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Compatibilizing PPE and PA6 with nitro-phthalimide derivatives

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Compatibilization of poly(2,6-dimethyl (PPE) with 1,4 phenylene-ether) PA6 has been achieved in two steps: first, (PPE) was functionalized with *N*-methyl-4-nitro-phthalimide; then, functionalized PPE was allowed to react, by melt blending, with the amine end group of PA6, giving a *trans*-imidation product. The reaction path was followed by torque measurements in a Brabender apparatus and the products characterized by infrared (i.r.) and nuclear magnetic resonance (NMR) spectroscopy. The above PPE/PA6 blends, modified with a suitable rubbery component (Kraton G), showed a remarkable Izod impact strength value, compared to the uncompatibilized mixture (170 versus 30 J m^{-1}). The maximum impact values were obtained with 1.65% functionalized PPE.

1. Introduction

The study of polymer blends and alloys is of great interest owing to the possibility of combining the main features of the different materials. A polymer blend is defined as a combination of two or more polymers resulting from processing steps, e.g. mixing the materials in the molten state, casting from a common solvent etc. For thermodynamic reasons, most polymer pairs are not miscible at a molecular level; however, several hundred miscible polymers, either in all proportions or over limited ranges, have been discovered [1–4]. Very few of them have reached commercial production, the most important one being high impact polystyrene (HIPS) /poly(2,6-dimethyl 1,4 phenylene-ether) (PPE) [5–8].

Quite often, immiscible blends show poor mechanical properties and their morphology depends strongly on the processing history, e.g. the dispersion of the components in an extruder, which, in turn, is linked to blend composition, product viscosity, melt temperature etc. The main dispersion modes are essentially

1. ribbons and lamellae (or strata),
2. rods and fibrils, and
3. droplets.

The formation of ribbons, rods or droplets of a disperse phase in a polymer mixture can be predicted on the basis of the VanOene theory [9]. Accordingly, in a binary blend, a droplet or fibril-like morphology of the dispersed phase is achieved if the deformability and the molecular weight of the dispersed phase are larger than those of the matrix. On the other hand, stratified morphology could be observed. Thus [9], dispersion depends on the deformability-elastic term, the molecular weight of the dispersed phase and the particle sizes of the starting materials.

According to Wu's research on toughened nylon and polyester [10], the dispersed drops are smaller when the interfacial tension is lower and the viscosity ratio is closer to unity. In their exhaustive study on LLDPE/HIPS blends, Plochocki *et al.* [11] found that the domain size of the dispersed phase goes through a minimum as the mixing energy is increased. The common route to overcome that problem and to lower the interfacial tension among the components is to add a proper "compatibilizing agent", usually a block or graft copolymer of suitable primary structure [12–17]. The use of a compatibilizing agent leads to a strong improvement of the mechanical properties of blends, thus rising their commercial interest. High impact polystyrene/polyethylene (HIPS/PE) blend is an example [16, 17]; in this case, the compatibilization is achieved by a proper styrene–butadiene block copolymer.

Another way for compatibilization, also extensively explored [12, 18–27], is *in situ* formation of the block or graft copolymer during blend extrusion. As an example, Triacca *et al.* [28] succeeded in compatibilization of ABS and nylon 6 by adding poly(styrene-co-maleic anhydride) (SMA), miscible with SAN phase but also able to react with the nylon 6 amine end groups.

Nylon has recently attracted the interest of researchers due to its peculiar features: it holds both basic (amine) and acid (carboxyl) groups; it is ductile, but exhibits a sharp tough–brittle transition at a critical particle size, the rubber content and rubber–matrix adhesion being constant [10, 27, 29, 30]. From an appreciative point of view, nylon holds good chemical resistance, due to its crystallinity; but, on the other hand, it has high water absorption and a low heat distortion temperature, due to its rather low T_g. These deficiencies can be partially overcome by blending nylon with PPE: PPE has a high T_g (214 °C), low water absorption and is ductile, with a shear yielding deformation mechanism. On the other hand, PPE has poor solvent resistance and difficult processability: for this last reason, PPE is usually blended with HIPS. In summary, the minuses of nylon can be balanced by the pluses of PPE and vice versa.

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In order to obtain a blend of practical interest, there is a need for both compatibilizer and an impact modifier. The latter must be properly chosen, owing to the high processing temperatures needed and, as well known, saturated block-copolymers are the best choice.

A typical sketch of nylon 6/PPE blend consists of a nylon 6 continuous phase and a PPE dispersed phase in order to achieve good chemical resistance (Fig. 1). The impact modifier is usually found in the PPE phase, but it could also be put in the nylon 6 phase or in both.

All these topics have been extensively studied by many researchers, mainly from the General Electric Co. [31–36].

1.1. PPE/PA compatibilization

As mentioned above, the compatibilization of the two matrices is the key point and many solutions have been proposed, e.g.

1. maleic anhydride,
2. fumaric and citric acid,
3. trimellitic anhydride, and
4. styrene-maleic anhydride copolymers.

