Melt Rheological Properties of Polypropylene–Maleated Polypropylene Blends. II. Dynamic Viscoelastic Properties

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Received 17 November 1997; accepted 9 May 1998

ABSTRACT: The dynamic viscoelastic properties of polypropylene (PP)-maleated PP blends in the molten state have been investigated with a dynamic mechanical thermal analyzer (PL-DMTA MKII) at a frequency range (ω) of 0.6 * 10⁻¹-3.14 * 10² rad s⁻¹. In the study, the blends were prepared by melt-blending in a twin-screw extruder, using homopolypropylene and an ethylene-propylene copolymer as a matrix, respectively, and PP grafted with maleic anhydride (PP-g-MA) as a second component. It has been found that the data of the blends do not obey the Cox-Merz rule; the plots of log *G'*-log *G''* for the both blends show a composition dependence. It is due to the fact that the two kinds of PP are immiscible with PP-g-MA. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1649–1656, 1999

Key words: polypropylene; polypropylene grafted with maleic anhydride; melt rheology; dynamic viscoelastic properties

INTRODUCTION

Blending polypropylene (PP) with maleated polypropylene (PP-g-MA) with low molecular weight and higher maleic anhydride content has led to materials with improved adhesiveness and mechanical properties.¹ In a previous article,² the melt rheological properties of PP–PP-g-MA blends were studied on steady flow by capillary. As part of our continuing effort for enhancing our understanding on the rheological behavior of the two-phase polymer blends with a large difference in melt viscosity between the two components, the dynamic viscoelastic properties of the blend melts will be presented in this article.

Materials and Preparation of Samples

In this study, the PP used was PP VC20 82C (homopolypropylene; M_{μ}/M_{n} , 225,000/52,000; T_{m} , 164°C) and PP SC13 11M (ethylene-propylene block copolymer; ethylene content in the copolymer, 6-13wt %; M_w/M_n , 265,000/58,000; T_m , 166°C) produced by Borealis Polymer Co. (Finland). The maleated PP was supplied by Eastman Chemical Co. (United Kingdom) with the following specifications: content of maleic anhydride (MA), 8-10 wt %; M_w/M_n, 9100/3900; T_m, 157°C; 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. Both PPVC-PP-g-MA and PPSC-PP-g-MA blends were prepared by a melt-mixing, in the requisite ratio, in the twin-screw extruder (Berstorff ZE 25 * 33D).

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EXPERIMENTAL

Blend		Measuring Temperature (°C)			
PP	230				
95/5 PP–PP-g-MA blend	230				
90/10 PP-PP-g-MA blend	230		200		
80/20 PP–PP-g-MA blend		210	200		
65/35 PP–PP-g-MA blend			200		
50/50 PP–PP-g-MA blend			200	185	
35/65 PP–PP-g-MA blend			200	185	
PP-g-MA					165

 Table I
 The Temperature at Which Rheological Measurements Were

 Performed for PPVC-PP-g-MA and PPSC-PP-g-MA Blends

Measurement

A dynamic mechanical thermal analyzer (Polymer Laboratories DMTA MKII) with parallel plates of radius 1.5 cm was used for torsional measurement at the dynamic displacement amplitude of $\pm 20 \ \mu$ m (within linear viscoelastic range) over frequency range of $0.6 * 10^{-1}$ -3.14 * 10^2 rad s⁻¹, in order to obtain storage modulus $G'(\omega)$, loss modulus $G''(\omega)$, and dynamic complex viscosity η^* . Since there was a large difference in melt viscosity between the PP and the PP-g-MA, we had to use a broad range of temperature for

the rheological measurements, which is shown in Table I to make a correlation of G' with G''.

The apparent viscosity η_{app} was measured using a capillary rheometer (Göttfert Rheograph 2001), and the length-to-diameter ratio of the capillary is 30.

RESULTS AND DISCUSSION

Figure 1 shows the shear rate $\dot{\gamma}$ dependence of the apparent viscosity η_{app} and the frequency ω de-



Figure 1 Plots of apparent viscosity η_{app} versus shear rate $\dot{\gamma}$ and complex viscosity η^* versus frequency ω at 230°C for PPVC: (+) η_{app} ; (\bigcirc) η^* . For PPSC; (\triangle) η_{app} ; (\square) η^* .



