Design of polymer blend rheology: 4. Effect of polymethacrylic ionomers on the melt viscosity of polyamide m x D,6

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Abstract
Rheological properties of blends of polyamide m x D,6 (PA) with random copolymers of methyl methacrylate and methacrylic acid (P(MMA-co-MAA)) and the related ionomers (P(MMA-co-metal MA)), respectively, have been investigated at 260°C. Addition of small amounts of suitable ionomers (up to 5 wt%) remarkably increases the melt viscosity of PA. At low shear rates and depending on the metal cation of the ionomer, the rheofluidity of PA is reduced by at least two orders of magnitude. The PA melt viscosity increases with the cation as follows: $Ni^{2+} < Ba^{2+} < Mg^{2+} < Li^+ < Na^+ < K^+ < Cs^+$. The major effect is believed to occur when the polymer compatibility is improved to the point where a finely dispersed two-phase system with a low interfacial tension is reached, as a result of strong ion—dipole interactions. Polyblends show a rheothinning behaviour which agrees with the reversibility of H-bonding and dipolar interactions.

Keywords: melt viscosity; poly(methyl methacrylate) ionomers; polyamide blend

INTRODUCTION

Rheology of polymer blends has been shown to be intimately dependent on the phase morphology and the interactions at the interface[1,2]. The viscosity-composition curve usually shows positive deviation from the logarithmic additivity rule in case of intimately mixed polymers and emulsion-type heterogeneous blends with a low interfacial tension and a long relaxation time of the structured morphology. In contrast, melt viscosity shows a negative deviation from the logarithmic additivity rule when there is no specific interaction between the phases, thus when no compatibilization agent is added. This classification is essentially empirical and relies upon a great deal of published data on the control of deformation and break up of dispersed polymer droplets in a simple shearing matrix[3-9].

The m × D,6 polyamide (PA) from Solvay Co. is a semi-crystalline polymer prepared by step-growth polymerization of m-xylene diamine and adipic acid. It has a characteristic low Newtonian melt viscosity (η_{260oc} = 170Pa s), which is usually a prerequisite for fast and easy processing. However, when moulding is concerned, a higher melt viscosity ($\eta_{260°c} > 850$Pa s) at low shear rates ($\gamma < 100$ s^{-1}) is still required, particularly for avoiding bur formation and an additional finishing step which is time and polymer consuming. A straightforward way to increase the melt viscosity of PA is the addition of a polymeric partner of high melt viscosity and able to interact with the amide functions through ion-dipole, dipole-dipole or hydrogen bonding interactions. Blends of copolymers of styrene and acrylic acid with aliphatic polyamides are examples of blends in which hydrogen bonding can take place between amide groups of the polymer backbone and/or the amine end-groups of the polyamide, and carboxylic acid groups of the copolymer which improves the interfacial properties of the blends[10,11]. Polyamide/polyamide blends[12] and blends of polyamide with poly(ethylene oxide)[13] are other examples in which dipole-dipole interactions are operative. Since ion-dipole interactions are usually stronger than either dipole-dipole interactions or hydrogen bonding, the use of polymers bearing a limited number of pendant ionic groups, i.e. ionomers, has potential in improving the compatibility of this polymer with other polar polymers. Numerous examples are known where polyethylene-based ionomers have been used as compatibilization agents in polyamide containing binary and ternary blends[14-24]. It has also been shown that polyamides can be compatibilized with sulfonated[25-28] and carboxylated[29] polystyrene ionomers.

This paper aims at reporting how rheology of the m x D,6 polyamide is modified by small amounts (up to 5wt%) of free-radical initiated copolymers of methyl methacrylate and methacrylic acid, P(MMA-co-MAA) and the related ionomers, P(MMA-co-metal MA). Compared to widely used ethylene and styrene-based ionomers, the chain flexibility of methyl methacrylate-based ionomers is expected to be lower, taking into account, e.g. the persistance length of PMMA, PS and PE which are 7.2 ± 0.5Å at 21°C, 9.1 ± 0.2Å at 25°C in toluene and 6.900 ± 100 Å at 145°C in bis-2-ethylhexyl-adipate, respectively. Furthermore, being more polar than polyethylene and polystyrene, poly(methyl methacrylate) could interact with the m x D,6 polyamide by dipoledipole interactions[30]. The experimental observations reported in this paper complement data published elsewhere[31].

EXPERIMENTAL

Materials

Polyamide m x D,6 (PA) was supplied by Solvay (IXEF PARA XOOO: M_w = 17400; 75x10^{-6}mol-NH$_2$/g; 55 x 10^{-6}mol-COOH/g; T_g = 88°C and T_m = 238°C). It was dried at 100°C for at least 18 h under reduced pressure prior to blending and rheological measurements. Methyl methacrylate, methacrylic acid and ethyl acetate (Janssen) were used without further purification, 2,2'-Azobis(2-methylpropionitrile) (AIBN) and metal acetates (Li, Na, K, Cs, Mg, Ba and Ni) were purchased from Merck. Pyridine and thionylchloride (Aldrich) were freshly distilled before use. Toluene, tetrahydrofuran and methanol were dried by refluxing over CaH$_2$, benzophenone-Na and Mg, respectively, and distilled just before use.

