

Compatibilization of a Polyolefin Blend through Covalent and Ionic Coupling of Grafted Polypropylene and Polyethylene. I. Rheological, Thermal, and Mechanical Properties

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ABSTRACT: A polypropylene/high-density polyethylene blend containing 70 wt % polypropylene was prepared and compatibilized via the addition of maleic anhydride grafted polypropylene and polyethylene. The functionalized polymer chains were coupled with two types of coupling agents. Dodecane diamine formed covalent bonds with the maleic anhydride, whereas two metallic salts, zinc acetate and sodium hydrogenocarbonate, formed ionic interactions with the carboxylic functions produced by the hydration of the

anhydride cycle. The coupling of the grafted polyolefin chains was successfully realized by a single operation in a twin-screw extruder. The coupling agents were efficient in improving the elongation at break and impact properties of the studied blends. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 312–320, 2005

Key words: blends; compatibilization; polyolefins

INTRODUCTION

Polypropylene (PP) and polyethylene (PE) are the most consumed of all polymers. For this reason, the question of their recycling is interesting. Generally, two main problems are encountered during the recycling of polymers. First, the multiple reprocessing of a material that is not virgin can cause its degradation. Furthermore, the fact that the polymers have usually been polluted during their use or have been subjected to aging makes the situation even worse. However, these difficulties may be overcome, to a certain extent, with antioxidants or stabilizers. Second, polymeric materials are more and more often made of several polymers to match the desired properties. Examples are encountered in the packaging industry, in which multilayer sheets and bottles are produced. These very efficient materials considerably complicate recycling. In such complex structures, the separation of the polymers is usually simply impossible, and one must think of recycling them as blends.

PP/PE blends have been studied for a long time and not only for recycling. When PP is the major component, there is a commercial interest in improving its fracture toughness at low temperature, and some authors have investigated a solution that consists of adding a component with a low glass-transition temperature to PP. Rubbers are obviously good candidates, but PE can also be used.^{1,2}

Like other immiscible polymer blends, PP/PE blends present mechanical properties generally inferior to those predicted by a simple additivity relation. Furthermore, the mechanical properties at a high deformation are more sensitive to the immiscibility of the system than those at a low deformation.^{3,4} Because of the semicrystalline nature of polyolefins, the crystallinity of the phases, the thermal history, and the processing conditions greatly influence the resulting blend properties. For these reasons, the properties of PP/PE blends are not easily predicted or reproduced.

However, some blends may have unexpected and interesting properties for certain compositions or certain types of components. For instance, the impact toughness of PP/high-density polyethylene (HDPE) blends is higher than that calculated by the additivity relation for the whole range of compositions,^{5,6} and it is improved by a smaller size of the dispersed phase.

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TABLE I
Characteristics of the Polymers

	Reference	M_n (g/mol)	M_w (g/mol)	PI	Grafting degree (wt %)	Fraction of grafted chains (%)
PE	HDPE B55-20	Blow-extrusion grade			—	—
PP	PP HS 200	Injection grade			—	—
PEg	PEgMA XA255	19,600	93,100	3.1	0.18	36
PPg	PPgMA XA 258	35,700	109,500	4.7	0.08	29

M_n = number-average molecular weight; M_w = weight-average molecular weight; PI = polydispersity index.

The PP/linear low-density PE blend presents unusual properties linked to the partial miscibility of its components.⁷ The special properties of some blends may also be explained by anchoring points at the interface in relation to the specific architecture of the polymer chains used.⁸ These unexpected properties often result from morphology or crystallization effects.

To overcome these difficulties, authors have described different compatibilization schemes in the literature. The addition of a preformed copolymer is a typical example. The copolymers used are statistical or block copolymers based on ethylene and propylene, and they generally present a rubbery character. As a result, if the impact toughness is actually improved, it is unfavorable for the modulus, which decreases because of the presence of a soft phase in the blend and because of the perturbed crystallinity of the components.^{9,10} The use of a PE-PP block copolymer limits the rigidity loss.¹¹ Adding such a copolymer at a 15% concentration to PP/HDPE blends multiplies by 3 the stress at break and by 2 the deformation at break without any modulus decrease.

