

Design of polymer blend rheology

III. Effect of maleic anhydride containing copolymers on the melt viscosity of polyamides

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Summary

Addition of small amounts of maleic anhydride containing copolymers remarkably increases the melt viscosity of the $m \times D,6$ polyamides (PA). Random copolymers of styrene and maleic anhydride, P(S-co-MA), have been melt blended with PA in a ratio ranging from 0.5 to 5 wt%. A linear dependence has been observed for the blend viscosity on the molar ratio of the maleic anhydride subunits in the copolymer and the amino end-groups of PA. This linear relationship holds even for blends containing a molar excess of anhydride compared to amine. These rheological effects are of prime importance for the highly desirable control of the PA processing.

Introduction

Nowadays a great research effort is devoted to polymer blends and alloys (PBA). This very fast shift in the plastics industry towards multicomponent and usually multiphase systems is due to the prohibitively high cost for the development of new polymers. Blending is a more straightforward and less expensive technology, whereas PBA properties can be designed to meet the large spectrum of customer demands. In this respect, processing plays a decisive role on the ultimate properties of PBA (1,2). Furthermore, in the range of extreme compositions for multiphase PBA, size and shape of the minor phase (3,4) are controlled by a complex interplay of blend composition, melt viscosity ratio, interfacial tension, shear stress, elasticity ratio and the traditional processing parameters (5-15). As an example, when the viscosity ratio between dispersed and continuous phases, $\eta_r = \eta_d/\eta_c$, highly exceeds 2, it is quite a problem to disperse finely the minor phase. There is rather formation of a cocontinuous two-phase morphology, which might be detrimental to the ultimate mechanical properties, because of delamination problems (7). The use of graft copolymers, P(A-g-B), hopefully formed by a reactive processing, is a convenient way to cope with this problem. Numerous examples are now available which support that block and graft copolymers can significantly enhance the interfacial adhesion. This strategy is particularly suitable for the melt blending of a polyamide terminated with primary amino groups and a maleic anhydride containing polyolefin used as a compatibilizer in ternary blends (16-24).

This paper aims at reporting on the deep change in rheology of $m \times D,6$ polyamides (PA) when melt blended with small amounts (0.5-5 wt%) of styrene-

maleic anhydride random copolymers, P(S-co-MA), of various compositions. The semi-crystalline PA under consideration results from the step-growth polymerization of *m*-xylene diamine and adipic acid. They display high mechanical properties and a low Newtonian melt viscosity ($\eta_{260^\circ\text{C}} = 170 \text{ Pa}\cdot\text{s}$). However, the high fluidity of PA has adverse effects on polymer molding. A previous study has shown that small amounts of methylmethacrylate-methacrylic acid random copolymers, P(MMA-co-MAA), can efficiently increase the melt flow resistance of PA (25). This beneficial effect has been accounted for by a condensation reaction of neighbouring carboxylic acid groups of the additive into anhydrides able to react with the primary amino end-groups of PA and formation of graft copolymers. Based on the evidence that carboxylic acid groups are less reactive towards amino end-groups than maleic anhydride units (26), a faster and more quantitative reaction is expected from the addition of maleic anhydride containing copolymers to polyamide chains. Accordingly, within the time of blending, a better improvement of the flow resistance of PA might be predicted.

Experimental

Material

Polyamides m x D,6 (PA) were supplied by Solvay (IXEF PARA 0000 : $M_n = 17,000$; $75 \cdot 10^{-6} \text{ mol-NH}_2/\text{g}$; $55 \cdot 10^{-6} \text{ mol-COOH/g}$ and IXEF PARA X000 : $M_n = 16,500$; $43 \cdot 10^{-6} \text{ mol-NH}_2/\text{g}$; $93 \cdot 10^{-6} \text{ mol-COOH/g}$, designated as PA-1 and PA-2, respectively). Because of hygroscopicity, PA were dried at 100°C for at least 18 hours under reduced pressure prior to melt processing. Styrene, maleic anhydride and ethylacetate were purchased from Janssen and used without further purification. Azo-bis-isobutyronitrile (AIBN) was purchased from Merck. Toluene was dried by refluxing over CaH_2 for 48 hours.