Synthesis ofP(MMA-co-MAA)

Random copolymers of methyl methacrylate and methacrylic acid, P(MMA-co-MAA), with a MAA content ranging from 0 to 31mo1%, were synthesized in ethyl acetate using AIBN (5gmol$^-$I of monomers) as an initiator. After careful removal of oxygen from the reaction medium, polymerization was initiated at 60°C under reduced pressure for 24 h. The copolymer was recovered by precipitation in heptane and dried up to constant weight. Methacrylic acid content was measured by potentiometric titration of carboxylic acid groups with a standard solution of tetramethylammonium hydroxide (TMAH) in a toluene—methanol mixture (from 9/1 to 7/3 depending on MAA content).

Neutralization of P(MMA-co-MAA)

Copolymers of methylmethacrylate and methacrylic acid, P(MMA-co-MAA), were dissolved in a toluene methanol mixture (2wt/v%). Toluene to methanol volume ratio was in the 9/1 to 7/3 range, depending on the MAA content. Stoichiometric amount of metal acetates was dissolved in a minimum of methanol (Li, Na, K, Cs, Mg and Ni acetates) or deionized water (Ba acetate) and added to the copolymer solution. Acetic acid formed as a by-product was removed from the reaction mixture together with water and methanol by three repeated azeotropic distillations of toluene under reduced pressure. Ionomers were stored under nitrogen.

Esterification of P(MMA-co-MAA)

Random copolymers of methylmethacrylate and methacrylic acid, P(MMA-co-MAA), were dissolved in pyridine (5wt/v%) and refluxed in the presence of a 10-fold molar excess of thionylchloride with respect to methacrylic acid for 1 h. Methanol (50 molar excess with respect to carboxylic acid groups) was then added and the reaction was continued for an extra 6 h. Polymer was recovered by precipitation in an excess of technical grade methanol, filtered and dried until constant weight.

Polymer blending

PA, neutralized and unneutralized P(MMA-co-MAA) copolymers were systematically dried under vacuum at 100°C overnight. Indeed, rheological measurements are known to be adversely affected by water absorption[32]. PA was melt blended with neutralized and unneutralized P(MMA-co-MMA) copolymers in a laboratory Braben-der Plasticorder mixing chamber (60 cm^3) using rather blades designed for high shear applications. The polymer mixture was added to the mixing chamber heated at 260°C under a mixing rate of 50 rpm. When the addition was complete, blending was maintained until the mixing torque was stabilized *(ca 10min)*. Blends were then rapidly transferred into a mould and pressed (15 bars) at 260°C for 3min. The final 2 mm thick compression-moulded sheets were then cooled down to room temperature in another hydraulic press for *ca* 3 min. In agreement with previously published data[23], the morphology of the blends was found to be the same as the morphology observed for a sample withdrawn from the mixing chamber and rapidly quenched at 0°C.

Measurements

I.r. spectra were recorded with a Perkin-Elmer 1600 FTIR. Samples were solvent cast on KBr. Size exclusion chromatography (s.e.c.) was performed in THF at 45°C using a HP 1090 liquid chromatograph equipped with a HB 1037A refractometer, index detector and four PL GEL columns of various pore sizes (10^5, l0^4, 500 and 100 A). Molecular weight distribution was calculated in reference to a polystyrene calibration curve. Glass transition temperature was measured with a differential scanning calorimeter (DuPont 9000), at a heating rate of 20°Cmin^{-1} under a nitrogen flow. Melt viscosity of samples finely ground and previously dried overnight under vacuum at 100°C was measured with a Gottfert Rheograph 2001 capillary rheometer at 260°C. When the temperature equilibrium was reached, the sample was forced through a capillary with the following characteristics: 1 mm diameter, length over diameter ratio 20 and entrance angle = 180°. The flow rate was controlled by the speed of the plunger, and the applied force was measured with a compression load cell. The apparent viscosity was calculated as the ratio of the shear stress at the wall over the shear rate assuming a Newtonian behaviour and

using the Rabinowitsch correction. Each measurement was repeated three times.

RESULTS AND DISCUSSION

Blends of PA with P(MMA-co-MAA)

A series of P(MMA-co-MAA) copotymers of various compositions have been synthesized by free-radical copolymerization of methyl methacrylate and methacrylic acid in ethyl acetate. The composition of these random copolymers has been analysed by the nonaqueous titration of the methacrylic acid subunits by TMAH. Molecular weight distribution has been determined by s.e.c, after the quantitative esterification of the methacrylic acid subunits by methanol *(Table 1)*.