Figure 2 Plots of apparent viscosity η_{app} versus shear rate $\dot{\gamma}$ and complex viscosity η^* versus frequency ω for PPVC–PP-g-MA blends at 200°C and varying PP-g-MA contents: $(\blacklozenge, \diamondsuit)$ 10; (\blacksquare, \Box) 20; $(\blacktriangle, \bigtriangleup)$ 35; (\diamondsuit, \bigcirc) 50. Open symbols are for η^* , and closed symbols are for η_{app} .

pendence of the dynamic complex viscosity η^* for PPVC and PPSC, respectively. It is very obvious that the both matrices data follow the Cox–Merz rule³:

$$\eta_{\rm app}(\dot{\gamma}) = \eta^*(\omega)\big|_{\omega = \dot{\gamma}} \tag{1}$$

For PPVC–PP-g-MA and PPSC–PP-g-MA blends, however, deviation between the two viscosities (as shown in Figures 2 and 3) is observed; that is, the curves of apparent viscosity versus shear rate locate above the ones of dynamic complex viscosity versus oscillatory frequency,

$$\eta_{\rm app}(\dot{\gamma}) > \eta^*(\omega)|_{\omega = \dot{\gamma}} \tag{2}$$

indicating that the data of the blends do not obey the Cox–Merz rule. It is due to that the blends of PP and PP-g-MA are immiscibile.⁴ The immiscibility in the blend of PP and PP-g-MA could be explained by the fact that PP is a nonpolar molecule, whereas the PP-g-MA used in the study contains a high maleic anhydride content (8–10 wt % MA), and the addition of maleic anhydride grafting increases the polarity of molecule. The dispersed PP-g-MA phase with very low viscosity in the capillary shearing flow is deformed easily in the direction of the shear stress, whereas in the oscillatory shearing flow, the shape of the dispersed phase will oscillate. Because the dynamic displacement varies between -20 and +20 μ m (the displacement is very small), it is difficult to visualize that the dispersed phase in the dynamic shearing flow is deformed as much as in the capillary shearing flow. It was known that an apparent viscosity is contributed by both inversely viscous flow and recoverably elastic deformation; the latter relates to deformation of melt. The obvious deformation of the PP-g-MA phase in the capillary flow results in higher melt elasticity. Therefore, the difference in the deformation of the dispersed phase in the two types of measurements causes the deviation between the apparent and the complex viscosity.

Figures 4 and 5 give logarithmic plots of G' versus ω and G'' versus ω , respectively, for PPVC and 95/5 PPVC–PP-g-MA and 90/10 PPVC–PP-g-MA blends at 230°C; for an 80/20 PPVC–PP-g-MA blend at 200°C; for 50/50 PPVC–PP-g-MA and 35/65 PPVC–PP-g-MA blends at 185°C; and for PP-g-MA at 165°C. Corresponding to PPVC–PP-



Figure 3 Plots of apparent viscosity η_{app} versus shear rate $\dot{\gamma}$ and complex viscosity η^* versus frequency ω for PPSC–PP-g-MA blends at 200°C and varying PP-g-MA contents: (\blacklozenge , \diamond) 10; (\blacksquare , \Box) 20; (\blacktriangle , \triangle) 35; (\blacklozenge , \bigcirc) 50. Open symbols are for η^* , and closed symbols are for η_{app} .



Figure 4 Storage modulus G' versus frequency ω for PPVC–PP-g-MA blends at various temperatures and PP-g-MA contents (wt %). At 230°C: (\Box) 0; (\triangle) 5; (\bigcirc) 10. At 210°C: (\diamond) 20. At 200°C: (+) 35. At 185°C: (\times) 50; (-) 65. At 165°C: (*) 100.



Figure 5 Loss modulus G'' versus frequency ω for PPVC–PP-g-MA blends at various temperatures and PP-g-MA contents (wt %). At 230°C: (\Box) 0; (\triangle) 5; (\bigcirc) 10. At 210°C: (\diamond) 20. At 200°C: (+) 35. At 185°C: (\times) 50; (-) 65. At 165°C: (*) 100.



Figure 6 Storage modulus G' versus frequency ω for PPSC–PP-g-MA blends at various temperatures and PP-g-MA contents (wt %). At 230°C: (\Box) 0; (\triangle) 5; (\bigcirc) 10. At 210°C: (\diamond) 20. At 200°C: (+) 35. At 185°C: (\times) 50; (-) 65. At 165°C: (*) 100.



Figure 7 Loss modulus G" versus frequency ω for PPSC–PP-g-MA blends at various temperatures and PP-g-MA contents (wt %). At 230°C: (\Box) 0; (\triangle) 5; (\bigcirc) 10. At 210°C: (\Diamond) 20. At 200°C: (+) 35. At 185°C: (\times) 50; (-) 65. At 165°C: (*) 100.



