homopolypropylene, M_w/M_n: 225,000/52,000) and PP SC13 11M (ethylene–propylene block copolymer, with the ethylene content in the copolymer as 6–13 wt %, and M_w/M_n as 265,000/58,000) produced by Borealis Polymer Co. (Finland). The maleated PP was supplied by Eastman Chemical

Figure 1   Melt viscosity of the PPVC–PP-*g*-MA blend as a function of shear stress at a varying PP-*g*-MA contents (wt %): (□) 0; (△) 5; (○) 10; (◇) 20; (+) 35; (×) 50.

Co. (United Kingdom) with the following specifications: content of maleic anhydride (MA) in the maleated PP, 8–10 wt %; M_w/M_n, 9100/3900; ring and softening point, 157°C; acid number, 47; viscosity (190°C), 0.4 Pa s. The three materials above are abbreviated as PPVC for PP VC20 82 C, PPSC for PP SC13 11M, and PP-*g*-MA for maleated PP.

Preparation of Blends

Both PPVC–PP-*g*-MA and PPSC–PP-*g*-MA blends were prepared by a melt-mixing, in the requisite ratios, in the twin-screw extruder (Berstorff ZE 25*33D) at a screw speed of 150 min^{-1} and the barrel temperatures (from the feeding zone to the die) of 210, 210, 220, 220, 220, 220, and 215°C. The blends contain 0.5 wt % antioxidant to ensure thermal stability of PP and PP-*g*-MA. The strands obtained from the extruder were cut into small granules in a granulator.

Measurement

Steady shearing flow properties were measured with a capillary rheometer (Göttfert Rheograph 2001) at three temperatures (200, 230, and 260°C). The length to diameter (*L/D*) ratio of the capillary is 30. The sample was preheated for 5 min at a test temperature before measuring. At least two parallel runs for every samples were made in order to get more accurate values. The relative standard deviation of the data is less than or equal to 0.01. The apparent shear stress

(τ_{app}) and the apparent shear rate (γ_{app}) were calculated from the experimental data using the conventional expression.[22,23] The Bagley correction on the apparent shear stress is neglected for the present case in which the *L/D* ratio of the capillary is 30; therefore, the apparent shear stress is taken approximately as the true shear stress (τ_w). The Rabinowitsch correction for non-Newtonian behavior was made. The diameter of the extrudate solidified (*D*) was measured with a micrometer.

Morphology of cryogenically fractured surface of the extrudate was observed with a scanning electron microscope (JEOL 100T).

RESULTS AND DISCUSSION

Melt Viscosity

Effect of Shearing

Figures 1 and 2 show logarithmic plots of melt viscosity versus shear stress at 200°C for both PPVC–PP-*g*-MA and PPSC–PP-*g*-MA blends. It is evident from the figures that melt viscosity decreases with increasing shear stress at a fixed blend composition. The slope of the curves in lower shear stress region varies with shear stress. Whereas, a power-law relationship between melt viscosity and shear stress is observed in higher shear stress region. The former is a character of transition from Newtonian flow in zero-shear rate region to power-law flow in higher shear rate

Figure 2   Melt viscosity of the PPSC–PP-*g*-MA blend as a function of shear stress at varying PP-*g*-MA contents (wt %): (□) 0; (△) 5; (○) 10; (◇) 20; (+) 35; (×) 50.

region. For the two matrices, the decreasing of the melt viscosity with an increase of shear stress is attributed to shear-induced change in molecular state, which is often described in terms of entanglement[22,23] between molecules. At low shear rates, the entanglement density is nearly that in the unperturbed state. At the shear rates where shear thinning is observed, the entanglement density decreases from that in the unperturbed state (zero shear limit). For the PPVC–PP-*g*-MA and PPSC–PP-*g*-MA blends, the curves of melt viscosity versus shear stress shift towards the left downward as PP-*g*-MA content increases, indicating that the PP-*g*-MA component in the blends possess an obvious effect of improving flow, which will be discussed in a subsequent section.

According to the power-law relationship between melt viscosity and shear stress in higher shear stress region, the general flow behavior of both PPVC–PP-*g*-MA and PPSC–PP-*g*-MA blends in the region can be described with Ostwald de Waele power law,[22] which is expressed as

$$\eta = K^{1/n}\tau_w^{(n-1)/n} \tag{1}$$

where η, τ_w, and K are melt viscosity, shear stress, and a constant, respectively, and n is a power-law exponent describing the character of the fluid. Table I shows n values calculated by using eq. (1). $n < 1$ is a characteristic of non-Newtonia, that is, the pseudoplastic behavior of the matrices and the blends. Values of n increase with an increase of PP-*g*-MA content and/or temperature, implying that the PP-*g*-MA component and temperature both can decrease the pseudoplasticity of the blend melts.