In the case of maleic anhydride, usually PPE is functionalized first and then the polymer chains, bearing the carboxylic or anhydride groups, are allowed to react with the amine moiety of nylon molecules, forming an *in situ* compatibilizer: a scheme of the reaction has been outlined in Fig. 2. However, the actual path occurring in the extruder is very complicated and a precise description, i.e. where and by what mechanism maleic anhydride is linked to the PPE unit, has not yet been published. Furthermore, limited information is available about the optimum ratios of the various reactants and the conditions of the reaction.

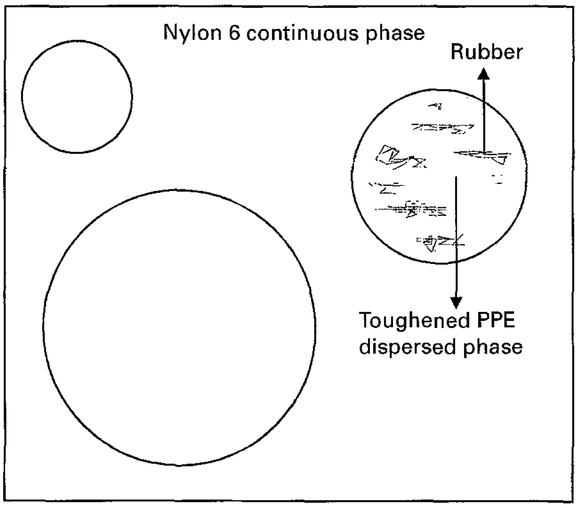


Figure 1 Sketch of PPE/PA6 blend.

Another very efficient way of compatibilization can be achieved by introducing a functional group in the PPE chain, reactive with nylon, such as carboxylic or anhydride groups. Trimellitic anhydride chloride particularly has been used as a compatibilizing agent, because it can react with the terminal hydroxylic groups of PPE, forming ester bonds [34].

In the laboratory the authors have recently studied the problem of compatibilization between PPE and nylon, and, in order to simplify the problem, have first functionalized PPE with nitrophthalimide derivatives, which are able to react, in a further step, with the terminal amino groups of nylon. PPE functionalization has been obtained by nucleophilic substitution

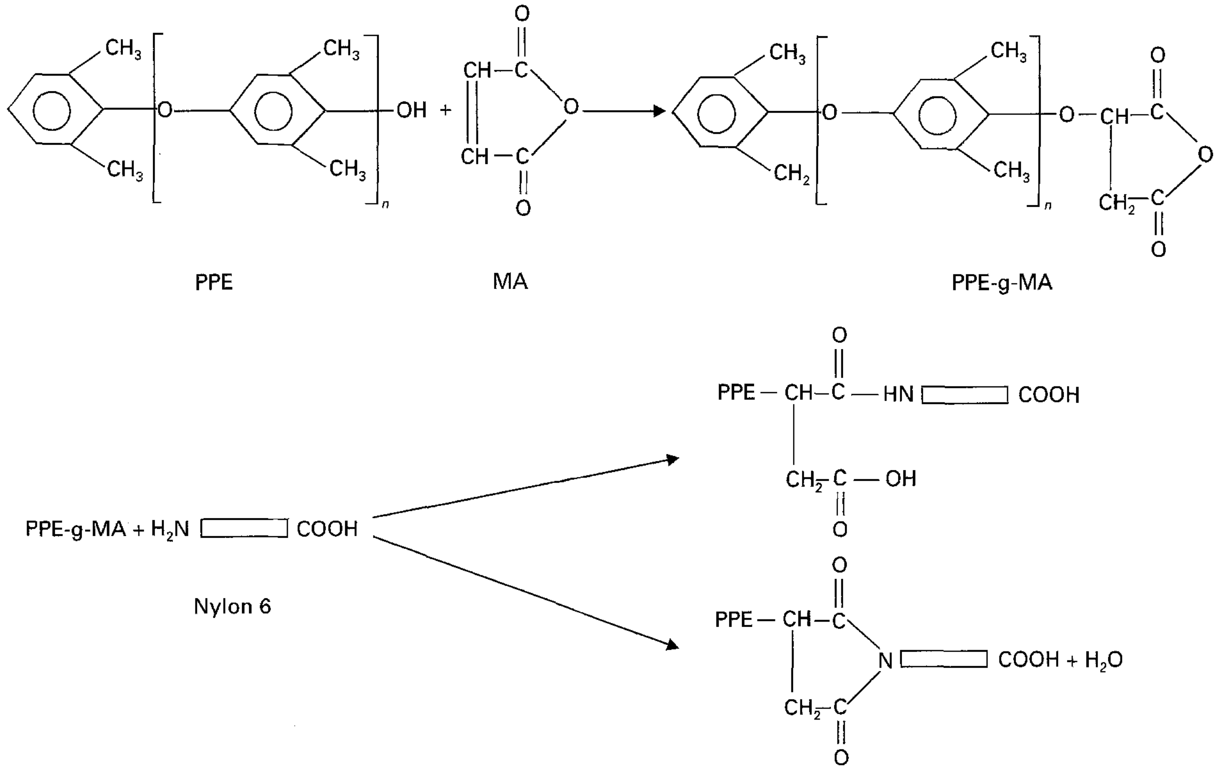
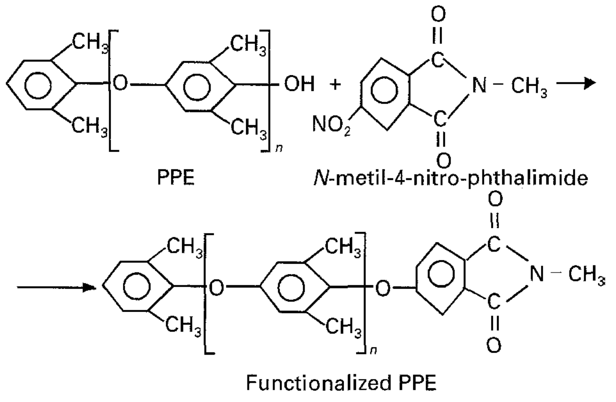