The copolymer may also be formed *in situ*. If a peroxide is added in the molten state, the viscosity of PP decreases because of β scission, whereas PE becomes more viscous as the recombination of macroradicals causes branching or even crosslinking. The rise of the viscosity ratio should normally lead to a coarsening of the structure, but actually a fine morphology is maintained by the crosslinking of the PE particles.¹² In addition, a small proportion of the copolymer may be formed at the interface. Its presence may counterbalance the negative effect of the viscosity ratio.¹³

One must keep in mind that this type of compatibilization has a great influence on the organization of the macromolecules, that is, on the crystallinity, which is often different from that of the pure polymers.

The different ways of compatibilizing PP/PE blends allow us to improve a specific property but often damage some other property. In addition, the control of the processing parameters appears to be a critical issue.

The aim of this work is to propose an alternative to the use of a peroxide for polyolefin-blend recycling. The proposed solution should ameliorate the proper-

ties of the blend (the quality and stability of the morphology and the mechanical properties).

For this reason, in PP/PE blends, small amounts of maleic anhydride grafted PE and PP (PEg and PPg, respectively) were added along with a chain coupling agent [covalent coupling: dodecane diamine ($C_{12}N_2$); ionic coupling: zinc acetate (ZnAc) and sodium hydrogenocarbonate (NaHy)]. In this way, copolymers were expected to be synthesized *in situ* at the interface and to act as compatibilizers.

Moreover, the processing method, reactive extrusion, being realizable in one step, should be easily performed on an industrial scale with nontoxic additives. The effects of coupling on the rheological and thermal properties of the blends were first analyzed. The compatibilization effects on the mechanical properties were then compared.

EXPERIMENTAL

Materials

Pure PE and PP and PEg and PPg were supplied by Solvay. Their characteristics are summarized in Table I.

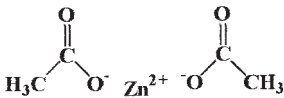
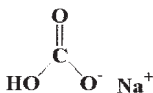
Three coupling agents were selected: $C_{12}N_2$ and two metallic salts, ZnAc and NaHy. All the reactants were purchased from Aldrich (France) and were used without further purification (Table II). These molecules reacted very quickly with the maleic anhydride functions of the grafted polyolefins, and so they were adapted for use in an extruder.¹⁴

Preparation and composition of the blends

The blends were prepared by twin-screw extrusion. The twin-screw extruder was a Clextral (France) BC21 instrument with a length/diameter ratio of 36 and a screw diameter of 25 mm. The screw configuration and temperature profile are given in Figure 1. The experimental conditions were as follows: screw speed = 150 rpm and throughput rate = 3 kg/h.

A dry blend of the polymer components was conveyed by a gravimetric feeder to the first zone of the extruder. The coupling agents were injected in section 5, just after the first kneading zone. The ionic coupling agents were dissolved in water, whereas the diamine

TABLE II
Characteristics of the Reactants

Name (abbreviation)	Formula	Properties
1, 12-Diaminododécane (C ₁₂ N ₂)	$\text{H}_2\text{N}-(\text{CH}_2)_{12}\text{NH}_2$	MW = 200 g/mol $T_m \approx 70^\circ\text{C}$ $T_b > 280^\circ\text{C}$
Zinc acetate (ZnAc)		MW = 220 g/mol Solubility in water at 20°C = 430 g/L
Sodium hydrogenocarbogenate (NaHy)		MW = 84 g/mol Solubility in water at 20°C = 100 g/L

MW = molecular weight; T_m = melting temperature; T_b = boiling point.

was dissolved in toluene before its injection. The injection zone was sealed. The excess of reactants and the solvents were degassed in section 8, either with a vacuum pump or by the venting zone being left open. The extruder was equipped with a 4-mm-diameter capillary die. The extrudate was pulled out through a water bath, dried, and granulated.

We always studied blends composed of 70 wt % PP/PPg and 30 wt % PE/PEg so that the global compositions of the blends would be fixed.

Two type of blends were prepared:

- Binary blends: PP/PE and PPg/PEg (70/30).
- Quaternary blends: PP/PPg(*a*)/PE/PEg(*b*), with 10–50% of the total weight being grafted polyolefins.

a and *b* are the proportions of grafted PP and PE, respectively.

The blends were prepared with or without a coupling agent. In this study, the blends with a coupling agent added are called compatibilized blends.

The stoichiometric ratio (*x*) is defined as the number of amine functions per anhydride function. For in-

stance, the PP/PPg(35)/PE/PEg(25)/2C₁₂N₂ blend contained the diamine coupling agent with a stoichiometry of 2 with respect to the anhydride functions.