Synthesis of P(S-co-MA)

Styrene-maleic anhydride random copolymers, P(S-co-MA), with a MA content ranging from 0 to $22 \cdot 10^{-4} \text{ mol/g}$, were synthesized in ethylacetate using AIBN (5 g/mol. of monomers) as an initiator. After the careful removal of oxygen from the reaction medium, polymerization was initiated at 60°C under reduced pressure for 24 hours. The copolymer was recovered by precipitation in heptane and dried up to constant weight. The molar percentage of maleic anhydride was determined by titration of the previously hydrolyzed copolymers with tetramethylammonium hydroxide in a toluene-methanol mixture. Anhydrides were hydrolyzed in a 5/1 tetrahydrofuran-water solution, for 72 hours at 60°C . Hydrolysis progress was followed by infrared spectroscopy ($\nu_{\text{COanhydr}} = 1856$ and 1780 cm^{-1} , $\nu_{\text{COO-H}} = 3450 \text{ cm}^{-1}$ and $\nu_{\text{CO acid}} = 1710 \text{ cm}^{-1}$).

Polymer blending

PA were mixed with P(S-co-MA) in a laboratory Brabender Plasticorder of 60 cm^3 at 260°C and 50 rpm until torque was stabilized, i.e. for approximately 10 minutes. Final blends were compression-molded as 2 mm thick sheets at 260°C for 3 minutes under a pressure of 15 bars.

Measurements

IR spectra were recorded by using a Perkin-Elmer 1600 FTIR. Size exclusion chromatography (SEC) was performed in tetrahydrofuran at 45°C using a Hewlett-Packard 1090 liquid chromatography equipped with a HP1037A refractometer index detector and four PL GEL columns of various pore sizes (10^5 , 10^4 , 500 and 100 Å). Molecular weight distribution was calculated in reference to a polystyrene calibration curve. Melt viscosity of previously molded and then finely grinded blends was measured by using a Gottfert Rheograph 2001 capillary rheometer at 260°C. Polymers and blends were carefully dried at 100°C for at least 18 hours before measurement. The capillary was of a 1 mm diameter, a length over diameter ratio of 20 and 180° entrance angle. The force of the plunger was measured at constant crosshead speeds.

Results and Discussion

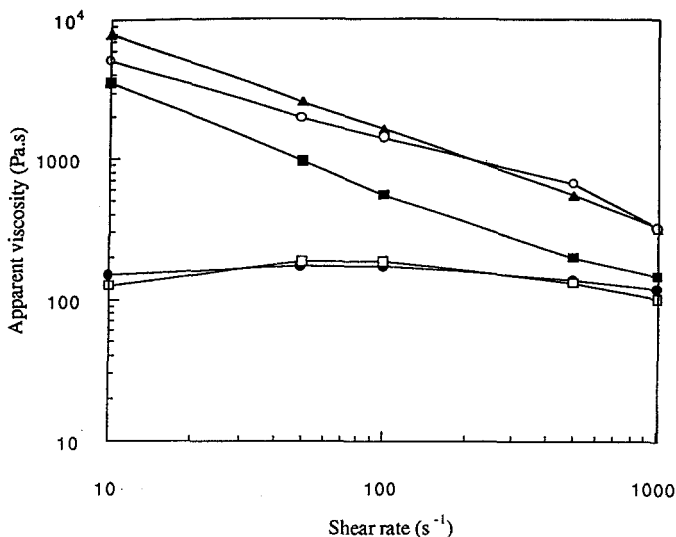
Random copolymers P(S-co-MA) of an increasing maleic anhydride content have been synthesized by a free-radical polymerization process (Table I). The maleic anhydride, MA, composition of the previously hydrolyzed copolymers has been measured by potentiometric non-aqueous titration of the carboxylic acid groups. It must be noted that only one carboxylic acid group per MA is neutralized with tetramethylammonium hydroxide (27,28).