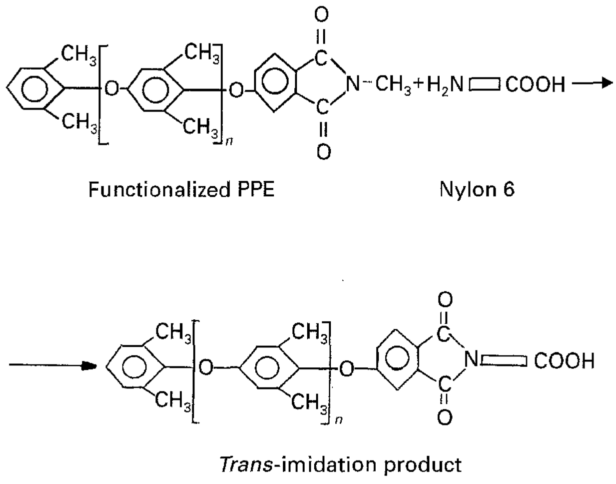
Figure 2 Scheme of the reaction.

of the nitrophenil derivative of *N*-methyl-4-nitrophthalimide on the hydroxyl end groups of the polymer. This is the scheme of the reaction



The functional end group is linked to the polymer with etherbonds, as clearly shown by spectral analysis. The ethereal bond formed is much more stable towards hydrolysis than an ester one.

During melt blending with nylon 6, the imide group can react with the terminal amine groups, leading to a *trans*-imidation reaction, according to the following suggested scheme



Also the imidic bond so formed is stable under the processing conditions.

2. Experimental procedure

2.1. Materials

Both poly(phenylene ether) (PPE) (experimental sample; intrinsic viscosity of 0, 53 dl g^{-1} in chloroform, 23 °C), and nylon 6 (Ternyl B 27: molecular weight, M_w, 18 000) were supplied by Enichem. Pertinent information about the impact modifiers used is summarized in Table I.

TABLE I Impact modifiers used in this study

Type	Structure	ST (%)	Source	Material
Kraton G 1701	Diblock	37	Shell	SEP
Kraton G 1702	Diblock	28	Shell	SEP
Kraton G 1651	Triblock	32	Shell	SEBS
Kraton G 1652	Triblock	29	Shell	SEBS

N-methyl-4-nitro-phthalimide was prepared as reported in the literature [37–40].

2.2. Synthesis of the functionalized polymer

The functionalized PPE was prepared as follows. A mixture of PPE sodium salt (400 g), dry dimethylsulphoxide (DMSO) [21] and *N*-methyl-4-nitrophthalimide (30 g; 0.15 mol) were refluxed for 5 h under stirring. The solution was then poured into methanol [21], and the polymer filtered off and purified twice by precipitation. After drying under vacuum, 375 g (yield 93.7% by weight) of functionalized polymer was collected, and then analysed by ^{1}H-NMR, ^{13}C-NMR and i.r. spectroscopy. The NMR spectra were acquired on a Bruker AC 300 spectrometer. The sample was dissolved in deuterochloroform and tetramethylsilane (TMS) was used as a reference. The following typical absorption band or chemical shifts were recorded

i.r. $\nu = 1717$ cm (C = O)
^{1}H-NMR $\delta = 3.1$ p.p.m. (s) (Fig. 3)
^{13}C-NMR $\delta = 151.3$ p.p.m. (Fig. 4)

By NMR analysis, a functionalization degree of 33% by weight was estimated.

2.3. Blending techniques

The blends were prepared in two steps: first 30 parts of rubber were incorporated in PPE + PPE-N-CH_3-phthalimide (70 parts, premixed), then PA6 was added. All the samples were mixed in a Brabender Plasticorder, model PLE 651, with a 300 cm^3 cell, recording the torque versus processing time at a fixed temperature (240 °C) and speed (100 r.p.m.) The blends were ground to a very fine form, and compression moulding specimens were obtained with a PHI machine (model 90). Immediately after moulding, the samples were introduced into a sealed plastic bag or a desiccator, in order to avoid moisture sorption. These samples were tested dry as-moulded.