Blends of PA and P(MMA-co-MAA) copolymers of various wt compositions (0, 25, 50, 75 and 100 wt% PA) have been prepared in formic acid and precipitated into deionized water. In the particular case where the MAA content of the copolymer is the highest (31 mol%), the PA/P(MMA-co-MAA) blend has been dissolved in a formic acid/tetrahydrofuran (2/l, v/v) mixture. The polyblends were dried at 100°C under reduced pressure for at least 1 week. The d.s.c, analysis (second scan after an isotherm of 5 min at 260°C) of these blends shows that only the copolymer with the highest methacrylic acid content (MAA31 in *Table 1*) is miscible with PA over the whole composition range. Indeed, a single composition-dependent glass transition temperature is observed together with depression of the PA melting temperature upon addition of increasing amounts of P(MMA-co-MAA) copolymer. It must be pointed out that anhydrides are formed upon heating the P(MMA-co-MAA) copolymers at 260°C. Indeed, *FTi.r.* shows two additional absorption bands at 1760 and 1830 cm^{-1}, respectively *(Figure 1)*. This observation is in agreement with the well known condensation of neighbouring methacrylic acid subunits into anhydrides at temperatures higher than 200°C[33].
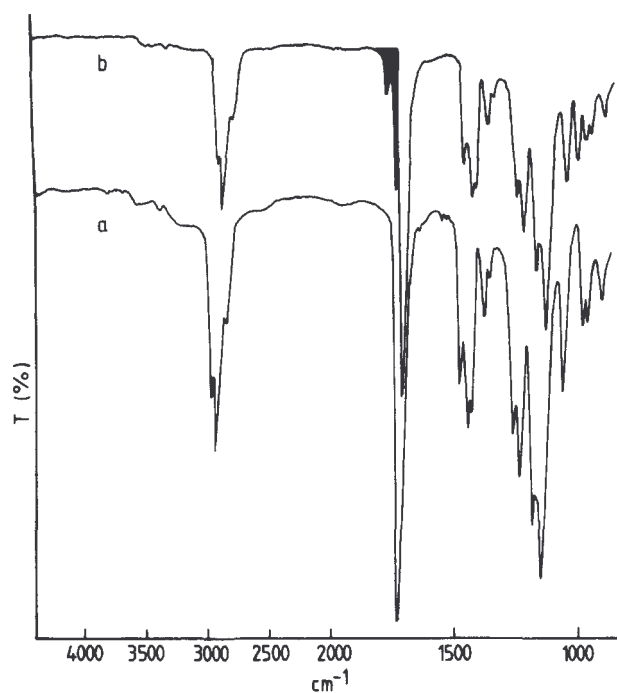

Figure 1 *FT*i.r. spectra of MAA14 (*Table 1*) before (a) and after annealing at 260°C for 15 min (b)

Table 1 Molecular characteristics of P(MMA-co-MAA) copolymers

Reference	M_n 10^{-3} (g mol^{-1})	M_w/M_n	MAA content (mol%)
MAA3	24.5	1.3	2.6
MAA5	28.0	1.4	4.8
MAA7	18.5	1.3	7.2
MAA12	19.0	1.4	12.1
MAA14	26.0	1.4	14.1
MAA20	39.5	2.1	20.0
MAA31	34.0	1.7	30.9

Thus, blending PA with P(MMA-co-MAA) at 260°C is liable for the formation of graft copolymers, as a result of the reaction between the amine end-groups of PA and the aforementioned anhydride functions [10,11,34,35]. A further evidence of the grafting reaction can be found in the selective extraction of the MAA7 copolymer previously melt blended with PA (50wt%) at 260°C for 10min. This blend has actually been finely ground and the copolymer has then been selectively extracted with dry THF in a Soxhlet apparatus for 48 h. Only half of the initial amount of MAA7 has been extracted which gives credit to the grafting of PA onto the polymethacrylate backbone through an amide or an imide bond (equation (1)). It is worth noting that the extraction results remain unchanged beyond 24 h of extraction time, which confirms that the extraction is actually complete.