For the metallic salts, *x* is the number of moles of cations per mole of carboxylic acid. For instance, *x* = 1 corresponds to one Zn²⁺ for one carboxylate. In this case, the system is not at electronic neutrality.

Rheological measurements

The molten viscosity of the components was measured by dynamic viscosimetry with a Rheometrics (New Castle, Delaware) RDA2 rheometer, with parallel-plate geometry with 25-mm-diameter plates. The temperature was set at 200°C.

Thermal properties

Differential scanning calorimetry measurements were carried out with a Mettler (Columbus, Ohio) TA300 instrument operated at a 10°C/min heating rate. Samples of about 10 mg were used for these experiments. Two consecutive temperature scans were run from 20 to 230°C. The melting temperature and enthalpy were

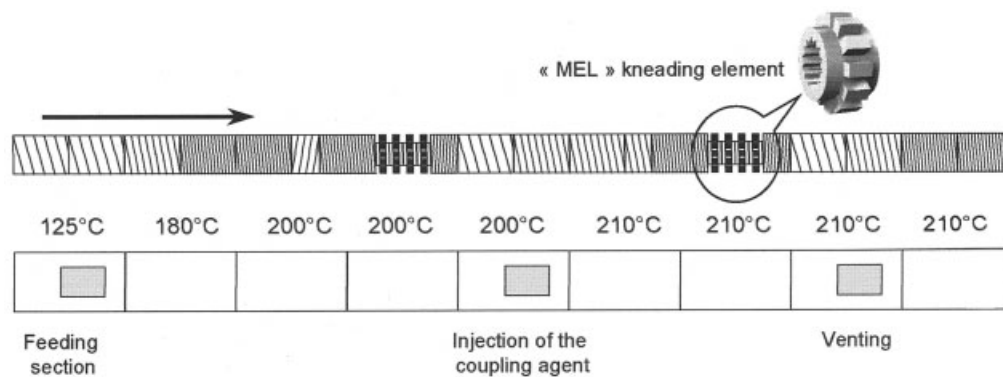


Figure 1 Screw configuration and temperature profile.

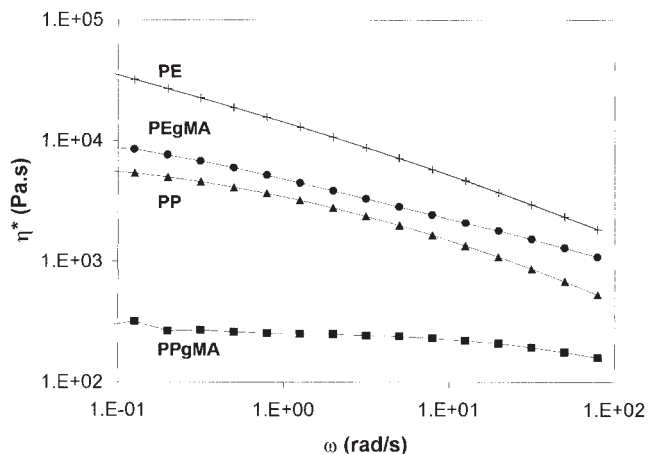


Figure 2 Complex viscosity (η^*) of the pure polymers at 200°C (ω = frequency).

measured during the second scan. The melting temperature was taken at the onset of the endotherm. The degree of crystallinity was calculated as the ratio of the enthalpy of melting of the polymer over the enthalpy of melting of a theoretically 100% crystalline polymer (ΔH_∞). ΔH_∞ was taken to be 293 and 209 J/g for PE and PP, respectively.¹⁵

Mechanical properties

The stress-strain properties were tested at 25°C on a J.J. Loyd (Southampton, UK) M30K tensile tester equipped with a Laserscan laser extensometer. The test specimens were prepared by injection molding in the form of microtensile test specimens according to the ISO 60 standard.