The Izod impact strength and Vicat temperatures were determined according to ASTM D 256 and ASTM D 1525 methods, respectively. Transmission electron microscopy (TEM) analysis of the samples was carried out with (Philips TEM EM 301 model), by staining with osmium tetroxide and ultramicrotoming [41]. Differential scanning calorimetry (DSC) analysis was performed under nitrogen using a Perkin Elmer DSC type 7 instrument (rate temperature: 20 °C min^{-1}).

3. Results and discussion

3.1. Torque measurements

All the samples were prepared in the Brabender apparatus, recording the torque after mixing for 3 min.

Rheological changes can be used, to a certain extent, to detect whether a chemical reaction is occurring [42]; in this study, torque measurements are an interesting way of testing the formation *in situ* of graft copolymers, e.g. PPE-g-PA6.

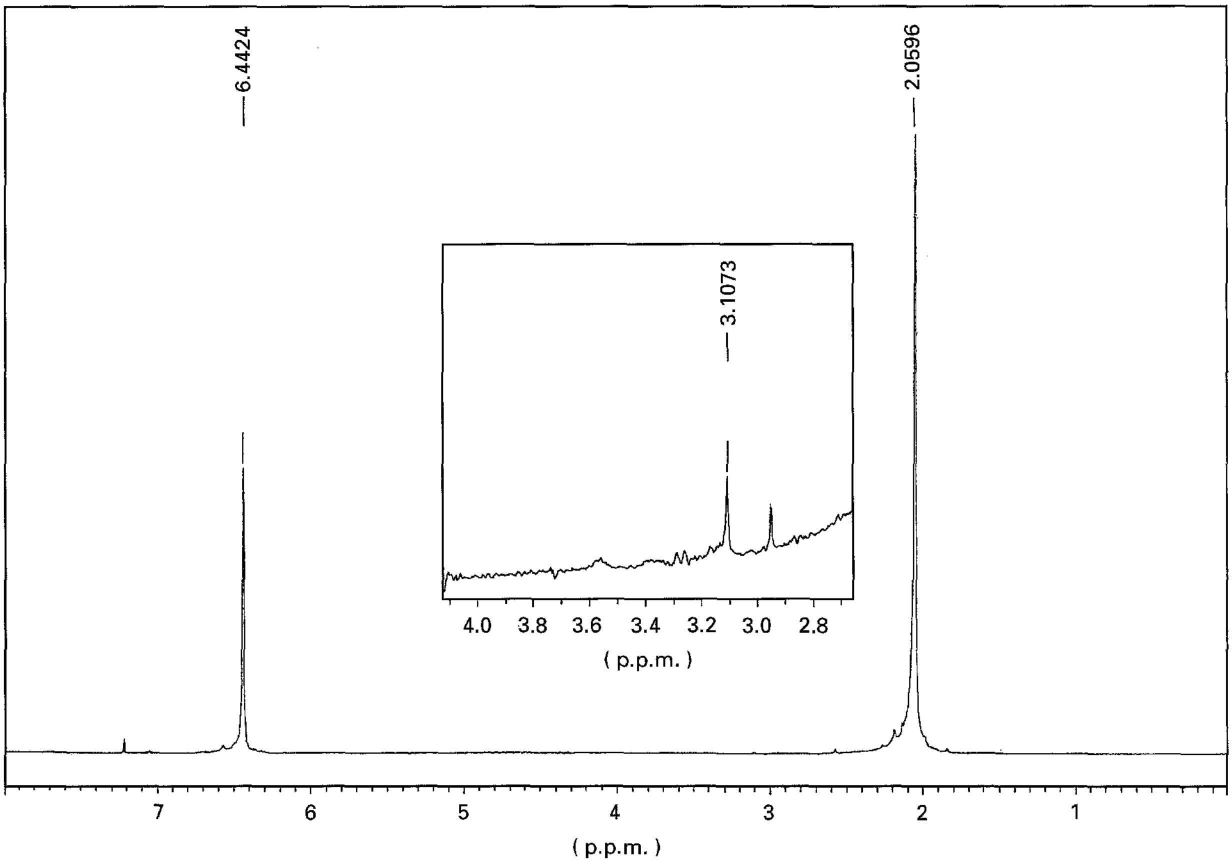


Figure 3 ^{1}H-NMR spectra of N-CH_3-phthalimide-PPE.