Figure 8 Log G'-log G'' plots for PPVC–PP-g-MA blends at various temperatures and PP-g-MA contents (wt %). At 230°C: (\Box) 0; (\triangle) 5; (\bigcirc) 10. At 210°C: (\diamond) 20. At 200°C: (+) 35. At 185°C: (\times) 50; (–) 65. At 165°C: (*) 100.



Figure 9 Log G'-log G'' plots for PPSC-PP-g-MA blends at various temperatures and PP-g-MA contents (wt %). At 230°C: (\bigcirc) 0; (\triangle) 5; (\bigcirc) 10. At 210°C: (\diamond) 20. At 200°C: (+) 35. At 185°C: (\times) 50; (-) 65. At 165°C: (*) 100.

g-MA blends, similar plots for PPSC-PP-g-MA blends at various blend ratios are also given in Figures 6 and 7, respectively. For the both blends, G' and G'' increase with increasing frequency. It is quite evident that the high-frequency region is dominated by the G' response, which is a characteristic of the approaching rubber plateau; the low frequency region is dominated by the G'' response where the slope of the curves approaches 1, which is a characteristic of well-defined terminal zone.⁵ From the point of view of polymer processing, theoretical prediction of the rheological properties of polymer is very essential. Han and Chuang⁶⁻⁸ used logarithmic plots of G' versus G''for studying the rheological compatibility of polymer blends; they found that such plots were independent of composition for compatible blends and dependent of composition for incompatible blends. Note in the study that G' and G'' rapidly decrease with increasing PP-g-MA content, and the data of PP-g-MA cannot be gotten above 165°C. Therefore, the rheological measurements of the blends

with different blend ratios had to be carried at different temperatures in order to make $\log G'$ - $\log G''$ plots of all the blends display in as same a range as possible. The measurement at different temperatures does not affect accuracy of correlations of G' with G'' for the blends with different compositions because such plots of G' versus G''give a temperature-independent correlations for both compatible and incompatible blend systems.^{6,7} Figures 8 and 9 show the log G'-log G''plots for PPVC-PP-g-MA and PPSC-PP-g-MA blends, respectively. It is observed that these plots become dependent of blend composition, and the curve shifts towards the left upward as the PP-g-MA content increases. It is also attributed to the two-phase morphology of the blends. In the oscillatory shearing flow, the oscillating deformation of the dispersed phase with very small viscosity should induce and improve the deformation of the continuous PP phase. The more prominent the deformation, the higher the PP-g-MA content. Consequently, ratio of the amount of energy stored (G') to the amount of energy dissipated (G'') increases with an increase of the PP-g-MA content in the blend; that is, the ratio varies with the blend composition.

Although both the PPVC and PPSC are immiscible with the PP-g-MA, dynamic mechanical and mechanical properties of the blends suggested interfacial interaction between the two phases.¹ The difference in log G'-log G'' plots between PPVC-PP-g-MA and PPSC-PP-g-MA blends can also been found from Figures 8 and 9. In Figure 8, the plots for PPVC, 95/5 PPVC-PP-g-MA, and 90/10 PPVC-PP-g-MA blends almost ride on one curve except for other PPVC-PP-g-MA blends, while Figure 9 shows that all of the plots for PPSC-PP-g-MA blends almost separate from each other. It is a symptom that the interfacial interaction between the two phases is stronger for PPVC-PP-g-MA than PPSC-PP-g-MA blends. The stronger interfacial interaction that PPVC-PP-g-MA blend displays is due to a more similar structure of the dispersed phase and the continuous phase. In the PPSC-PP-g-MA blend, the structural difference between the ethylene block of PPSC molecular chains and the propylene segment of PP-g-MA molecular chain results in the reduction of the interaction between the two phases.

CONCLUSIONS

In the present work, the dynamic viscoelastic properties in the molten state for the blends of PPVC (homopolypropylene) with PP-g-MA (polypropylene grafted with maleic anhydride) and PPSC (ethylene–propylene copolymer) with PP-g-MA have been studied. In the both blends, PPVC and PPSC are immiscible with PP-g-MA. The results obtained are as follows.

- 1. The data of the blends do not obey the Cox–Merz rule since there is a larger deviation between dynamic complex and apparent viscosities; that is, $\eta_{\rm app}(\dot{\gamma}) > \eta^*(\omega)|_{\omega=\dot{\gamma}}$.
- 2. Double logarithmic plots of G' versus G'' for the blends gives composition-dependent correlations.
- 3. The storage modulus G' and loss modulus G'' for the blends increase as the frequency increases. In frequency range studied, the high-frequency region is dominated by the G' response; the low-frequency region is dominated by the G'' response, where terminal relaxation occurs.

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