To characterize the impact resistance of the blends, we performed a multiaxial impact test on injected disk

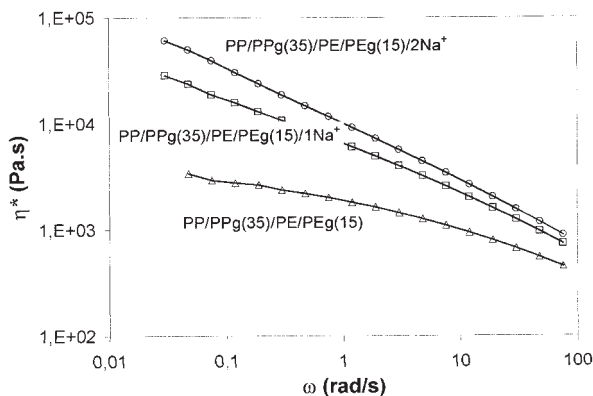


Figure 4 Effect of the stoichiometry ratio of NaHy on the complex viscosity (η^*) of the PP/PPg(35)/PE/PEg(15) quaternary blend (temperature = 200°C; ω = frequency).

specimens (diameter = 60 mm, thickness = 2 mm). The temperature was 23°C. The average data were calculated from five measurements.

The tensile tests were run on a Zwick (Ulm, Germany) servohydraulic machine at 1 m/s at room temperature.

RESULTS AND DISCUSSIONS

Rheological properties

The viscosity of the pure polymers is plotted in Figure 2. PP, which is the matrix of the studied blend, is always less viscous than the PE dispersed phase.

The effect of the coupling was first studied through rheological measurements under the same experimental conditions used for the pure polymers. The results presented here concern a binary blend, PPg(70)/PEg(30), and a quaternary blend, PP/PPg(35)/PE/

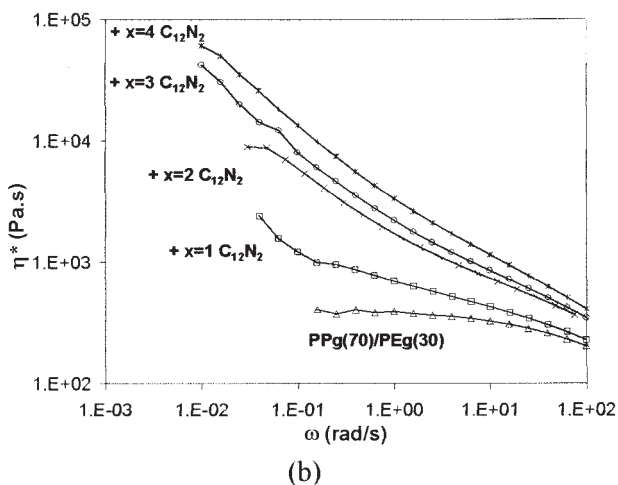
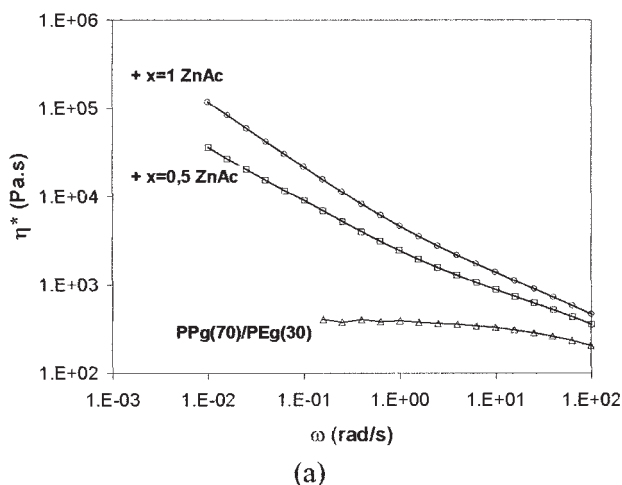


Figure 3 Effect of the stoichiometry ratio of the coupling agent on the complex viscosity (η^*) of the PPg(70)/PEg(30) binary blends coupled with (a) ZnAC and (b) C₁₂N₂ (temperature = 200°C; ω = frequency).