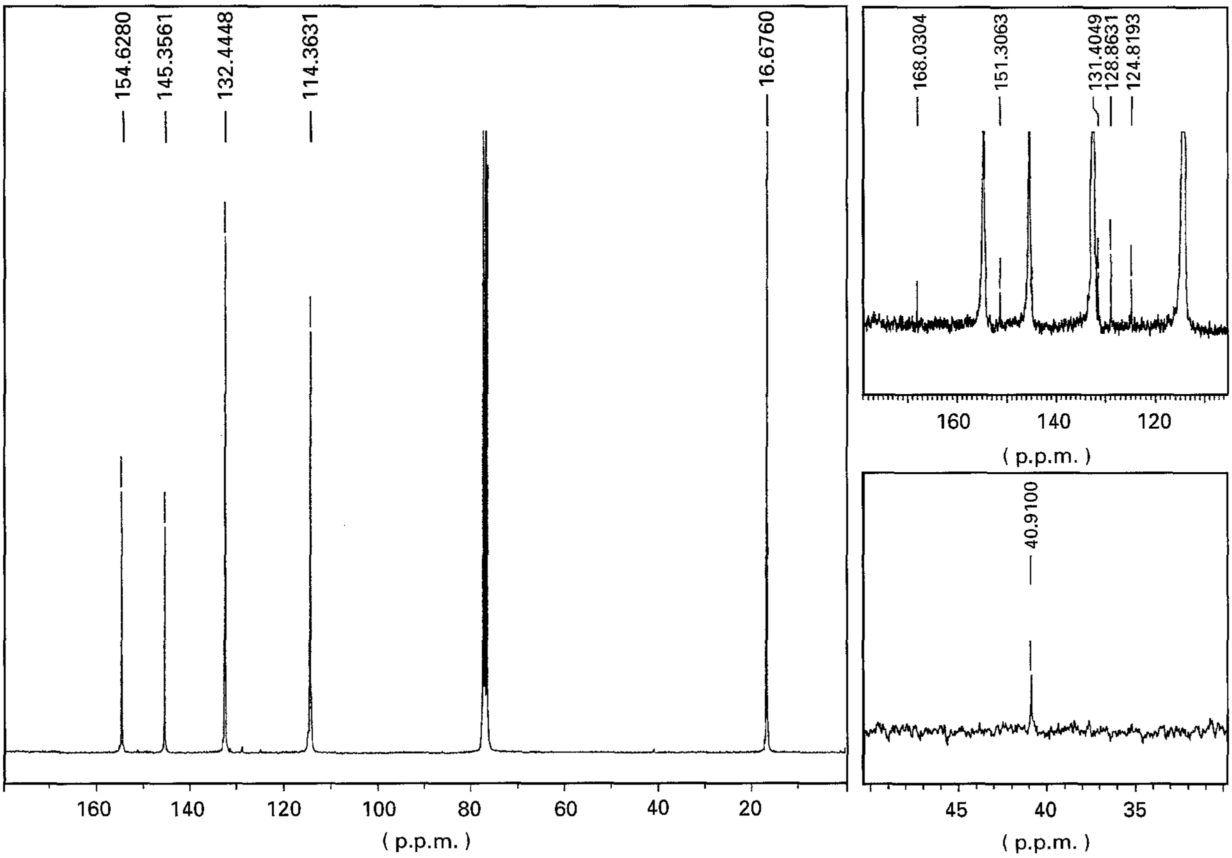


Figure 4 ^{13}C-NMR spectra of N-CH_3-phthalimide-PPE.

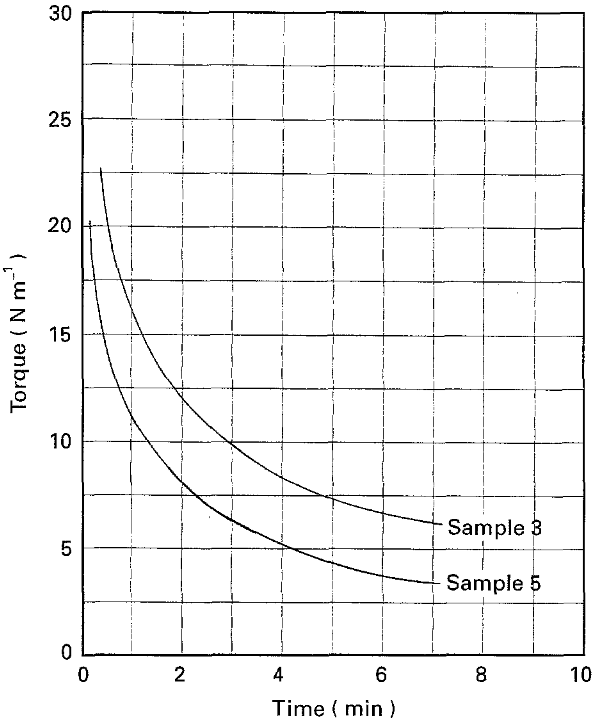


Figure 5 Torque–time evaluation at 240 °C 100 r.p.m.

TABLE II Blends

Sample	1	2	3	4	5
Ternyl B 27, %	41.0	41.0	41.0	41.0	41
Kraton G 1651, %	10.0	–	–	–	–
Kraton G 1652, %	–	10.0	–	–	–
Kraton G 1701, %	–	–	10.0	–	10
Kraton G 1702, %	–	–	–	10.0	–
PPE-N-CH_3-phthalimide, %	0.2	0.2	0.2	0.2	–
PPE, %	48.8	48.8	48.8	48.8	49
Izod, J m^{-1}	70	80	120	95	20

In extruding PPE/PA6 blends, the viscosity and therefore the torque value is very high in the feeding stage at the beginning of mastication. When plastification is over, a plateau is reached; for longer processing times the torque values tend to decrease smoothly, owing to slow polymer degradation.

