

FROM INCOMPATIBLE POLY(ARYL ETHER SULFONE)/POLYAMIDE
4.6. BLENDS TO NEW IMPACT RESISTANT ALLOYS BY A
SYNERGISTIC COMBINATION OF A BLOCK COPOLYMER
EMULSIFIER AND AN IMPACT MODIFIER.

C.E. Koning¹, R. Fayt², W. Bruls¹, L.v.d. Vondervoort¹, T. Rauch¹ and Ph. Teyssié^{2*}

¹DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands.

²Center for Education and Research on Macromolecules, University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium.

Abstract : The compatibilization and impact modification of blends of a relatively new engineering plastic polyamide 4.6 (PA 4.6) and a poly(aryl ether sulfone) (PSU) are investigated. PSU-b-PA6 block copolymers, which can be easily synthesized by ring opening polymerization of ϵ -caprolactam in the presence of a commercial PSU, were found to be very efficient emulsifiers for these incompatible blends. Small amounts (1-4%) of copolymer are sufficient to significantly reduce the particle size and to improve the tensile and impact properties. Combinations of the copolymer and an impact modifier (ethylene-propylene rubber grafted with maleic anhydride) are synergistic and high impact PSU/PA 4.6 alloys are obtained in that way.

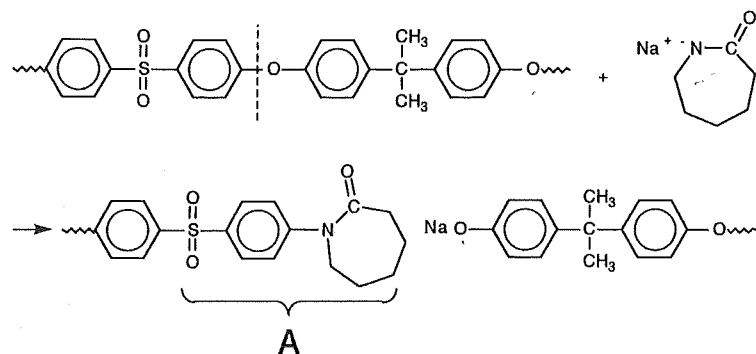
INTRODUCTION

Multiphase polymer blends based on amorphous and crystalline engineering plastics have received particular attention during these two last decades, owing to specific benefits resulting from their combinations. For instance, in poly(aryl ether sulfone)/polyamide (PSU/PA) blends in which the PA forms the continuous phase, the good processability, the good tensile properties and the good chemical resistance of PA are combined with the high glass transition temperature, the low moisture absorption and the good dimensional stability of PSU. In this work, we have studied blends of PSU and a relatively new engineering plastic polyamide 4.6 (melting point = 293°C). However, these blends are incompatible and an adequate compatibilizing agent is needed to control the particle size, interfacial adhesion and ultimate mechanical properties. In situ compatibilization chemistry by a reactive processing or the use of a preformed copolymer emulsifier are actually the two main ways to compatibilize immiscible polymer blends (Ref. 1). For the system PSU/PA6, Myers describes an anhydride endcapped PSU as an efficient reactive compatibilizer (Ref. 2). Older works have demonstrated that PSU-b-PA6 block copolymers are efficient emulsifiers for corresponding PSU/PA6 blends (Ref. 3). The compatibilizing effect of these copolymers in PSU/PA4.6 blends rich in PA4.6 (60-70%) is investigated in this work.

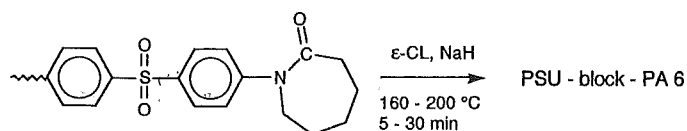
EXPERIMENTAL

The following polymers were used in this study : polyamide 4.6 Stanyl TW 300 (DSM), polysulfone Udel P1700 (Union Carbide) and an ethylene-propylene rubber grafted with maleic anhydride, EPR-MA, Exxelor VA 1803 (Exxon).