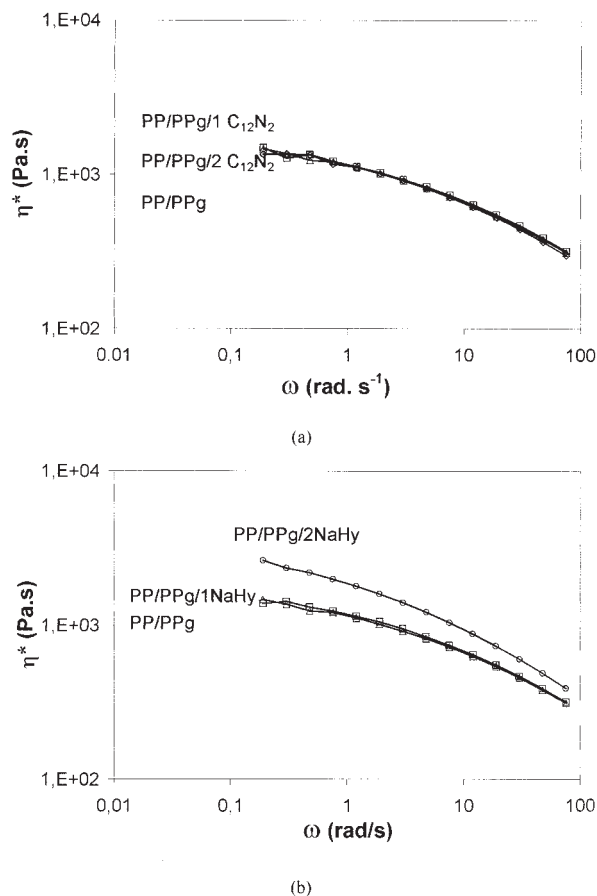


Figure 5 Effect of the coupling agent on the complex viscosity (η^*) of the PP/PPg(50) blend coupled with (a) $C_{12}N_2$ and (b) NaHy. This blend is the matrix of the PP/PPg(35)/PE/PEg(15) blend (ω = frequency).

PEg(15), with variable proportions of the two coupling agents [Figs. 3(a,b) and 4]. Whatever the type of coupling, the viscosity of the compatibilized blend increases over that of the noncompatibilized one, especially at low frequencies. Because the quaternary blend contains fewer functional chains, the viscosity rise is lower. These observations may be attributed to the presence of an *in situ* formed copolymer at the interface. The other hypothesis, which can lead to an equivalent qualitative evolution of the viscosity, is the formation of high-molecular-weight branched chains inside the PE- or PP-rich phase. The extent of the

viscosity rise may help to decide which explanation is most likely to be the right one. To determine this, we have measured the viscosity of a PP/PPg(50) blend corresponding to the composition of the matrix of the quaternary blend. The PP/PPg blend was extruded without a coupling agent and with $C_{12}N_2$ and NaHy in variable proportions [Fig. 5(a,b)]. The coupling is inexistent in the case of the diamine and very low with the sodium salt. Moreover, we have measured a viscosity increase of a factor of 15 for PEG alone with a stoichiometry of $x = 1$ in ZnAc.¹⁴ Because the composition of the PP/PPg blend is identical to the matrix of the quaternary PP/PPg(35)/PE/PEg(15) blend, the viscosity data may be compared. The viscosity rise of the quaternary blend with $x = 2$ NaHy is more than one order of magnitude at 0.01 rad s^{-1} (Fig. 4) and is not due to the modification of the matrix alone because the coupling effect on the matrix is much lower. This amplification when PPg is blended with PEG may perhaps be attributed to a predominant reaction at the interface rather than inside the phases.

To clarify the situation, we determined the insoluble fraction of the material with an extraction technique. The blends were extracted into a Kumagawa device, and the solvent was xylene. The noncompatibilized blends were totally and rapidly dissolved after only a few extraction cycles. As for the compatibilized blends, the material started to swell, and then the dissolution was very slow. The high swelling of some of the blends rendered extraction impossible. This was the case for the PPg(70)/PEg(30)/ $3C_{12}N_2$ blend. The theoretical insoluble fraction was calculated under the assumption that the grafted chains had the same molecular weight distribution as the nongrafted one and that every grafted polymer chain reacted. The measured insoluble fraction and the calculated fraction are in good agreement and are proportional to the percentage of the grafted polymer present into the blend. This would be expected if every functionalized chain had reacted and had become insoluble (Table III). These observations indicate that we actually have a coupling reaction between the amine and anhydride functions and the formation of insoluble molecules, as is the case for PEG alone.¹⁴ However, the extraction does not allow us to identify the nature of the coupled molecules. These molecules may be PPg and PEG that

TABLE III
Measured and Theoretical Insoluble Fractions of the Blends with Diamine Coupling

Blend	Insoluble fraction (insoluble mass/total mass)	Estimated theoretical insoluble fraction
PPg(70)/PEg(30)/ $3C_{12}N_2$	Impossible to measure	31%
PP/PPg(35)/PE/PEg(25)/ $2C_{12}N_2$	14%	15%
PP/PPg(17.5)/PE/PEg(7.5)/ $2C_{12}N_2$	6%	8%
PP/PPg(7)/PE/PEg(3)/ $2C_{12}N_2$	<1%	2%