Fig. 5 shows a Brabender torque experiment for two blends (samples 5 and 3, Table II). The behaviour of sample 5 (blend without compatibilizer) has been taken as the "*reference*", and its profile as the baseline for the following sample 3, where a small amount of compatibilizer (0.2%) has been introduced. The torque–time plot of sample 3 is always higher than that of sample 5, suggesting that reaction between functionalized PPE and PA6 chain ends is occurring in the melt. The reaction is rather fast at 240 °C; similar torque–time plots have been observed at different temperatures (220–260 °C); the highest plot being obtained at the lowest temperature (220 °C) (15 N m^{-1} after 3 min mastication) and the lowest plot at 260 °C (4 N m^{-1} after 3 min mastication). The decrease of the mastication speed (from 100 to 80 r.p.m.) shows a similar torque–time plot, with slightly lower torque values (8 N m^{-1} after 3 min mastication), Fig. 6.

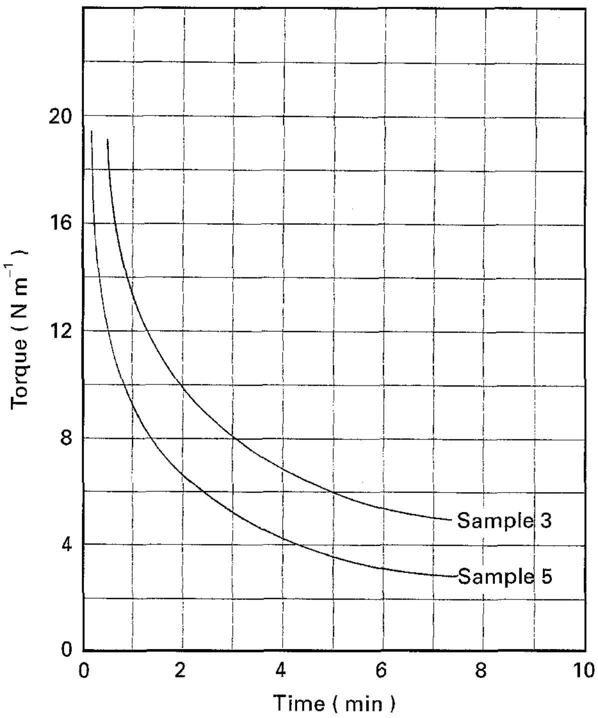


Figure 6 Torque–time evaluation at 240 °C 80 r.p.m.

TABLE III Blends

	6	7	8	9	10
PPE-N-CH_3-phthalimide, %	0.8	1.65	5	10	23
PPE, %	48.2	47.35	44	39	26
Kraton G 1701, %	10.0	10.00	10	10	10
Ternyl B 27, %	41.0	41.00	41	41	41
Izod 3.2 mm, J m^{-1}	130	170	150	110	30
Vicat 1 kg, °C	200	201	204	208	209
Vicat 5 kg, °C	177	178	180	182	185

Different amounts (0.8–23%) of functionalized PPE have been charged, with the same PA6 and impact modifier (Kraton G 1701) levels (41 and 10%, respectively, see Table III). The torque value (at 100 r.p.m. and 240 °C) has been recorded from 0 to 5% of functionalized PPE in the blend; it increases steadily within the range (Fig. 7). Again, the torque of the blend without functionalized PPE has been taken as the reference.

3.2. Concentration of the compatibilizer

The levels of PA6 and the impact modifier (Kraton G 1701) were fixed at 41 and 10%, respectively. Different amounts of functionalized PPE were tested, extruding at 240 °C and 100 r.p.m. (see Table III for the main mechanical and thermal properties of the blends).

Izod impact strength raises suddenly by adding 0.2% functionalized PPE from 20 to 120 J m^{-1} (see Fig. 8), and still increases with compatibilizer content, up to a maximum of 170 J m^{-1} with 1.65% functionalized PPE. Further amounts of compatibilizer do not improve further the mechanical property and some degradation occurs, as suggested by the colour shift to dark, for amounts of compatibilizer higher than 1.65%.

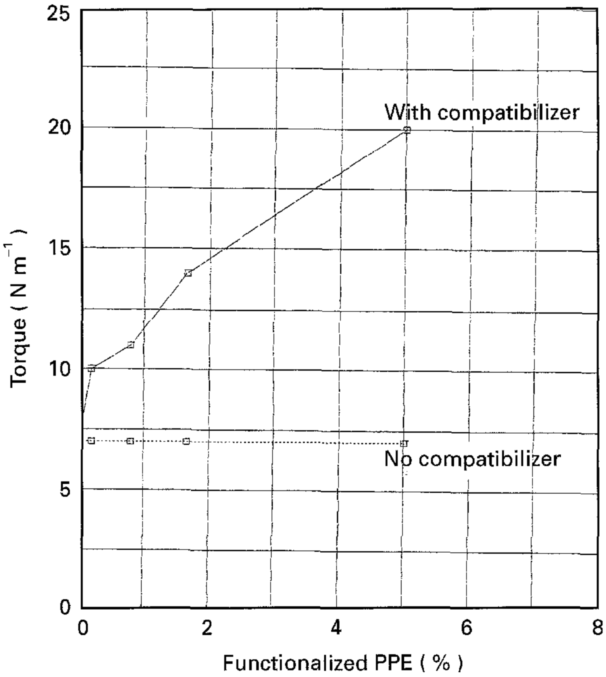


Figure 7 PPE/PA6 compatibilization (nylon 6, 41%, Kraton G 1701, 10%).