PSU-b-PA6 block copolymers (ca. 50/50 wt composition) were synthesized by ring-opening polymerization of ϵ -caprolactam in presence of PSU Udel (Ref. 3-6) : PSU was dissolved in ϵ -CLA in excess and block copolymerization occurred upon addition of NaH mainly by PSU chain scission, according to the following scheme :



Group A = activator for the anionic polymerization of ϵ -caprolactam



The crude products contain 10-30% homo-PSU (extracted by chloroform) and 10-20% "homo" PA6 (extracted by HCOOH). The PSU block length was evaluated by viscosity measurement and by GPC after complete hydrolysis of the PA6 block with hydrochloric acid. The following results were found : $[\eta]$ 25°C/CHCl₃ = 0.20-0.25 dL/g, M_{peak} (GPC, PS calibration) = 18,000-22,000. Viscosity and M_{peak} of the initial PSU Udel are 0.51 and 56,000 respectively. A treatment of pure PSU with HCl resulted in $[\eta]$ = 0.52 dL/g and M_{peak} = 56,000

All blends were compounded in a Haake twin-screw extruder at 310°C. Tensile and Izod impact tests were performed on injection molded bars, according to ISOR527 and ISOR580, respectively.

SEM of room temperature or liquid nitrogen fracture surfaces was performed on a Philips SEM 501B. Dynamic mechanical measurements were carried out on a DMA built at DSM.

RESULTS AND DISCUSSION

a) **General behavior of PSU/PA4.6 blends**

Blending polyamide 4.6 with 30% PSU results in a material displaying in particular a lower moisture absorption (25% less), a higher modulus at temperatures intermediate between the Tg's of PA4.6 and PSU (77°C and 186°C respectively) and, as a result, a HDT value 10-13°C higher than pure polyamide 4.6 (Tab. 1). Unfortunately, the high incompatibility of PSU and PA 4.6 is responsible for a coarse dispersion of the phases and a lack of interfacial adhesion, as illustrated in Fig. 1.a. Consequently, tensile and impact properties significantly lower than those of PA 4.6 are recorded (Tab. 1). Such a deleterious effect on both morphology and properties is also observed at other compositions which are not discussed in this paper.

Table 1 : Some properties of PA 4.6/PSU blends

	PA 4.6 100	PA 4.6/PSU 70/30	PA 4.6/PSU/copo 68/28/4	PSU 100
Moisture absorption(1) (%)	2.3	1.7	-	-
Heat Distortion Temperature (°C) (method A)	144	157	-	173
Izod Impact resistance (kJ.m ⁻²)	7.9	1.8	7.2	5.2
Tensile strength (MPa)	80	71	85	68
Elongation at break (%)	34	10	16	19

(1) after 24h in water at 23°C

b) **Compatibilizing effect of a PSU-b-PA 6 block copolymer**

The addition of a PSU-b-PA 6 block copolymer (53% PSU, MW_{tot} ≈ 40000) to these incompatible blends greatly alleviates that situation. Indeed, the modification of the blends by 4% copolymer results in a strong reduction of the particle size together with an improvement of the interfacial adhesion. A better interfacial adhesion is expected in view of the much higher PSU block molecular weight (M_{peak} ≈ 20,000) than the entanglement molecular weight of PSU, being ca. 2250 (Ref. 7). These features are evidenced by comparing, for instance, the SEM micrographs of fracture surfaces in Fig.

1a and 1d. It is shown that upon addition of 4% copolymer, the particle size of the 70 PA4.6/30 PSU blend is reduced by a factor of more than 10, from 5-10 μm for the pure blend to less than 1 μm for the emulsified blend. This finer dispersion results in improved mechanical properties. Results gathered in Tab. 1 show that both tensile and impact properties are significantly enhanced. The very low Izod impact resistance (1.8 $\text{kJ}\cdot\text{m}^{-2}$) recorded for the pure 70 PA4.6/30 PSU blend is raised to a value (7.2 $\text{kJ}\cdot\text{m}^{-2}$) very close to that of pure polyamide 4.6 (7.9 $\text{kJ}\cdot\text{m}^{-2}$). Furthermore, a tensile strength even higher than that of pure PA4.6 is obtained; on the other hand improvement in ductility is unexpectedly limited.

