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ORIGINAL PAPER

The effect of polypropylene/polyamide 66 blending modification on melt strength and rheologic behaviors of polypropylene

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Abstract Common linear polypropylene (PP) was modified by blending with polyamide 66 (PA66) under the act of compatibilizer in a twin-screw extruder in an attempt to improve the melt strength (MS) of PP. The MS of pure PP and modified PPs were measured by MS testing unit at three temperature of 190, 210, and 230 °C, and the MS improvement of PP was verified. The MS of the modified PPs increased with increasing the content of PA66. The steady- and dynamic-shear rheological behaviors of pure PP and modified PPs were investigated using a capillary rheometer and a parallel-plate rotating rheometer. The steady-shear rheological analysis results revealed that modified PPs had higher melt shear viscosity, stronger non-Newtonian behaviors, and higher zero shear-rate viscosity. The dynamic-shear rheological analysis showed modified PPs had higher melt complex modulus and smaller phase angle, which indicated that the melt viscosity and melt elasticity of PP were also enhanced. The modified PPs was characterized by DSC. DSC results revealed that the PA66 phase and PP phase of the modified PPs were in state of crystallization. The enhancement of MS, melt viscosity, and melt elasticity of modified PPs could be due to undisaggregated PA66 crystallization phase within the melt of PP blends.

Keywords Melt strength · Melt elasticity · Polypropylene · PA66

Introduction

Common PP has attractive advantages over other thermoplastics, such as polyethylene and PVC, due to its good comprehensive properties. However,

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polypropylene (PP) exhibits weak melt strength (MS) and no strain-hardening behavior in the melt-state due to its linear architecture, which results in difficulties in the process of thermoforming, blow molding, and extrusion foaming. The MS drawback of common linear PP could be overcome by several ways. One method is to form long chain branching on common PP macromolecules using an irradiation process [1–5]. The other option is to form a minute quantity of crosslinking entanglement onto common PP chains by using organic peroxide and crosslinking reagent [6–8]. In addition, blending PP with other polymers has been considered as a potential method to improve the MS of common PP while maintaining the cost and processing advantages [9–11].

It has been reported widely that it is a fruitful and an applicable way to produce modified PP with higher MS by blending common PP with other polymers which have a high MS or a strain-hardening behavior, such as polyethylene (PE) [9, 11]. Since the melt point of PE is lower than PP, the PE phase of PP/PE blends with improved MS is in melt-state in the course of PP/PE blends melt processing for thermoforming or extrusion foaming. However, few cases have been studied on the MS of linear PP modified by polymers with a higher melt point than that of PP, such as PA66, the melt point of which is about 260 °C and higher than the temperature (190–220 °C) of PP melting processing used regularly.

It is well known that it is immiscible between PP phase and polyamide (PA) phase in PP/PA blends, therefore, compatibilizers is needed in PP/PA blends. Poly (ethylene 1-octene) grafted with maleic anhydride (POE-g-MA) and polypropylene grafted with maleic anhydride (PP-g-MA) are the desirable compatibilizers of PP/PA blends, as have been validated widely by other studies. [12–14].

Within PP/POE-g-MA/PA66 blending systems prepared through melting blending, PA66 phase is dispersed in the PP-rich substrate of PP/PA66 blends under the action of compatibilizers, and maleic anhydride groups of POE-g-MA would react with amido groups of PA66. While the PP/POE-g-MA/PA66 undergoes melt reprocessing at range of 190–230 °C which is the PP regularly used processing temperature, PA66 phase in the blend is not to be molten, and the microstructure of PA66 phase tends to be maintained because of high melt point of PA66 being about 260 °C. Therefore, the undisaggregated PA66 components with reacted POE-g-MA in PP could tend to result in a certain morphology, which could be resembling "physical crosslinking net" in PP melt. These microscopic characteristics within the modified PP melt could be helpful to increase PP macromolecules slippage movement resistance and improve PP melt deformation resistance and, thus, could be effective to enhance MS of PP.

On the basis of the above mentioned knowledge and theoretic hypotheses, in this study, we aimed at developing an approach for improving MS of PP by blending common PP with high MP crystalline polymer. The key objective was to investigate the improvement effects of PA66 modification on the MS of PP, and to ascertain whether above mentioned hypotheses is correct or not.