The Vicat softening point slightly increases by adding more compatibilizer, but further experiments are needed to explain this result.

3.3. Structure of the impact modifier

Four grades of saturated impact modifiers were tested (see Table I for the structures) at the same level (10%). Miscibility of the styrenic block of Kraton G with PPE phase is complete over the whole composition when M_w is higher than 10 000–12 000 [43]. In fact, the T_g of the blend falls between the T_gs of the PS block and PPE, in good agreement with Fox's equation. For M_w lower than 10 000, two T_gs can be observed, corresponding to PS and PPE phases, each one shifted towards the T_gs of the pure materials (100 and 214 °C, respectively).

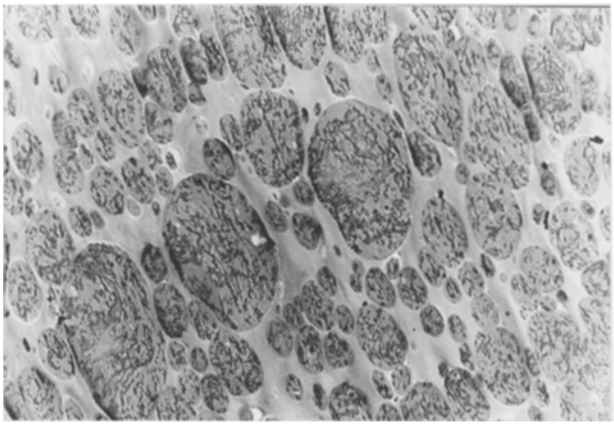


Figure 9

The DSC analysis has been carried out on premixed PPE/rubber 70/30 blends, concerning the preparation of samples 1 and 2. Two T_gs have been detected in the premixed blend concerning sample 2 at 127 °C (PS rich phase) and 209 °C (PPE rich phase), in good agreement with Tucker *et al.*'s studies [43] regarding SEBS copolymers with PS blocks of low M_w (7500). The premixed blend concerning sample 1, where SEBS copolymer was introduced at high M_w (29 000) showed, on the other hand, a single hardphase T_g (204 °C).

The PS blocks of Kraton G seem, therefore, not completely miscibile with the PPE phase, probably owing to the rather low M_w.

The best toughening efficiency has been obtained by using SEP copolymers, as suggested by patents.

Izod impact strength reaches 120 J m^{-1} with 10% Kraton G 1701; Kraton G 1702 is less efficient, in spite of the higher EP content (72%).

The dispersion of Kraton G rubber in the PPE phase is very good, as shown in Fig. 9 (TEM at 11 250).

The boundary between PPE and PA6 (continuous phase) is sharp and adhesion is good, owing to the graft PPE-g-PA6 formed *in situ* during the extrusion.

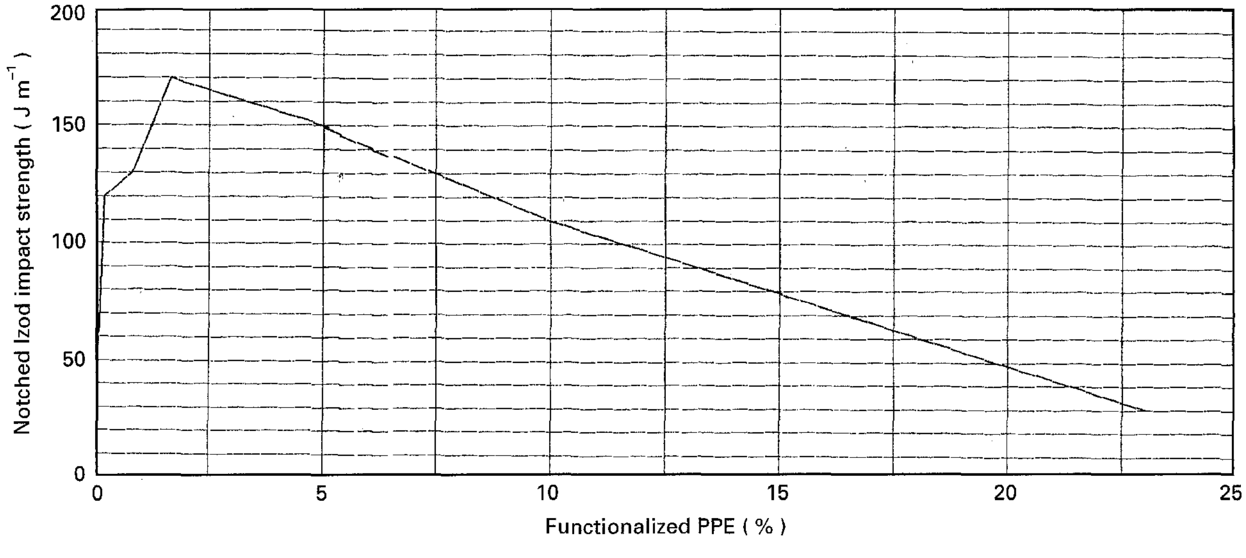


Figure 8 PPE/PA6 compatibilization (nylon 6, 41%, Kraton G 1701, 10%).