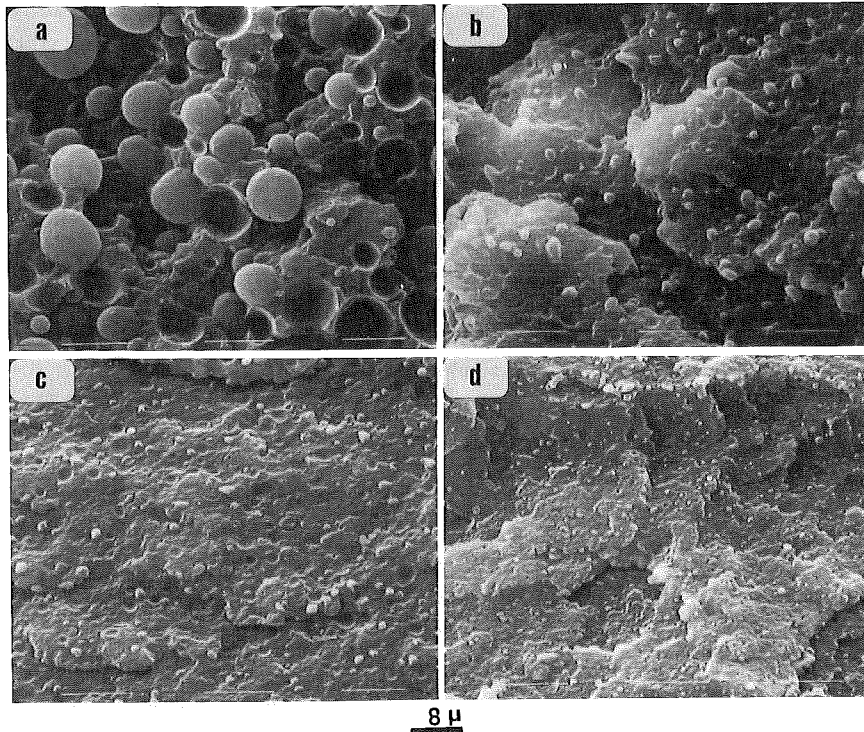


Fig. 1 : SEM of cryofracture surfaces of PA4.6/PSU blends (70/30) : (a) no copolymer, (b) 1%, (c) 2% and (d) 4% copolymer added

Morphology and mechanical properties of 70/30 blends were also evaluated as a function of the amount of copolymer added. Fig. 1a, b, c, d clearly show that the particle size gradually decreases as the amount of copolymer is increased from 1 to 4%. Considering the mechanical properties, it is noteworthy that the maximum improvement in both the strength and elongation at break is already obtained after addition of 1% copolymer only (Fig. 2 and 3). On the other hand, the Izod impact resistance continuously increases with the amount of copolymer (Fig. 4). This is also accompanied

by the gradual decrease of the particle size (see Fig. 1), and most likely by an increasing interfacial adhesion. In other words, these results indicate that for a good impact resistance, much smaller PSU particles and a much better interfacial adhesion are required than for good tensile properties, in case of this PA4.6/PSU (70/30) blend. The importance of adhesion for impact properties was already demonstrated by Campbell et al (Ref. 8) for PA6.6/PPO blends in which the PA forms the continuous phase. All these morphological and mechanical features demonstrate that PSU-b-PA6 copolymers are very efficient emulsifiers for PA4.6/PSU blends, despite the facts that the PSU block length is much lower than that of the homopolymer but still much higher than the entanglement MW of PSU, and that the PA6 block is not truly miscible with PA4.6 (Ref. 9). The latter observation suggests therefore that the emulsifying efficiency of the PA6 block results from interchange reactions with PA4.6 during the melt processing at 310°C.