Experimental

Materials

Linear polypropylene (T30S PP) with 3.28 g/10 min of melt flow index is supplied by Maoming Petrochemical Corporation. A commercial grade PA66 (1300S) obtained from Asahi Kasei Corporation is used. POE-g-MA (Bondyram 7103) with grafting ratio of 0.7–0.9% manufactured by Israel's Polyram Corporation is used as received without further purification. Irganox B215 manufactured by Ciba Company is used as antioxidant of the PP/PA66 blends.

Preparation of modified PPs

According to the desired composition (as shown in Table 1), PP pellets were tumble-premixed with PA66, POE-g-MA, and a regular amount of B215. Before premixing with other materials, PA66 had already been dried at 120 °C for 8 h with an electric blast drying oven. The mixtures were extruded in a corotating twin-screw extruder, with 25-mm screw diameter and a length/diameter ratio of 42/1, manufactured by Brabender Corporation. The temperatures profiles from the feeding zone to the die zone were set as follows: 250, 260, 265, 265, 260, 250, 250, and 230 °C. The screw rotating speed was kept constant at 140 rpm. After the granulation and being dried at 100 °C for 4 h, the properties of modified PPs were examined.

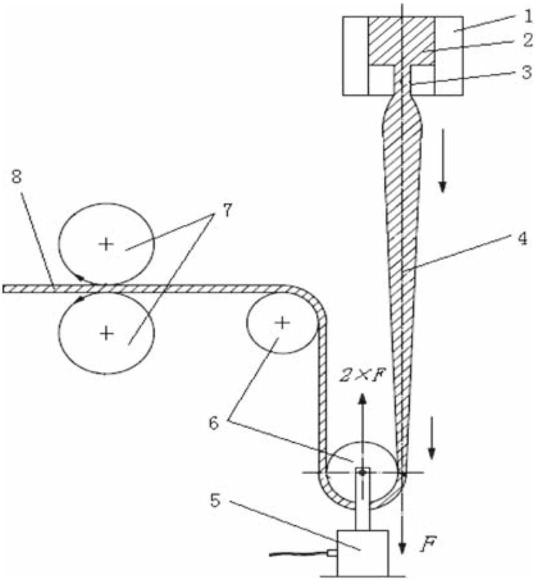
Measurement and characterization

Melt strength

According to ISO 16790 Standard, MS was measured by using a "take-off after return pulley" melt-strength tester module from RHEOLOGIC-5000 rheometer manufactured by Ceast Corporation. The schematic diagram of the MS tester is shown in Fig. 1. Pure PP and modified PPs samples were molten in the barrel of the rheometer ($D = 15$ mm), and the melt was extruded through a capillary die ($D = 1$ mm, $L = 30$ mm) into melt strand using a plunger ($D = 15$ mm). The

Table 1 Samples and compositions (by weight)

Samples	T30S PP	POE-g-MA	PA66
PP	100	0	0
PP/POEgMA	100	20	0
PP/15PA66	100	20	15
PP/20PA66	100	20	20
PP/25PA66	100	20	25
PP/30PA66	100	20	30
PP/35PA66	100	20	35



1-rheometer; 2-melt; 3-capillary die; 4-axis; 5-force transducer;
6-return pulleys; 7-drive rollers; 8-driven, pinched extrudate

Fig. 1 Schematic diagram of the Ceast RHEOLOGIC-5000 MS tester

downward extrusion velocity of the plunger was 0.10 mm/s. The melt strand was pulled downward by using a pair of drive rollers with increasing velocity (at a constant acceleration of 1.2 cm/s^2). The pull-down force was measured, and recorded till the rupture of the melt strand occurred. The pull-down force at the melt strand rupture was defined as Melt Strength (MS). The MS measurement was conducted at three test temperatures of 190, 210, and 230 °C.