Figure 2 shows the melt viscosity dependence on shear rate for 100/5 (wt/wt) PA blends with P(MMA-co-MAA) copolymers of various methacrylic acid content. All these blends have been prepared with a Brabender internal mixer at 260°C. The addition of P(MMA-co-MAA) copolymers to PA is responsible for a general increase in melt viscosity (except for the MAA 31 copolymer at shear rates higher than *ca* 250 s^{-1}). It also triggers a rheo-thinning behaviour in contrast to the Newtonian behaviour of PA. The effect of the methacrylic acid content of the copolymer on the viscosity ratio, i.e. the relative increase in the melt viscosity of PA (η_{blend}/η_{PA}), at a constant shear rate of 10 s^{-1} is shown in *Figure 3*. Surprisingly enough, this plot passes through a maximum for a MAA content of *ca* 12mol%.
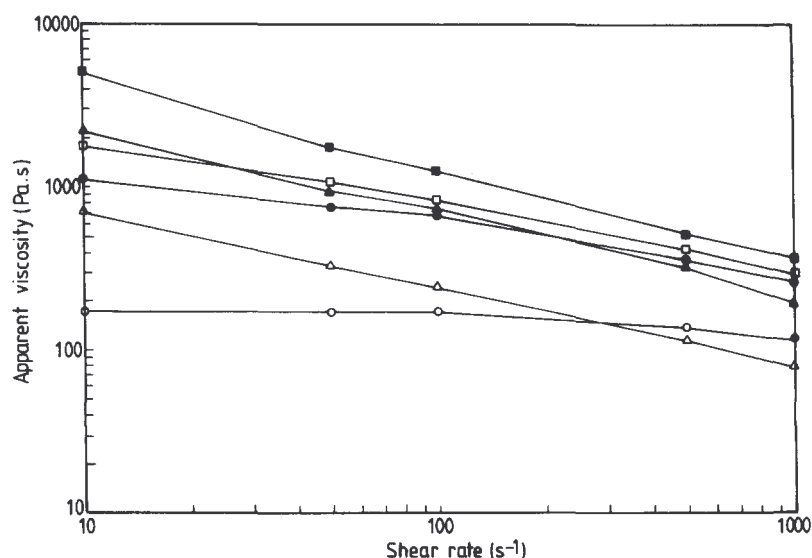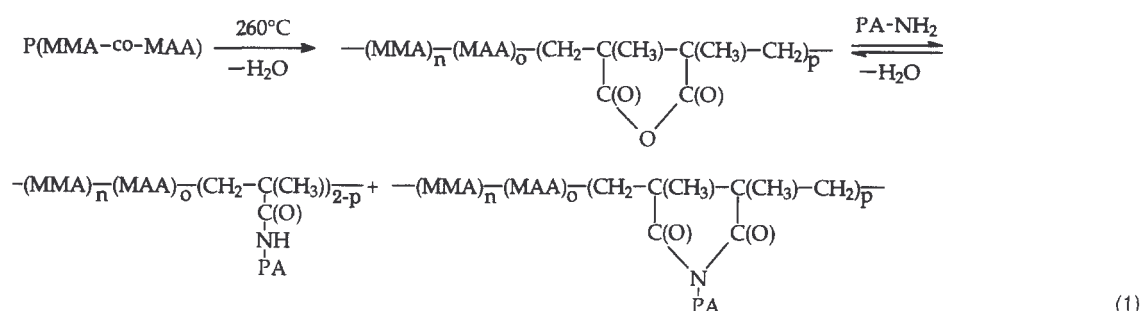

Figure 2 Shear rate dependence of melt viscosity for 100/5 (wt/wt) PA/P(MMA-co-MAA) blends in relation to methacrylic acid content in mol% (○: PA; ●: MAA3; □: MAA5; ■: MAA12; ▲: MAA20 and △: MAA31)

(1)

It is believed that an increase in the MAA content of the copolymer is responsible for a steadily improving compatibility of the PA/PMMA blend as a result of more extensive grafting and hydrogen bonding between the two constitutive components. In parallel, a positive deviation of the melt viscosity with respect to the logarithmic additivity rule is expected to occur and to reach a maximum when the compatibility of the two-phase polyblend is optimum. Beyond that point, thus beyond *ca* 12mol% methacrylic acid in the copolymer, the viscosity ratio decreases as rapidly as the miscibility is increased and the binary blend tends to a one-phase system.

Blends of PA with P(MMA-co-metal MA)
The P(MMA-co-MAA) copolymers listed in *Table 1* have been neutralized with stoichiometric amounts of Na, Ba and Ni acetates, respectively. *FTi.r.* spectroscopy shows that the neutralization reaction is complete, since the absorption characteristic of the carboxylic acid function (v_{COO_H} 3260cm^{-1} and $v_{c=o}$: 1705cm^{-1}) have completely

disappeared and are replaced by absorptions typical of metal carboxylates ($v_{c=o}$: 1560— 1615cm^{-1} depending on the cation) *(Figure 4)*. PA has been melt blended with each ionomer in a 100/5 (wt/wt) ratio prior to analysis by capillary rheometry at 260°C.

Effect of metal methacrylate content. Figure 5 shows the dependence of the viscosity ratio, η_{blend}/η_{PA} measured at a constant shear rate of 10 s^{-1}, on the metal carboxylate content and the metal cation. Although the divalent Ba and Ni ionomers do not change very significantly the PA melt viscosity, Na ionomers have a remarkable effect on the viscosity ratio. Compared to the unneutralized P(MMA-co-MAA) copolymers *(Figure 3)*, bell-shaped curves are observed for both PA/Na ionomers and the parent PA/P(MMA-co-MAA) blends. Nevertheless the maximum in the viscosity ratio is increased by at least a factor of 2 and shifted from 12mol% of MAA subunits down to *ca* 7mol% of Na methacrylate upon neutralization of the acid groups. The half-height width of the curves is also much smaller for Na ionomers than for the acid precursors, which suggests that the transition from a completely immiscible two-phase system to a monophase one at 260°C occurs in a rather narrow range of metal methacrylate content. In other words, the interactions of Na carboxylate groups with PA appear to be more efficient in promoting the PA/PMMA compatibility than combination of carboxylic acid/amide hydrogen bonding and partial grafting. Since the maximum viscosity ratio is so different in the two series of blends *(Figures 3* and 5), the phase morphology and the interfacial tension are expected to be different when the apparent optimum compatibility is promoted by either the P(MMA-co-MAA) copolymers and the counterparts neutralized with Na.