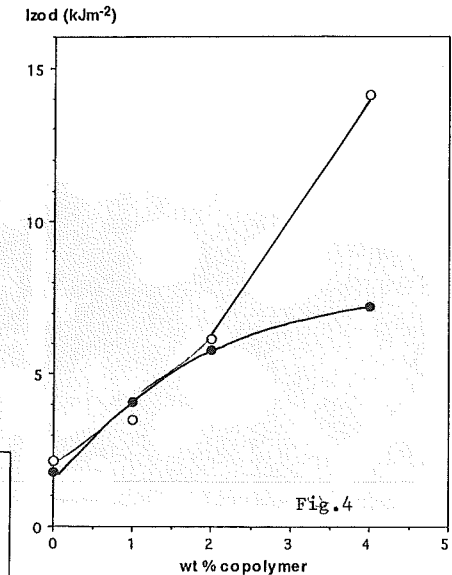
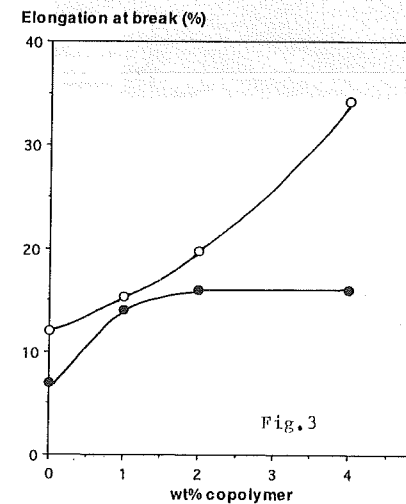
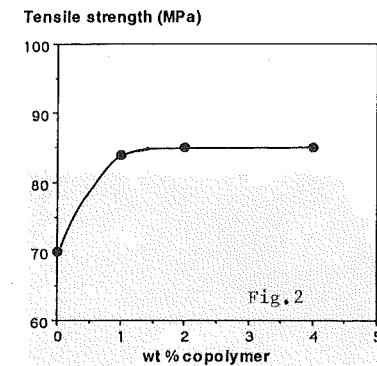


Fig. 2 : tensile strength; Fig. 3 : elongation at break, and Fig. 4 : Izod impact resistance of (●) PA4.6/PSU (70/30) and (○) PA4.6/PSU/EPR-MA (60/30/10) blends as a function of the amount of PSU-b-PA6 copolymer added

c) Effect of an impact modifier

Above results show that the compatibilization of a PA4.6/PSU (70/30) blend results in a real alloy, keeping in particular the rather high impact resistance of the PA4.6 matrix. It was also of interest to investigate the possibility of improving the toughness of this material more by introducing a specific impact modifier. Actually, polyamides are efficiently toughened by polyolefin rubbers grafted with maleic anhydride (Ref. 10). The in situ compatibilization resulting from the reaction of the anhydride groups with e.g. the amine terminal groups of polyamides promotes the dispersion and anchoring of the rubber in the polyamide matrix. By blending in the Haake twin-screw extruder PA4.6 with 10% of an ethylene-propylene rubber containing around 1% of maleic anhydride, the Izod impact resistance is increased from 7.9 to 12.5 kJ.m⁻². On the other hand, the addition of the same amount of rubber to the 70 PA4.6/30 PSU binary blend has no beneficial effect on the impact resistance : an Izod value (2.1 kJ.m⁻²) close to that of the pure blend (1.8 kJ.m⁻²) is indeed recorded. In other words, the brittleness of the incompatible PA4.6/PSU blend is not alleviated by the presence of the rubber. In addition, the SEM micrograph in Fig. 5a confirms that the presence of the rubber has no effect on the particle size nor on the interfacial situation of the blend (compare to Fig. 1a).