Steady-shear rheological behaviors

Steady-shear rheological behaviors at the range of shear rate varied from 30 to 1,500 s^{-1} were carried out by using a CEAST Rheologic 5000 rheometer. The inner diameter and the length of the capillary die used were 1 and 30 mm, respectively. Studies were done at four test temperatures of 190, 210, 230, and 250 °C. The wall shear stress (τ_w) of the capillary can be expressed by the following equation

$$\tau_w = \frac{\Delta PD}{2L} \tag{1}$$

where ΔP is the total pressure drop during die extrusion, and D and L is the diameter and length of the die, respectively. The wall shear rate (γ_w) is defined as

$$\dot{\gamma}_w = \frac{32Q}{\pi D^3} \tag{2}$$

where Q is the volumetric flow rate. Steady-shear rheological behaviors at the range of steady-shear rate varied from 0.01 to 10 s^{-1} were examined by a Gemini 2000 rotational rheometer manufactured by Bohlin Instruments. The measurements were performed at a temperature of 210 °C under nitrogen atmosphere using a plate–plate geometry of 25 mm in diameter and a gap of 1 mm. Cylindrical samples of a thickness of 2 mm and a diameter of 25 mm were prepared in a hot press at a temperature of 200 °C.

Dynamic rheological properties

The Gemini 2000 rotational rheometer mentioned earlier was used for the measurements of dynamic rheological properties, such as complex modulus, loss angle, and complex viscosity, conducted at a temperature of 210 °C under nitrogen atmosphere with a plate–plate geometry of 25 mm in diameter and a gap of 1 mm. The applied dynamic oscillation frequency range was chosen from 0.01 to 100 Hz, and the strain was kept at 1%. Cylindrical samples of 2-mm thickness and 25-mm diameter were prepared in a hot press at a temperature of 200 °C.

Thermal properties

Differential scanning calorimetry (DSC) measurements were performed using a DSC-204C manufactured by Netzsch Corporation. Pure PP was heated from room temperature to 210 °C at a scanning rate of 10 °C/min, kept for 5 min at 210 °C, then cooled to 20 °C at a rate of 20 °C/min under nitrogen atmosphere. PA66 and modified PPs were heated from room temperature to 280 °C at a scanning rate of 10 °C/min, kept for 5 min at 280 °C, then cooled to 20 °C at a rate of 20 °C/min under nitrogen atmosphere.

Results and discussion

Effect of PA66 addition on the MS of modified PPs

The MSs of the pure PP and modified PPs are listed in Table 2. It is clear from Table 2 that the MS of the modified PPs were affected by the addition of PA66 and POE-g-MA. However, the MS of modified PP addedwith POE-g-MA only without PA66 decreased slightly. With the acts of POE-g-MA compatibilizer, the MS of the modified PPs increased with increasing content of PA66. When the amount of PA66 was 35, the MS measured at the temperature of 190 °C was up to 8.35 CN, which was 127% higher than that of pure PP. The results revealed that PA66 could play a positive role in improving MS of common PP. However, it did not mean that the higher the content of PA66, the better the properties the modified PPs could have. When the additional amount of PA66 reached 40, the modified PP melt strand was easy to be broken when stretched during MS measurement process, which indicated little use in application. It is found from Table 2 that the ratios of the MS of

Table 2 MS of pure PP and modified PPs at different temperature

Samples	190 °C		210 °C		230 °C	
	MS (CN)	R[a]	MS (CN)	R[a]	MS (CN)	R[a]
PP	3.68	1	2.21	1	1.54	1
PP/POEgMA	3.46	0.94	–	–	–	–
PP/15PA66	6.33	1.72	3.71	1.68	2.71	1.76
PP/20PA66	6.81	1.85	4.13	1.87	2.74	1.78
PP/25PA66	7.40	2.01	4.64	2.1	3.14	2.04
PP/30PA66	7.95	2.16	4.46	2.02	3.28	2.13
PP/35PA66	8.35	2.27	4.33	1.96	3.17	2.06

[a] R is the ratios of MS of modified PPs to that of pure PP at a certain temperature

modified PPs to that of pure PP did not change too much as the testing temperature varied at the range of 190–230 °C, although the MS of both pure PP and modified PP decreased with the testing temperature increasing. This result indicated that PA66 melt could play its role to improve the MS of modified PPs even at a higher temperature.