Effect of the metal counterion. The effect of the metal cation used in the neutralization of the P(MMA-co-MAA) copolymers has been first investigated by substituting Na by a smaller (Li) and bigger (K, Cs) alkaline cations, respectively. It is well known that the strength of the mutual dipolar interactions in ionomers increases as the ionic radius of the metal cation decreases, at least in the series of alkaline and alkaline-earth metal carboxylates[36]. The intermolecular PA/ionomer interactions responsible for improved compatibility can only be formed at the expense of the intramolecular dipolar interactions in the ionomer. This process is thus expected to be as favourable as the radius of the metal cation is large. This expectation is confirmed by the shear rate dependence of the viscosity ratio, η_{blend}/η_{PA}, at constant alkaline methacrylate content, which increases from Li to Na, K and finally Cs carboxylate ionomers *(Figure 6)*. At a constant shear rate of 10s^{-1}, the viscosity ratio is increased by a factor of *ca* 9 upon substitution of Li by Cs. The same tendency is observed when alkaline-earth cations are compared (e.g. Mg and Ba), since the bigger metal cation gives rise to a higher viscosity ratio *(Figure 7)*. There is however a dramatic decrease in the efficiency of the ionomer to increase the PA melt viscosity when divalent alkaline-earth cations are substituted for alkaline ones. It must be emphasized that the thermal dissociation of ionic multiplets in ionomers releases unpaired carboxylate groups in case of monovalent cation.
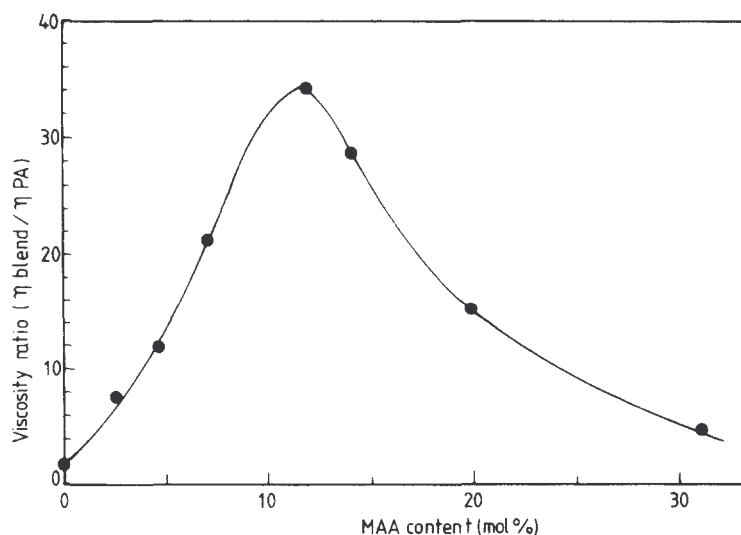

Figure 3   Dependence of the viscosity ratio, η_{blend}/η_{PA}, on the methacrylic acid content in mol%, for 100/5 (wt/wt) PA/P(MMA-co-MAA) blends at 260°C and a shear rate of 10 s^{-1}

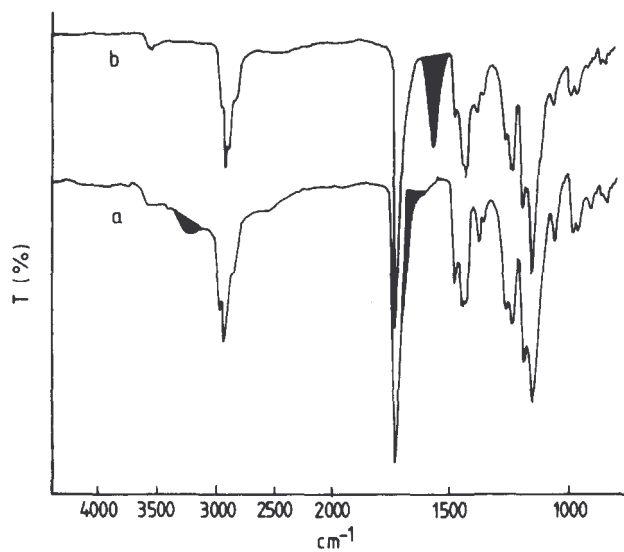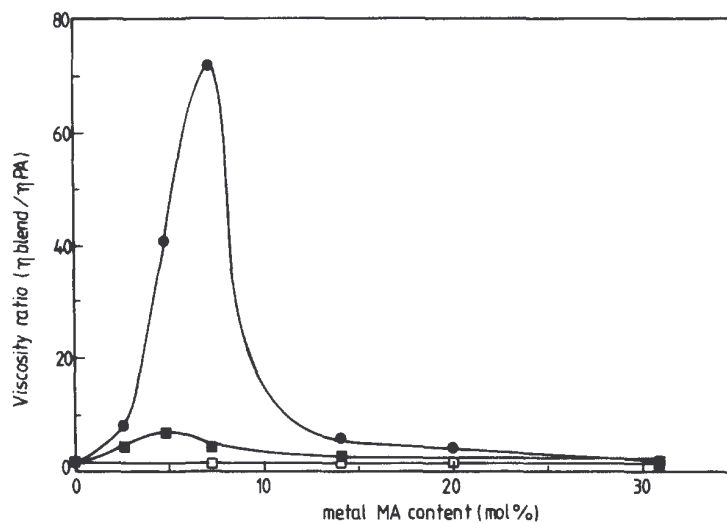**Figure 4** *FT*i.r. spectra of MAA14 (a) compared to the related Na ionomer (b)