TABLE IV
Melting Temperature (T_m) and Crystallinity of the Compatibilized and Noncompatibilized PPg/PEg Blends ($\Delta H_\infty = 209$ J/g for PP; $\Delta H_\infty = 293$ J/g for PE)

	PPg phase		PEg phase	
	T_m (°C)	Degree of crystallinity (%)	T_m (°C)	Degree of crystallinity (%)
PPg(70)/PEg(30)	151	35	119	31
PPg(70)/PEg(30)/0.5ZnAc	151	29	118	42
PPg(70)/PEg(30)/1ZnAc	152	27	118	48
PPg(70)/PEg(30)/0.5C ₁₂ N ₂	151	34	119	35
PPg(70)/PEg(30)/2C ₁₂ N ₂	152	31	119	37
PEg			121	59
PEg/2AcZn			118	53
PEg/2C ₁₂ N ₂			119	46

have reacted together at the interface, but they may also be PPg and PEg that have reacted individually into their respective phases.

Thermal properties of the blends

The thermal properties of the blends were determined only for the binary blends. PP/PE blends are very complex from the point of view of crystallization. There exist at least two crystalline phases and two amorphous phases. Even if it can be shown that no cocrystallization exists in PP/HDPE,¹⁶ the literature reports that the crystallinity of each phase in a mixture is different from that of the pure polymer taken separately.¹⁷

The presence of PE in PP involves a reduction of the size of the spherulites of PP. This effect is perhaps related to the role of nucleating agent played by the chains of PE.¹⁸ In addition, the thermal properties of each phase are influenced by the composition of the blend and by the cooling process adopted. The two phases crystallize neither at the same temperature nor at the same speed.¹⁹ For instance, when a peroxide is used to compatibilize a blend, in general, a reduction of the heat of melting is observed. The thickness of the lamellae and the crystallinity of each phase decrease because of the presence of crosslinking points acting as structural inhomogeneities.^{20,21}

The general trend observed for our system is the following: although the melting temperatures are not modified by the compatibilization of the blend, the crystallinity of the PPg phase decreases and the crystallinity of the PEg phase increases. The effect is more pronounced for ionic coupling. The results for some of the blends are shown in Table IV. Surprisingly, the pure PEg did not show the same trend. Its crystallinity actually decreased and its melting point decreased in the presence of the two types of coupling agents.

This could be evidence of the presence of copolymer chains in the PPg-rich phase that modify the crystalline arrangement. The coupling concerns not only the

interface but also the PPg phase. Even if the *in situ* coupling can only occur at the interface, some of the prepared copolymer does not stay at the interface and acts as a compatibilizer but goes into the PPg phase.

Although rheological and thermal characterization and extraction allow us to conclude about the efficiency of the coupling reaction, it is not possible to assert whether the coupling occurs at the interface or into the phases. We may hypothesize that both processes exist in a proportion that depends on the partial solubility of the chemical reagents in the PE and PP phases and on their ability to diffuse toward the interface.

Mechanical properties of the blends

Generally, the mechanical properties of PP/PE blends present a negative deviation from a simple additivity law. The evolution of a mechanical property according to the composition goes through a minimal value. This has been noted for the properties at a low deformation, but this negative effect is even more important for the ultimate tensile properties and the impact resistance.^{16,17,22} The properties at a high deformation, being more sensitive to the incompatibility of the system, thus represent significant parameters for study.

The nature of the coupling agent has an effect on the impact resistance of the binary blend (Fig. 6). Although NaHy increases the fracture energy of a blend in comparison with that of a noncompatibilized one, the diamine reduces it.

The analysis of the binary compatibilized blend provides information about the effects of the coupling agent on the mechanical properties of the material. However, this study was performed for recycling, and the idea was to compatibilize a PP/PE blend through the addition of a low proportion of grafted polyolefins and a coupling agent. Hence, it is interesting to consider the case of a quaternary blend (Fig. 7). No significant differences can be noted in the fracture energy data. This indicates that if the presence of the grafted olefins and the existence of