Steady-shear rheological behaviors analysis

Steady-shear flow behaviors of pure PP and modified PPs at four temperatures of 190, 210, 230, and 250 °C are shown in Fig. 2. At same shear rate, the shear stress for modified PPs were higher than that for pure PP, and increased with increasing PA66 concentration. That is to say, the apparent viscosity of modified PPs are higher than pure PP, and increased with increasing PA66 addition. The flow curves in Fig. 2 were obtained by fitting the experimental data of $\lg \tau_{\mathrm{w}}$ and $\lg \dot{\gamma}_w$. At the range from 30 to 1,500 s^{-1} of wall shear rate, $\lg \tau_{\mathrm{w}}$ and $\lg \dot{\gamma}_w$ have good linear relationship which could be observed in Fig. 2.

For most polymer melts, the relationship between shear stress and shear rate can be described as

$$\lg \tau_{\mathrm{w}} = \lg K + n \lg \dot{\gamma}_{\mathrm{w}} \tag{3}$$

Here, K is the consistency and n is the non-Newtonian index. According to Eq. 3, the K and n values can be obtained with the flow curves in Fig. 2. Table 3 listed the K and n values of pure PP and modified PPs at different temperatures. It is clear from Table 3 that the n values of both pure PP and modified PPs were less than 1, which indicated that both pure PP and modified PPs exhibited shear-thinning rheological behaviors. With increasing testing temperature, the n value increased, and K values decreased. Under all conditions, the n value for modified PPs, except for sample PP/15PA66, were less than pure PP, and the K values for modified PPs, except for sample PP/15PA66, were obviously higher than pure PP. The n value for modified PPs decreased with increasing PA66 content, and the K value increased with PA66 addition increasing. These results revealed that the melt of modified PPs presented stronger non-Newtonian rheological behavior and elasticity than that of

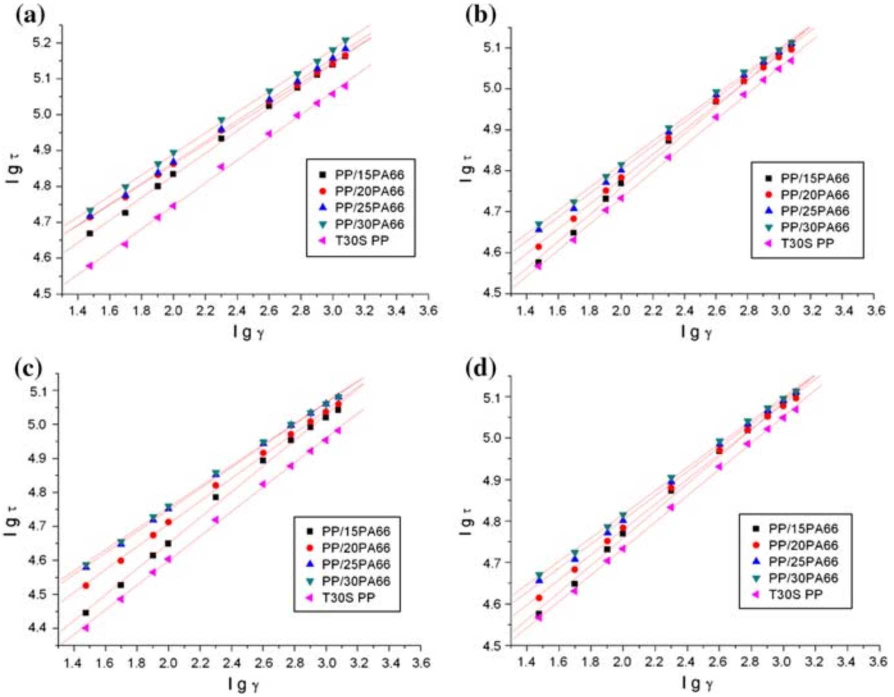


Fig. 2 The steady-shear flow behavior of pure PP and modified PPs at different temperature (**a** 190 °C, **b** 210 °C, **c** 230 °C, **d** 250 °C)