Figure 5 Dependence of the viscosity ratio, η_{blend}/η_{PA}, on the metal methacrylate content in mol% for 100/5 (wt/wt) PA/ionomer blends at 260°C and a shear rate of $10\,s^{-1}$ (●: Na; ■: Ba and □: Ni)
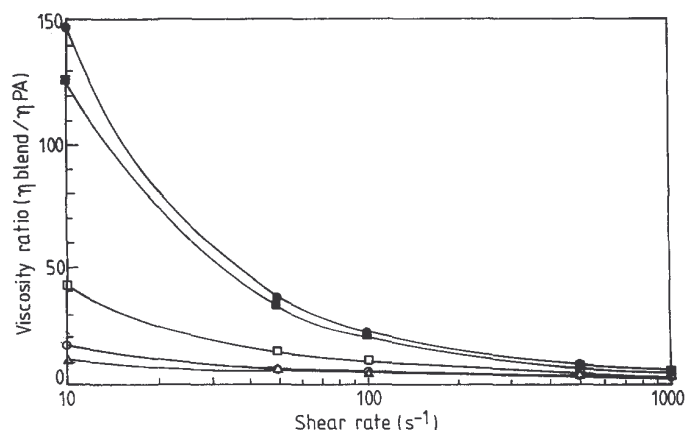
Figure 6 Shear rate dependence of the viscosity ratio, η_{blend}/η_{PA}, for various 100/5 (wt/wt) PA/P(MMA-co-alkaline MA5) blends at 260°C ($\triangle$: H in MAA, $\bigcirc$: Li; $\square$: Na; $\blacksquare$: K and $\bullet$: Cs)

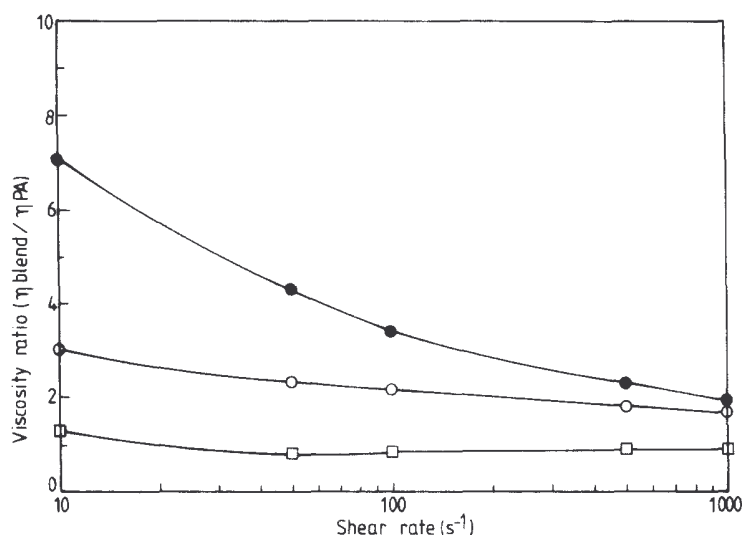**Figure 7** Shear rate dependence of the viscosity ratio, η_{blend}/η_{PA}, for 100/5 (wt/wt) PA/P(MMA-co-divalent MA5) blends at 260°C ($\bigcirc$: Mg; $\bullet$: Ba and $\square$: Ni)

In contrast, dielectric measurements have shown that divalent cation carboxylates are released at higher temperatures as species of a zero or at least very small dipole moment. These species are more likely triplets, possibly in equilibrium with a set of doublets and anions[37]. Thus, even though K and Ba have the same cation radius, Ba carboxylate containing copolymers are less prone to form strong iondipole interactions with PA than the K counterparts, as a result of more stable ionic multiplets and more sterically hindered metal carboxylate ion pairs in ionomers containing divalent metal cations rather than monovalent ones, as recently confirmed for PMMA-based ionomers[30]. Ni is another divalent metal cation which belongs to the series of transition metals and which accordingly forms much less ionic bonds with carboxylates. Compatibilization cannot be promoted any more by ion—dipole interactions but rather by intrinsically weaker dipole—dipole interactions which, in this case, have to accommodate the common six-fold coordination of the Ni cations. Therefore, it is not surprising that the PA melt viscosity is not significantly improved by Ni carboxylate-based ionomers.