Table I : Molecular characteristics of P(S-co-MA) random copolymers

| Copolymers | MA content ($\times 10^4$ mol/g) | Mn ($\times 10^{-3}$ g/mol) | Mw/Mn |
|------------|-----------------------------------|------------------------------|-------|
| SMA-1 | 7.4 | 5.0 | 2.5 |
| SMA-2 | 16.8 | 4.6 | 2.2 |
| SMA-3 | 22.0 | 3.0 | 2.5 |

Figure 1 shows how rheology of PA-1 is modified at 260°C upon the addition of 5 wt% of P(S-co-MA) of various MA contents. In contrast to the Newtonian behavior of the neat PA-1, the addition of P(S-co-MA) promotes a sharp increase in the melt viscosity at low shear rates, which however seems to level off when the MA content exceeds ca. 20×10^4 mol/g. Indeed, the viscosity ratio, $\eta_{\text{blend}}/\eta_{\text{PA}}$, at 10 s^{-1} is 24, 37 and finally 34 when the MA content of the additive is 7.4×10^4 , 16.8×10^4 and 22.0×10^4 mol/g, respectively. For the sake of comparison, a homopolystyrene prepared by an anionic process (PS : Mn = 16,000; Mw/Mn = 1.1) has been melt blended with PA-1. It is clear that the addition of 5 wt% of PS does not significantly affect the melt viscosity of PA-1 ($\eta_{\text{blend}}/\eta_{\text{PA}} = 0.9$ at 10 s^{-1}). As a second effect of blending, a rheothinning behavior is observed to occur, i.e. a decrease in the PA-1/P(S-co-MA) blend viscosity upon increasing shear rates.

Figure 1 : Viscosity versus shear rate for PA-1 melt blended with 5 wt% of P(S-co-MA) of various MA contents at 260°C (● PA-1; □ (PA-1-b-PS); ■ (PA-1-b-SMA-1); ▲ (PA-1-b-SMA-2); ○ (PA-1-b-SMA-3))



This general feature is of the utmost importance since it nicely fits the target of this research : a substantial increase in the melt viscosity at low shears ($\eta_{\text{blend}}/\eta_{\text{PA}} = 37$ at 10 s^{-1}) while preserving a high injectability at high shear rates ($\eta_{\text{blend}}/\eta_{\text{PA}} = 2.7$ at 1000 s^{-1}). This non-Newtonian power-law behavior at low frequency is usually attributed to long branching components in multiphase PBA (29,30). Accordingly, the high reactivity of PA amino end-groups towards the anhydride subunits of P(S-co-MA) more likely results in graft copolymers during the melt mixing (equ. 1). In this respect, it is worth examining whether the melt flow resistance is related to the extent of the amine-maleic anhydride reaction. The maleic anhydride to amino end-group molar ratio, ($\text{MA}_{\text{SMA}}/\text{NH}_{2\text{PA-1}}$), is listed in table II along with the viscosity ratio of blends of a constant composition (5 wt% of P(S-co-MA) additive).

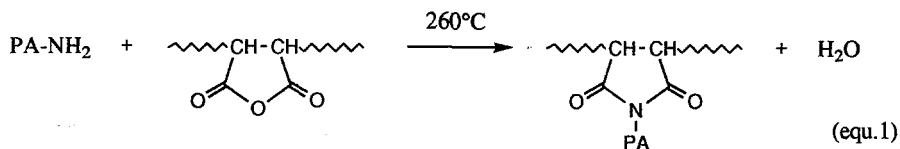


Table II : Molecular and rheological characteristics of PA-1/P(S-co-MA) blends (95:5)

| Blends | ($\text{MA}_{\text{SMA}}/\text{NH}_{2\text{PA-1}}$) | ($\eta_{\text{blend}}/\eta_{\text{PA-1}}$) at 10 s^{-1} |
|----------------|---|---|
| (PA-1-b-PS) | 0.00 | 0.9 |
| (PA-1-b-SMA-1) | 0.49 | 24.0 |
| (PA-1-b-SMA-2) | 1.12 | 37.1 |
| (PA-1-b-SMA-3) | 1.47 | 34.0 |

From these results, it is clear that the melt viscosity of blends increases with the MA content of the additive up to a (MA_{SMA}/NH_{2PA}) molar ratio close to 1. When the MA content is higher than the number of available amino end-groups, the apparent viscosity does not change anymore. This implies that the reaction between amino groups and maleic anhydride subunits to form N-alkylmaleimide, is quantitative within the time devoted to melt mixing, i.e. approximately 10 minutes at 260°C.