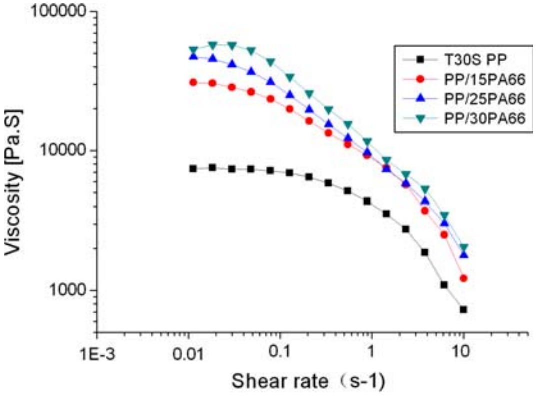
Table 3 The *K* and *n* values of pure PP and modified PPs at different temperatures

Samples	190 °C		210 °C		230 °C		250 °C	
	n	*K*	*n*	*K*	*n*	*K*	*n*	*K*
T30SPP	0.318	12,852	0.318	12,489	0.361	7,535	0.377	6,227
PP/15PA66	0.312	16,079	0.328	12,664	0.379	7,813	0.458	4,120
PP/20PA66	0.283	19,710	0.303	14,910	0.336	10,855	0.350	8,774
PP/25PA66	0.291	19,271	0.291	16,642	0.316	13,083	0.349	9,298
PP/30PA66	0.292	20,216	0.283	17,782	0.310	13,664	0.320	12,364

the pure PP melt, and that the higher the content of PA66, the stronger the non-Newtonian rheological behavior and elasticity of the modified PPs.

Steady-shear rheological behaviors of pure PP and modified PPs at low shear rate (from 0.01 to 10 s^{-1}) are shown in Fig. 3. It is observed from Fig. 3 that the viscosity of both pure PP and modified PPs increased sharply with decreasing shear rate from 10 to 0.1 s^{-1}. With shear rate decreasing from 0.1 to 0.01 s^{-1}, the viscosity increases for both pure PP and modified PPs were not so obvious. Over the entire range of shear rate studied, the viscosity of modified PPs were much higher than that of pure PP, especially at the lower shear rate range of 0.1–0.01 s^{-1}. The

Fig. 3 The rheological behavior of pure PP and modified PPs at the shear rate range of 0.01–10 s^{-1}



viscosity of modified PPs increased with increasing PA66 concentration. The results indicated that the melt of modified PPs could have higher zero shear-rate viscosity than pure PP, and that the higher the content of PA66, the higher the zero shear-rate viscosity of the modified PPs.

Dynamic rheological behaviors analysis

Dynamic rheological behaviors of pure PP and modified PPs are shown in Fig. 4. It is seen from Fig. 4 that the complex modulus of pure PP and modified PPs increased

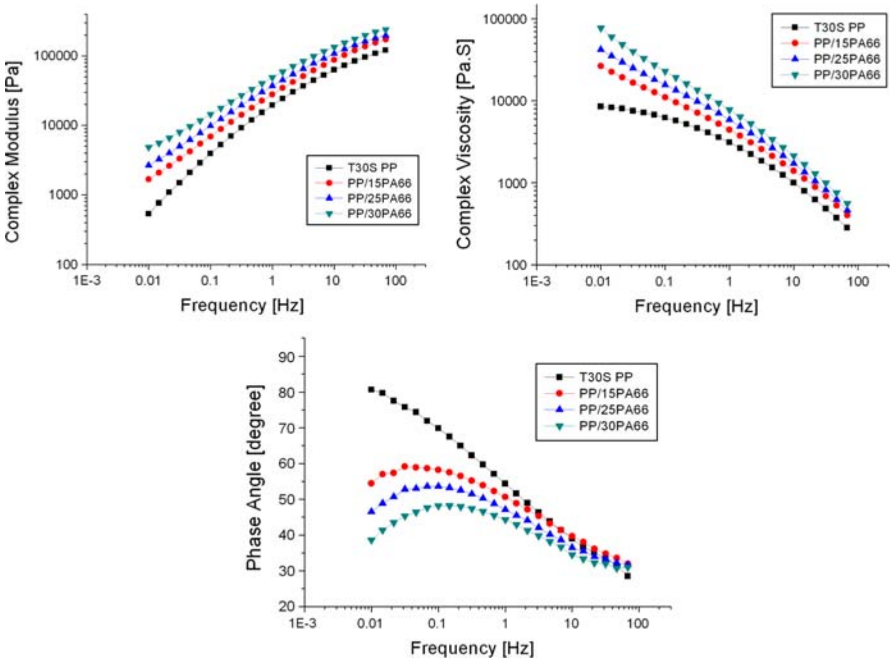


Fig. 4 Dynamic rheological behaviors of pure PP and modified PPs

with increasing frequency applied. The complex viscosity of pure PP and modified PPs decreased with increasing frequency. Over the entire range of frequency studied, the complex viscosity of modified PPs were higher than that of pure PP, especially at the low frequency region. The complex viscosity of modified PPs increased with increasing PA66 concentration in the blends. These results are in agreement with the analysis results of steady-shear rheological behaviors discussed earlier.