Table I   Values of Power Law Exponent *n*

| | n | | | | | |
| | 200°C | | 230°C | | 260°C | |
PP–PP-*g*-MA	A[a]	B[b]	A	B	A	B
100/0	0.344	0.323	0.382	0.350	0.419	0.359
95/5	0.338	0.344	0.391	0.359	0.491	0.437
90/10	0.370	0.345	0.408	0.384	0.50	0.426
80/20	0.388	0.382	0.466	0.434	0.569	0.451
65/35	0.546	0.515	0.511	0.476	0.593	0.589

[a] PPVC–PP-*g*-MA blends.
[b] PPSC–PP-*g*-MA blends.

Figure 3   Melt viscosity of the PPVC–PP-*g*-MA blend as a function of the PP-*g*-MA content at varying shear rates (s^{-1}): (□) 50; (△) 100; (○) 400; (◇) 2000.

Effect of PP-g-MA

Melt viscosity as a function of PP-*g*-MA content at 200°C and any given shear rates, in general, decreases monotonously with increasing PP-*g*-MA content as depicted in Figures 3 and 4. It is obvious that the melt viscosity decreases prominently with increasing PP-*g*-MA content at lower shear rates. However, the curve of melt viscosity versus PP-*g*-MA content trends towards flatness at higher shear rate, indicating that the effect of PP-*g*-MA on the melt viscosity weakens. Although rheological data of the pure PP-*g*-MA cannot be obtained in the experimental condition, the melt

viscosity of PP-*g*-MA above 200°C, which could be estimated from the melt viscosity at 190°C (0.4 Pa s at 190°C), should be very low. The PP-*g*-MA used in the study has extremely low molecular weight (M_w = 9100) and contains a higher content of maleic anhydride grafting (8–10 wt % MA in PP-*g*-MA). Maleic anhydride grafting might exist as a short-chain branch because a long-chain branch was produced with difficulty during the graft polymerization due to the space hindrance and the structural symmetry of maleic anhydride. Therefore, much low viscosity of PP-*g*-MA is attributable to the presence of low molec-

Figure 4   Melt viscosity of the PPSC–PP-*g*-MA blend as a function of the PP-*g*-MA content at varying shear rates (s^{-1}): (□) 50; (△) 100; (○) 400; (◇) 2000.

Figure 5   Scanning electron micrographs of fractured surfaces of extrudates: (a) 80/20 PPVC–PP-*g*-MA blend; (b) 80/20 PPSC–PP-*g*-MA blend.

ular weight and short-chain branching. At low molecular weight and low branch lengths, the zero shear viscosity of a branched polymer is considerably smaller than that of that of linear polymer of the same M_w.[23] This is the result of fewer entanglements. Figure 5 displays the two-phase structure of the PP–PP-*g*-MA blends, that is, the droplets of PP-*g*-MA dispersed in the continuous PP phase in the blend ratio. González-Montiel et al.[20] examined the morphology of PP–PP-*g*-MA blends by using transmission electron microscopy (TEM). They found that PP blends with the PP-*g*-MA containing 3.1 wt % MA show a phase-separated morphology. In the present study, the MA content of the PP-*g*-MA is above 3.1 wt %; thus, the PP–PP-*g*-MA blends should possess a two-phase structure. In polymer blends with no large difference in the melt viscosity between two phases, melt viscosity usually goes through a minimum/or maximum at some blending ratio.[22] In the blends studied, monotonous decreasing of the melt viscosity, with increasing PP-*g*-MA content, assigns a very large difference in melt viscosity between the two phases. The dispersed phase with very low viscosity in the blend melt easily become anisotropic in shape as it goes through the die, possibly forming elongated droplets/or shear planes, which will give less resistance to flow. It might be main cause of the reducing of the melt viscosity due to addition of PP-*g*-MA to PP. When the shear rate is lower, it is quite difficult for the entanglement network of PPVC or PPSC to deform (or disentangle), while elongated droplets or shear planes of PP-*g*-MA in the melt acts as an obvious function that is in favor of the flow. Therefore, the melt viscosity at lower shear rates decrease rapidly with an in-

creasing PP-*g*-MA content. When the shear rate is higher, shear stress corresponding to the shear rate has resulted in obvious deformation of the continuous phase, making a reduction of the PP-*g*-MA role in decreasing melt viscosity. With an increase of the PP-*g*-MA content in the blend, the power-law relationship between melt viscosity and shear stress is progressively spread to lower shear stresses (as shown in Figs. 1 and 2). It might be due to the fact that when the two-phase polymer blend melt is subjected to the shear forces in the given flow field, notable deformation of the dispersed phase also improves deformation of the continuous phase. The more obvious the effect, the higher the PP-*g*-MA content.