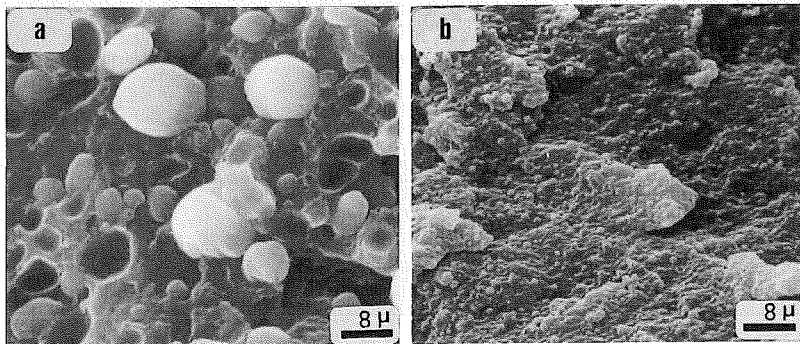


Fig. 5 : SEM of fracture surfaces of (a) PA4.6/PSU/EPR-MA (60/30/10) and (b) PA4.6/PSU/EPR-MA/copolymer (58/28/10/4)

The addition of 1 or 2% PSU-b-PA6 copolymer to the PA4.6/PSU/EPR-MA (60/30/10) ternary blend leads to a material displaying the same impact resistance as the PA4.6/PSU (70/30) binary blends similarly emulsified (Fig. 4), whereas the ductility is only moderately improved (Fig. 3). On the contrary, the addition of 4% copolymer raises both the ductility and impact resistance, the latter to values close to those of the toughened PA 4.6. Indeed, Izod impact resistance of PA4.6/EPR-MA (90/10) and of PA4.6/PSU/EPR-MA/copolymer (58/28/10/4) is 12.8 and 14 kJ.m⁻² respectively. It is noteworthy that an Izod value as high as 25 kJ.m⁻² was obtained by replacing, in the latter blend, PA 4.6 Stanyl TW300 by a more viscous grade, Stanyl KS400. That feature

is probably related to the molecular weight dependence of the ductile-brittle transition behavior of polyamide as described by Dijkstra et al. (Ref. 11) and it also demonstrates that the proper choice of the polymer grade is an important parameter for the design of high impact alloys. The above results indicate therefore that the impact modification of the PA 4.6/PSU (70/30) blend by the EPR-MA rubber is efficient only when the adequate emulsification of the PA 4.6 and PSU phases is achieved. 4% of copolymer appears to be necessary to fulfil these morphological and interfacial adhesion related requirements, in the actual case. We can therefore conclude that this copolymer/rubber combination is synergistic with respect to the binary PA 4.6/PSU blend, since nor the rubber, nor the copolymer is able to impart a so high toughness to the blend, when they are used separately. A SEM micrograph of the emulsified ternary blend is reported in Fig. 5b and shows a phase dispersion quite similar to that observed for the emulsified blend containing no rubber (Fig. 1d). Deeper examinations should be performed in order to differentiate the fine morphologies of these blends. Currently we are performing TEM examinations in order to fully elucidate the rubber position in these complicated four component systems. Finally, the storage modulus, G' of the various blends was also investigated. In Tab. 2 are gathered the values of G' at 110 and 170°C, i.e. in the region intermediate between the T_g 's of PA4.6 and PSU. As expected, the stiffness of PA4.6 is increased by blending it with PSU, whereas it is very significantly lowered by toughening it with 10% rubber. When PA4.6 is blended with both PSU (30%) and EPR-MA (10%), an intermediate value of G' is obtained at 110°C, whereas a value slightly higher than that of pure PA4.6 is recorded at 170°C. The beneficial effect of the block copolymer emulsifier is therefore obvious. It stabilizes a ternary blend displaying a rather high modulus while keeping the high impact resistance of toughened PA4.6. A better balance in terms of stiffness and toughness is therefore obtained thanks to the strong emulsifying activity of the copolymer.

Table 2 : Storage modulus values of PA 46-based blends

Blend	Storage modulus G' (MPa) 110 °C	Storage modulus G' (MPa) 170 °C
PA4.6	350	250
PA4.6/PSU (70/30)	430	390
PA4.6/EPR-MA (90/10)	190	170
PA4.6/PSU/EPR-MA (60/30/10)	300	270
PA4.6/PSU/copo (68/28/4)	450	380
PA4.6/PSU/EPR-MA/copo (58/28/10/4)	300	250

CONCLUSIONS

These results demonstrate that PSU-b-PA6 block copolymers are very efficient emulsifiers for incompatible PA4.6/PSU blends. Small amounts (1-4%) of copolymer are sufficient for controlling the particle size and interfacial adhesion and for improving the tensile and impact properties of these blends. Suitable combinations of the copolymer and a specific impact modifier for polyamides are synergistic; a higher impact PA4.6/PSU alloy exhibiting in addition a higher stiffness than a toughened PA4.6 between 80 and 180°C is obtained in that way. Such synergistic combinations are certainly of more general application. Therefore, efforts are now devoted to fully understand the morphology-properties relationship of these blends, a prerequisite to optimize their behaviour and to extend that concept to other systems.