Effect of ionomer content. The processing and moulding requirements are such that an at least tenfold increase in the melt viscosity of PA at low shear rates ($\gamma \sim 10s^{-1}$) is desirable and that the material is as fluid as the PA matrix at high shear rates ($\gamma > 300s^{-1}$). According to *Figure 5,* the first requirement can be met with a small amount of Na carboxylate containing copolymer, which is advantageous for keeping the mechanical properties of the extruded PA essentially unchanged. A more complete information is reported in *Figure 8,* which shows the melt viscosity vs shear rate of PA/P(MMA-co-NaMA 5) blends in relation to the ionomer content. As expected, the increase in the PA melt viscosity decreases with the ionomer content in the Whole range of shear rates investigated. This behaviour is emphasized in *Figure 9,* for the extreme shear rates $\gamma = 10$ and $10^{3}s^{-1}$, respectively. As an example, the PA melt viscosity is increased by one order of magnitude at l0 s^{-1} when blended

with 1.8 wt% P(MMA-co-NaMA 5) while the viscosity ratio is kept as low as 1.9 at 10^3 s^{-1}. It also appears from *Figure 6* that a comparable situation could be reached with a still smaller ionomer amount by substituting the Na cation by K and Ca cations, which promote more favourable ion-dipole interactions.
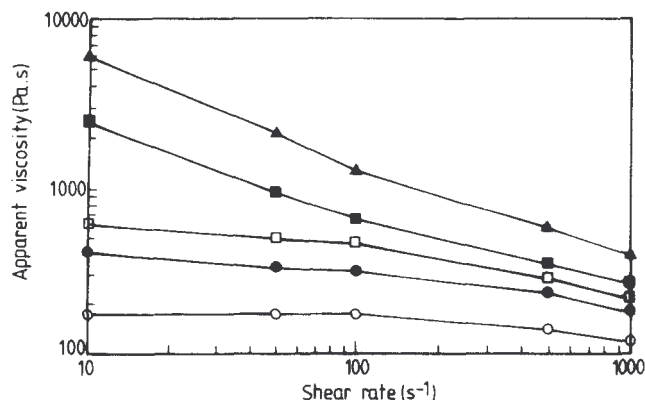

Figure 8 Shear rate dependence of the melt viscosity for PA/P(MMA-co-NaMA5) blends of various ionomer content (wt %) at 260°C (○: 0.0; ●: 0.5; □: 1.5; ■: 2.5 and ▲: 5.0)
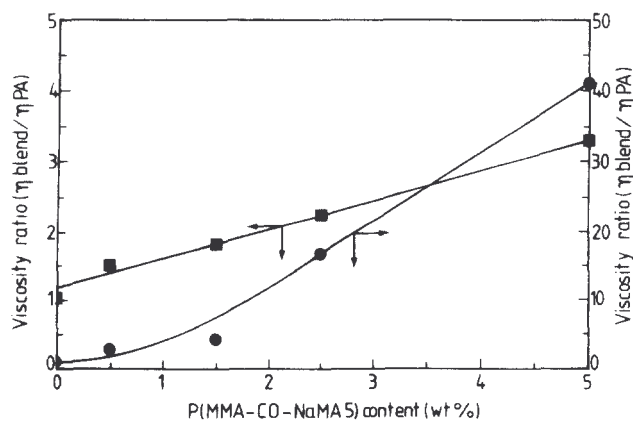

Figure 9 Composition dependence of the viscosity ratio for PA/P(MMA-co-NaMA5) blends at 260°C and two shear rates: $\gamma = 10$ s^{-1} (●) and 10^3 s^{-1} (■)

CONCLUSIONS

Blending polyamide m × D,6 (PA) with a small amount (up to 5 wt%) of suitable carboxylated ionomers is a very efficient strategy for complying the rheology of the PA matrix with the processing and moulding requirements. Copolymers of methyl methacrylate with methacrylic acid P(MMA-co-MAA) and metal methacrylates P(MMA-co-metal MA) have been melt blended with PA. At low shear rates and depending on the metal cation of the ionomer, the rheofluidity of PA at 260°C can be dramatically reduced. In the case of complete immiscibility and complete miscibility, the rheological effect of the additive is quite negligible. The best is observed in the intermediate situation when the polymer compatibility is improved to the point where a finely dispersed multiphase blend of a low interfacial tension is reached. Hydrogen bonding and long chain branching of PA amino end-groups onto carboxylic acid pendant groups of the P(MMA-co-MAA) copolymers as well as ion-dipole interactions between PA and the ionomers are at the origin of the compatibilization effect. When ionomers are considered, alkaline cations are the most effective metal cations in increasing the melt viscosity of PA. In this series, Cs promotes the more pronounced effect. Alkaline-earth cations have a comparatively small beneficial activity, while transition metal containing ionomers appear to be less efficient than the parent unneutralized copolymers. Blends exhibit a rheothinning behaviour which agrees with the slip of phase interactions at increasing shear rates. Rheological effects and trends reported in this paper are thus of a prime interest for the highly desirable control of the PA processing.