Effect of Temperature

As shown in Tables II and III, melt viscosity of both PPVC–PP-*g*-MA and PPSC–PP-*g*-MA blends decrease with an increasing shearing temperature from 200 to 260°C, demonstrating that increasing temperature improves the flow behavior of the melt. However, the effect of temperature on melt viscosity changes with shear rate. The data indicate more temperature sensitivity of shear at lower shear rates, and that temperature sensitivity of shearing reduces at higher shear rates. The temperature dependence of melt viscosity can be stated using the following Arrhenius equation:

$$\eta = \eta_0 e^{E/RT} \tag{2}$$

where η is the melt viscosity, η_0 is a constant, and E, R, and T are the activation energy for viscous flow, the universal gas constant, and the absolute temperature, respectively. Flow activation energy

Table II Experimental Viscosity of PPVC–PP-*g*-MA Blends at Various Temperatures and Shear Rates

PPVC–PP-*g*-MA	Shear Rate (s^{-1})	Melt Viscosity (Pa s)		
		200°C	230°C	260°C
100/0	100	390.0	266.9	215
	400	188.8	139.9	115.5
	2000	62.8	51.4	44.2
	4000	39.1	31.4	28.2
95/5	100	325.5	221.3	110.6
	400	155.7	117.1	72.4
	2000	53.7	44.3	31.6
	4000	33.5	26.9	20.7
90/10	100	273.4	182.0	84.6
	400	131.8	99.3	55.9
	2000	47.9	38.1	26.8
	4000	29.6	23.3	17.7
80/20	100	118	123.6	52.1
	400	66.2	73.2	39.1
	2000	27.4	29.3	19.5
	4000	18.8	18.9	13.1
65/35	100	73.6	60.5	39.7
	400	37.4	34.2	21.1
	2000	18.9	16.0	11.1
	4000	13.5	10.9	7.6

E, which can calculated from the slope obtained by linear regression of log η versus $1/T$, is shown in Table IV. It is clear that activation energy for viscous flow decreases with an increasing shear rate. It is assigned to the reason that the shearing favors destroying the coupling point of the entanglement network and, hence, results in a decrease of interaction between chain segments. However, variation of the activation energy with the blend composition is quite different from that of the activation energy with shear rate. In both the blends, the activation energy increases as the PP-*g*-MA content increases from 0 to 20 wt % and then drops down for further increasing PP-*g*-MA content. The following two factors affect the flow activation energy: the aggregate of maleic anhydride groups of PP-*g*-MA molecular chain in the blends and the interaction between the two phases enhance flow activation energy; while the dispersed PP-*g*-MA phase in the blend induce disentanglement or deformation of entanglement network of continuous PP phase, leading to a reduction of the activation energy. The activation energy is dominated by the former when the PP-*g*-MA content is below 20 wt %, and by the latter at above 20 wt % PP-*g*-MA content.

It is very interesting to note that although the flow activation energy of the blend at all blend compositions studied is higher than that of the matrix, the melt viscosity decreases monotonously with increasing PP-*g*-MA content. It is because the temperature dependence of melt viscosity are both, by and large, independent of chain length, but the melt viscosity is largely dependent on chain length.[24] The average chain length of the blend decreases as the PP-*g*-MA content increases, causing a progressively decrease in melt viscosity.

Melt Elasticity

Figure 6 shows the composition dependence of the die swell ratio D/D_0 (D_0 is the diameter of the die) at 200°C for PPVC–PP-*g*-MA and PPSC–PP-*g*-MA blends using shear stress as a parameter. The die swell ratio increases obviously with an increasing shear stress at a constant PP-*g*-MA content and slightly with an increasing PP-*g*-MA content at a constant shear stress. It is noteworthy that D/D_0 of the both blends at low shear stress, that is, $1.2*10^4$ Pa, is smaller than 1. Assume that

Table III Experimental Viscosity of PPSC–PP-*g*-MA Blends at Various Temperatures and Shear Rates