In order to have a better insight into the dependence of the melt viscosity on the (MA_{SMA}/NH_{2PA-1}) molar ratio, PA-1 and PA-2 have been melt blended with various amounts of SMA-2. Combination of two different PA and various amounts of SMA-2 (from 0 to 5 wt% with respect to PA) is indeed an easy way to modulate the maleic anhydride to primary amine molar ratio for the PA/additive pair under consideration (Table III). For the sake of a straightforward comparison, the rheological data have been plotted versus the (MA_{SMA}/NH_{2PA}) molar ratio in figure 2.

Table III : Effect of maleic anhydride to amine molar ratio on the viscosity ratio and the solubility of the extrudate in formic acid (S : soluble; I : insoluble)

| PA | SMA-2 content (wt%) | (MA_{SMA}/NH_{2PA}) | (η_{blend}/η_{PA}) at 10 s^{-1} | Solubility |
|------|---------------------|-----------------------|---|------------|
| PA-1 | 0.0 | 0.00 | 0.9 | S |
| | 0.5 | 0.11 | 3.2 | S |
| | 0.9 | 0.20 | 7.3 | S |
| | 1.2 | 0.27 | 9.4 | S |
| | 3.0 | 0.67 | 23.4 | I |
| | 5.0 | 1.12 | 37.1 | I |
| PA-2 | 0.0 | 0.00 | 1.0 | S |
| | 0.6 | 0.23 | 1.9 | S |
| | 1.3 | 0.51 | 3.9 | S |
| | 2.5 | 0.98 | 14.1 | I |
| | 5.0 | 1.96 | 27.0 | I |

Although PA-1 and PA-2 have the same rheology, thus independent of the content of the amino and carboxylic acid end-groups, this similarity disappears when they are melt blended with the same amount of SMA-2. In the whole range of shear rates, the melt flow resistance is expectedly higher for blends of PA-1 compared to PA-2. This is in a direct connection with the amino functionality of PA, which is higher for PA-1 ($75 \cdot 10^{-6} \text{ mol/g}$) than for PA-2 ($43 \cdot 10^{-6} \text{ mol/g}$). More surprisingly, figure 2 shows a linear dependence for the blend viscosity versus the amine to maleic anhydride molar ratio. This linear relationship holds even at (MA_{SMA}/NH_{2PA}) ratios higher than 1, which might be in contradiction with the observations reported in table II. There is however a marked difference in the two series of measurements. Indeed, the (MA_{SMA}/NH_{2PA}) ratio has been changed while keeping constant the additive content (5 wt% of P(S-co-MA)) in table II, although data in table III and figure 2 have been reported for an increasing content of SMA-2. In the latter case, the additive may form a dispersed phase,

Conclusions

Addition of small amounts of maleic anhydride containing copolymers is a convenient way for tailoring rheology of polyamide m x D,6 (PA). This has been shown by melt blending copolymers of styrene and maleic anhydride, P(S-co-MA), with PA in a ratio ranging from 0.5 to 5 wt%. At low shear rates, the rheofluidity of PA at 260°C is greatly reduced in relation to the molar ratio of maleic anhydride subunits in the copolymer and PA amino end-groups. Grafting of PA onto P(S-co-MA) is responsible for this increase in melt flow resistance, as a result of condensation of the primary amino end-groups of PA with the anhydride functions of the additive. Interestingly enough, blend viscosity is linearly dependent on this maleic anhydride over amine molar ratio. Hydrolysis of PA branches during melt blending is responsible for cross-linking reaction.

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