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References

1. S. KRAUSE, *J. Macromol. Sci. Rev. Macromol. Chem.* **C7** (1972) 251.
2. A. RUDIN, *ibid.* **C19** (1980) 267.
3. H. J. KARAM, in "Polymer Compatibility and Incompatibility", edited by K. Sole (Harwood Academic, New York, 1982).
4. T. SHIOMI, F. E. KARASZ and W. J. MacKNIGHT, *Macromol.* **19** (1986) 2274.
5. A. F. YEE, *Polym. Engng Sci.* **17** (1977) 213.
6. S. NAKASCHIO, US Patent 3 658 945 (1972).
7. G. LEE, *ibid.* 4 239 673 (1980).
8. A. KATCHMAN, *ibid.* 4 128 602 (1978).
9. H. VANOENE, *J. Colloid and Interface Sci.* **40** (1972) 448.
10. S. WU, *Polym. Engng Sci.* **27** (1987) 335.
11. A. P. PLOCHOCKI, S. S. DAGLI and R. D. ANDREWS, *ibid.* **30** (1990) 741.
12. D. R. PAUL, in "Polymer Blends", edited by D. R. Paul and S. Newman (Academic Press, New York, 1978) Ch. 12.
13. *Idem*, in "Thermoplastic Elastomers: a Comprehensive Review", edited by N. R. Legge, G. Holden and H. E. Schroeder (Hanser, Munich, 1987) Ch. 12, section 6.
14. R. JEROME, R. FAYT and P. TEYSSIE, in "Thermoplastic Elastomers: a Comprehensive Review", edited by N. R. Legge, G. Holden and H. E. Schroeder (Hanser, Munich, 1987), Ch. 12, section 7.
15. S. D. SJOERDSMA, A. C. A. M. BLEIJENBERG and D. HEIKENS, *Polymer* **22** (1981) 619.
16. R. FAYT, R. JEROME and P. TEYSSIE, *ACS Symp. Ser.* **395** (1989) 38.
17. P. TEYSSIE, *Macromol. Chem., Macromol. Symp.* **22** (1988) 83.
18. M. XANTHOS, *Polym. Engng Sci.* **28** (1988) 1392.
19. M. RATZSCH, *Macromol. Chem., Macromol. Symp.* **12** (1987) 165.
20. M. LAMBLA, R. X. YU and S. LOREK, *ACS Symp. Ser.* **395** (1989) 67.
21. R. E. BAKER and M. SALEEM, *Polymer* **28** (1987) 2057.
22. D. V. HOWE and M. D. WOLKOWICZ, *Polym. Engng Sci.* **27** (1987) 1582.
23. S. Y. HOBBS and M. E. J. DEKKERS, *J. Mater. Sci.* **24** (1989) 1316.
24. R. J. M. BORGGREVE, R. J. GAYMANS and H. M. EICHENWALD, *Polymer* **30** (1989) 78.
25. R. J. M. BORGGREVE and R. J. GAYMANS, *ibid.* **30** (1989) 63.
26. A. MARGOLINA and S. WU, *ibid.* **29** (1988) 2170.
27. S. WU, *ibid.* **26** (1985) 1855.
28. V. J. TRIACCA, S. ZIAEE, J. W. BARLOW, H. KESKKULA and D. R. PAUL, *ibid.* **32** (1991) 1401.
29. S. WU, *J. Polym. Sci., Polym. Phys. Ed.* **21** (1983) 699.
30. R. J. M. BORGGREVE, R. J. GAYMANS, J. SCHIJER and J. F. INGEN HOUSZ, *Polymer* **28** (1987) 1489.
31. T. S. GRANT, European Patent Application 226 910 (1985).
32. G. LEE, PCT WO 87/05 311 (1986).
33. V. ABOLINS, US Patent 4 269 950 (1980).
34. G. F. LEE, J. M. H. HENSCHEN and R. VAN DER MEER, PCT WO 05 311 (1987).
35. M. MAWATARI, T. ITOH, S. TSUCHIKAWA and S. KIMURA, European Patent 244 090 (1987).
36. S. VEDA, H. HARADA and K. YOSHIDA, Japanese Patent 62 151 456 (1987).
37. F. J. WILLIAMS and P. E. DONAHUE, *J. Org. Chem.* **43** (1978) 1608.
38. R. L. MARKEZICH, US Patent 4 020 089 (1977).
39. N. C. COOK and G. C. DAVIS, *ibid.* 3 933 852 (1976).
40. *Idem, ibid.* 4 005 102 (1977).
41. K. KATO, *Polym. Engng Sci.* **7** (1967) 38.
42. D. GHIDONI, G. C. FASULO, D. CECCHELE, M. MERLOTTI, G. STERZI and R. NOCCI, *J. Mater. Sci.* **28** (1993) 4119.
43. P. S. TUCKER, J. W. BARLOW and D. R. PAUL, *Macromol.* **21** (1988) 2794.

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