PPSC–PP-*g*-MA	Shear Rate (s^{-1})	Melt Viscosity (Pa s)		
		200°C	230°C	260°C
100/0	100	449.1	306.0	266.9
	400	193.6	146.4	130.2
	2000	64.1	51.8	46.5
	4000	40.2	31.6	29.1
95/5	100	332.0	234.3	136.7
	400	148.1	116.8	78.1
	2000	54.1	42.6	33.2
	4000	31.3	—	20.3
90/10	100	299.4	188.8	123.6
	400	136.7	100.9	73.2
	2000	46.9	36.8	29.6
	4000	29.0	23.3	18.9
80/20	100	195.3	123.6	—
	400	97.7	70.0	50.5
	2000	35.2	27.3	20.5
	4000	22.5	17.7	13.8
65/35	100	78.1	56.1	39.1
	400	39.4	37.1	24.4
	2000	18.9	—	12.7
	4000	13.2	10.7	8.3

Table IV   Activation Energy for Viscous Flow at Various Blend Ratios and Shear Rates

| | Activation Energy (kJ/mol) | | | | | | | |
| | $100\ s^{-1}$ | | $400\ s^{-1}$ | | $2000\ s^{-1}$ | | $4000\ s^{-1}$ | |
PP–PP-g-MA	A[a]	B[b]	A	B	A	B	A	B
100/0	21.1	18.5	17.3	14.1	12.4	11.4	1.6	11.5
95/5	37.7	31.1	26.8	22.4	18.5	15.3	16.9	—
90/10	41.0	31.1	29.9	21.9	20.3	16.2	18.0	15.1
80/20	46.2	32.2	31.9	23.2	—	19.0	20.9	17.2
65/35	21.5	24.3	19.8	16.6	18.6	—	20.1	16.3

[a] PPVC–PP-g-MA blend.
[b] PPSC–PP-g-MA blend.

the flow induced anisotropy of the dispersed phase would contribute positively to die swell as the dispersed phase relax after the melt got out of the die. Thus, the main factors that affect the die swell in the system studied might involve the melt elasticity of the continuous phase, the extent of deformation of the dispersed phase, and the difference in the volume contraction between PP and PP-g-MA due to the increase of density after the strand cools to room temperature. When the shear stress is lower, the continuous phase in both the melt blends store in themselves less elastic energy supplied; anisotropy of the dispersed phase is also unobvious. The volume contraction

of the strand should be for the entire strand after the strand cools to room temperature, including the matrix phase, not just the dispersed phase. However, the rate of the volume contraction is larger for PP-g-MA than the PP due to the strong interaction of maleic anhydride (MA) groups of the PP-g-MA, which would affect the diameter D of the strand. In the situation, the last factor dominates over the die swell, resulting in D/D_0 $<$ 1. When shear stress at a constant PP-g-MA content increases, the continuous phase can store higher elastic energy, and the dispersed phase deforms notably. Therefore, the recovery of elastic energy of the continuous phase and the relaxation

Figure 6 Dependence of the die swell ratio D/D_0 on the PP-g-MA content at varying shear stresses (Pa): (□, ■) 50,000; (△, ▲) 20,000; (○, ●) 12,000. Open symbols are for PPVC–PP-g-MA, and closed symbols are for the PPSC–PP-g-MA blend.

of the anisotropic dispersed phase dominate over the die swell, causing an increase of die swell ratio with increasing shear stress. At higher shear stresses, the extent of the volume contraction of the strand increases as the PP-*g*-MA content increases. The negative contribution of the volume contraction to the die swell almost counteracts the positive contribution of the relaxation of the anisotropic dispersed phase to the die swell; thus, the die swell ratio for the blends is close to 1 for the matrix when shear stress is higher.

CONCLUSIONS

Homopolypropylene (PPVC) and ethylene–propylene copolymer (PPSC) were melt-blended with MA-grafted polypropylene (PP-*g*-MA), respectively, using a twin-screw extruder. The steady shearing flow behavior of the both blends were studied using a capillary rheometer. The following conclusions are obtained.

1. The melts of PP–PP-*g*-MA blends behave pseudoplasticity, which reduces with an increasing PP-*g*-MA content and/or flow temperature. At the same blend composition, the pseudoplasticity of the PPVC–PP-*g*-MA blend is slightly weaker than that of the PPSC–PP-*g*-MA blend.
2. Melt viscosities of the both blends decrease with increasing shear stress and/or flow temperature and/or PP-*g*-MA content. Of the three factors, the effect of PP-*g*-MA content on decreasing melt viscosity is more prominent, especially in the lower shear rate region.
3. The activation energy for viscous flow increases with an increase of the PP-*g*-MA content from 0 to 20 wt % and then falls down with a further increasing PP-*g*-MA content. At the same blend composition, the activation energy is larger for PPVC–PP-*g*-MA than for PPSC–PP-*g*-MA blends, implying that the PPVC–PP-*g*-MA blend is more temperature-sensitive.
4. The die swell ratio of the both blends increases obviously with increasing shear stress and slightly with increasing PP-*g*-MA content.

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