ACKNOWLEDGEMENTS

REFERENCES

1. Utracki, L. A., *Polym. Eng. Sci.,* 1983, 23, 602.
2. Utracki, L. A., *Polym. Network Blends,* 1991,1, 61.
3. Chin, H. B. and Han, C. D., *J. Rheol.,* 1979, 23, 557.
4. Chin, H. B. and Han, C. D., *J. Rheol.,* 1980, 24, 1.
5. White, J. L. and Min, K., *Makromol. Chem., Macromol. Syrup.,* 1988,16, 19.
6. Wu, S., *Polym. Eng. Sci.,* 1987, 27, 335.
7. Favis, B. D., *Makromol. Chem., Macromol. Symp.,* 1992,56, 143.
8. Zhang, Z. and Qiao, J., *Polym. Eng. Sci.,* 1991, 31, 1553.
9. Elmendorp, J. J., *Polym. Eng. Sci.,* 1986, 26, 418.
10. Kuphal, J. A., Sperling, L. H. and Robeson, L. M., *J. Appl. Polym. Sci.,* 1991,42,1525.
11. Jo, W. H., Kim, H. G. and Chae, S. H., *Polym. J.,* 1993, 2,5, 1023.
12. Ellis, T. S., *Polym. Eng. Sci.,* 1990, 30, 998.
13. Coleman, M. M., Hu, J., Serman, C. J. and Painter, P. C., *Polym. Mater. Sci. Eng.,* 1988, 59, 231.
14. US 3,373,223 (1968), Continental Can Co., Amstrong, R. G.; C.A. 68,87958 (1968).
15. JP 78,108,151 (1977), Asachi Chem. Ind., Matsuki M., Kawasaki, H. and Yoshida K.; C.A. 90,24264 (1979).
16. US 4,078,014 (1978), du Pont de Nemours, Starkweather, K.; C.A. 88,192150(1978).
17. US 4,346,194 (1982), du Pont de Nemours, Roura M.J.; C.A. 97,183489 (1982).
18. JP 57,198,748 (1982), Allied Corp.; C.A. 98,199175 (1983).
19. JP 78,101,048 (1977), Toray Ind., Chiba, K., Yamada, K. and Muraki, T.; C.A. 90,7276 (1979).
20. US 5,200,468 (1993), Hoechst Celanese Corp., Pickton, J.; C.A. 119,74513(1993).
21. US 5,209,958 (1992), du Pont de Nemours, Katsaros, J. and Mehra, V.; C.A. 119,119147 (1993).
22. Willis, J. M. and Favis, B. D., *Polym. Eng. Sci.,* 1988, 28, 1416.
23. Willis, J. M., Favis, B. D. and Lavalée, C., *J. Mater. Sci.,* 1993, 28, 1749.
24. Favis, B. D., *Polymer,* 1994, 35, 1552.
25. Weiss, R. A. and Lu, X., *Polymer,* 1994, 35, 1963.
26. M61nar, A. and Eisenberg, A., *Macromolecules,* 1992, 25, 5774.
27. Yoshikawa, K., Mö1nar, A. and Eisenberg, A., *Polym. Eng. Sci.,* 1994, 34, 1056.
28. Lu, X. and Weiss, R. A., *Macromolecules,* 1991, 24, 4381.
29. Lee, B. H., Park, J. K. and Song, H. Y., *Adv. Polym. Technol.,* 1995, 3, 75.
30. Ma, X., Sauer, J. A. and Hara, M., *Macromolecules,* 1995, 28, 3953.
31. FR 2723745 (1996), Solvay, Vankan, R., Deg6e, Ph., J6r6me, R., Teyssi6, Ph.
32. Mar6chal, Ph., Ph.D. thesis, Universit6 Catholique de Louvain (UCL), Belgium, 1993.
33. Gueskins, G., Hellenekx, E. and David, C. *Eur. Polym. J.,* 1971, 7, 561.
34. Takeda, Y., Keskkula, M. and Paul, D. R., *Polymer,* 1992, 33, 3394.
35. Chang, F. C. and Hwu, Y. C., *Polym. Eng. Sci.,* 1991,31, 1609.
36. Horrion, J., Jérôme, R., Teyssi6, Ph., Marco, C. and Williams, C. E., *Polymer,* 1988, 29, 1203.
37. Boiteux, G., Foucart, M. and Jérôme, R., *Polymer,* 1992,33,4242.