ACKNOWLEDGMENT

The authors are very much indebted to Mrs. Palumbo for skilful technical assistance in electron microscopy.

REFERENCES

- (1) L.A. Utracki, in "Polymer Alloys and Blends" Hanser Publishers, 1989, part 2, 124.
- (2) C.L. Myers, in "SPE Conference Proceedings of ANTEC 1992", Detroit, vol.1, 1420.
- (3) J.E. McGrath, L.M. Robeson and M. Matzner, Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem. 14(2), 1032 (1972).
- (4) J.E. McGrath, and M. Matzner, US Patent 3.655.822 (1972).
- (5) M. Matzner, L.M. Robeson, R.J. Greff and J.E. McGrath, Ang. Makromol. Chem., 26, 137 (1972).
- (6) J.E. McGrath, L.M. Robeson and M. Matzner, Polym. Sci. Technol., 4, 195 (1974).
- (7) S. Wu, J. Pol. Sci., Polym. Phys. Ed., 27, 723 (1989).
- (8) J.R. Campbell, S.Y. Hobbs, T.J. Shea and V.H. Watkins, Pol. Eng. Sci., 30, 1056 (1990).
- (9) T.S. Ellis, Macromolecules, 22, 742 (1989).
- (10) R.J.M. Borggreve, R.J. Gaymans, J. Schuijjer and J.F. Ingen Housz, Polymer 28, 1489 (1987).
- (11) K. Dijkstra, "Deformation and fracture of Nylon 6/Rubber blends", Ph.D. Thesis, University of Twente, 1993.

CROSSLINKED POLYOLEFINS AS MATRICES FOR TWO-PHASE MATERIALS

Ivan Chodák, Igor Chorváth

Polymer Institute of the Slovak Academy of Sciences
842 36 Bratislava, Slovak Republic

This paper gives a review of the results of investigation of the effect of crosslinking on the properties of LDPE/PP^{a)} blends and LDPE filled with particulate silica. Tensile and impact properties, crystallization behaviour, crosslinked portion formation and crack growth rate have been investigated.

Crosslinking results in an increased compatibility of originally incompatible LDPE/PP blends apparently due to an *in situ* formation of a compatibilizer, leading to improved deformability and better impact resistance. Changes in the morphology as revealed by crystallization behaviour, and the increased number of tie molecules in amorphous region due to crosslinking result in better impact resistance of LDPE/silica mixtures, as well as to the improvement of other properties of two-phase materials, so as resistance to crack growth.

Crosslinking of polyolefins is a rather broadly used mode of modification of these polymers. Especially if polyethylene is considered, many applications of crosslinked materials have been commercialized, e.g. shrinkable products or cable insulation. The crosslinking is usually initiated by thermal decomposition of peroxides or by high energy radiation, less often by UV irradiation (Ref. 1). Crosslinking initiated by moisture introduces more complicated chemistry including a grafting of silane groups on the polyethylene chain (Ref. 1). Higher thermal resistance is the main advantage of crosslinking in all these cases. Crosslinking of poly(propylene) is much more difficult because of extensive fragmentation of macroradicals formed leading to decrease of molecular weight and inferior mechanical properties (Ref. 2). Efficient poly(propylene) crosslinking can be reached by addition of another component to initiating system. Polyfunctional monomers are the most common coagents of poly(propylene) crosslinking (Ref. 3) and the system based on addition of hydroquinone or benzoquinone was shown to be most efficient (Ref. 4).

a) LDPE: Low-density polyethylene; PP: poly(propylene).