In Fig. 4, it is observed that the phase angle of pure PP increased monotonically with decreasing frequency applied. In contrast, with decreasing frequency , the phase angle of modified PPs increased at high frequency but decreased at low frequency. Nevertheless, the phase angle of all modified PPs were smaller than that of pure PP over the range of frequency from 0.01 to 6.8 Hz, which indicated that the modified PPs presented more melt elasticity.

Thermal analysis

The melting parameters determined from DSC heating scan for pure PP and modified PP are given in Table 4. It is found from Table 4 that the PA66 phase and PP phase of the modified PP samples were in state of crystallization. The melt points of PP phase and PA66 phase of the blends were very close to the corresponding melt points of pure polymers, and the heat of fusion (ΔH_f) of PP phase and PA66 phase of the blends were a little higher than that of pure polymers. These results indicated that, during the process of MS testing, PA66 phase of modified PP did not disaggregate and remained in solid state due to crystallization, which could have effective influences on enhancing MS of modified PP. The crystallization parameters determined from DSC cooling scan for pure PP and modified PP are shown in Table 5. It is observed from Table 5 that the onset temperature of crystallization (T_{onset}) and the peak temperature of crystallization (T_c) is of PP phase and PA66 phase of the modified PPs were higher than those of pure polymers.

Table 4 The DSC heating scan results of pure PP and modified PPs

Samples	PP melting peak		PA66 melting peak	
	Melt point (°C)	ΔH_f^a (J/g)	Melt point (°C)	ΔH_f^a (J/g)
T30S PP	168.1	79.8	–	–
PA66	–	–	262.6	57.6
PP/15PA66	168.2	85.2	261.5	56.3
PP/20PA66	167.6	86.5	261.8	59.4
PP/25PA66	167.6	86.2	262.5	62.3
PP/30PA66	168.1	84.7	262.2	60.2
PP/35PA66	168.2	84.8	262.3	59.1

[a] $\Delta H_f = \Delta H_{f-\text{DSC}} \times \frac{100}{X}$, here $\Delta H_{f-\text{DSC}}$ is the heat of fusion of PP phase or PA66 phase determined by DSC directly,and X is the percentages of PP or PA66 amount to total amount of all components in modified PP

Table 5 The DSC cooling scan results of pure PP and modified PPs

Samples	PP crystallization peak		PA66 crystallization peak	
	T_{onset} (°C)[a]	T_c (°C)[b]	T_{onset} (°C)	T_c (°C)
T30S PP	112.7	105.7	–	–
PA66	–	–	235.0	225.6
PP/15PA66	117.8	111.3	238.6	230.5
PP/20PA66	117.3	110.4	238.2	231.6
PP/25PA66	118.2	110.6	238.8	232.4
PP/30PA66	118.0	109.7	238.2	231.9
PP/35PA66	117.5	110.8	239.6	232.7

[a] T_{onset} is the onset temperature of crystallization

[b] T_c is the peak temperature of crystallization

Conclusions

Linear PP was modified by blending with PA66 under the act of POE-g-MA compatibilizer. The MS of PP were improved by PA66 addition in the range of temperature from 190 to 230 °C. The MS of the modified PPs increased with increasing the content of PA66. In comparison with pure PP, the modified PPs presented higher melt shear viscosity, stronger non-Newtonian rheological behaviors, higher zero shear-rate viscosity, and melt elasticity. PA66 phase and PP phase of the modified PPs were in state of crystallization. The enhancement mechanism of MS, melt viscosity, and melt elasticity of modified PPs could be due to solid-state PA66 crystallization phase within PP blends melt.

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