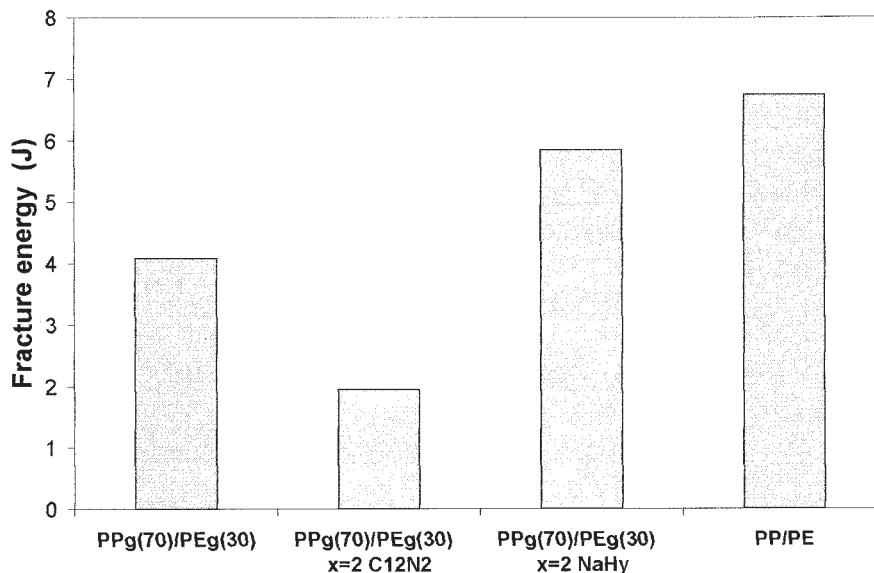


Figure 6 Effect of the covalent or ionic compatibilization on the fracture energy of PPg(70)/PEg(30) blends.

coupling reactions are not favorable for the impact resistance of the materials, they do not degrade it either.

A more positive effect of the coupling has been observed on the elongation at break (Figs. 8 and 9). The coupling considerably ameliorates the properties. With the diamine, very good results were obtained at low concentrations of grafted polyolefins (10 and 25%). With NaHy, 25–50% of the grafted chains were added to obtain better properties.

CONCLUSIONS

The process developed in this study to produce a compatibilized PP/PE blend is a simple, single-step

reactive-extrusion process. The used coupling agents are easily injected into the extruder and dissolved either in a small quantity of toluene for the amines or in water for the metallic salts.

For the compatibilized blends, the high reactivity of the coupling agents allows us to ensure chain coupling into the twin-screw extruder. The effects of the coupling reactions have been observed because of the rheological measurements, the extraction of the insoluble fraction, and the mechanical properties. From these data, we can conclude that the PPg and PEG macromolecules react. Nevertheless, it is difficult to establish whether PPg reacts with PEG, forming a copolymer, or if the two polymers react in their respec-

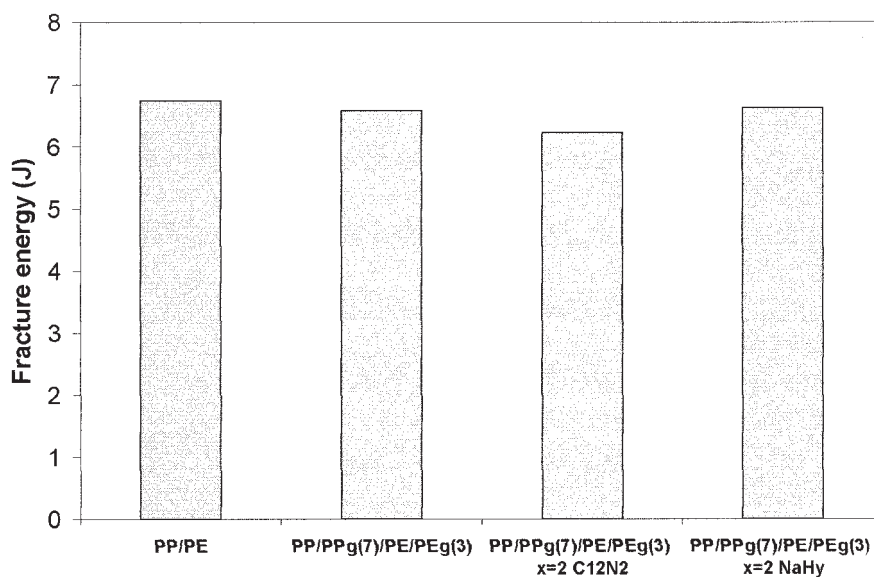


Figure 7 Effect of the covalent or ionic compatibilization on the fracture energy of the PP/PPg(7)/PE/PEg(3) blends.

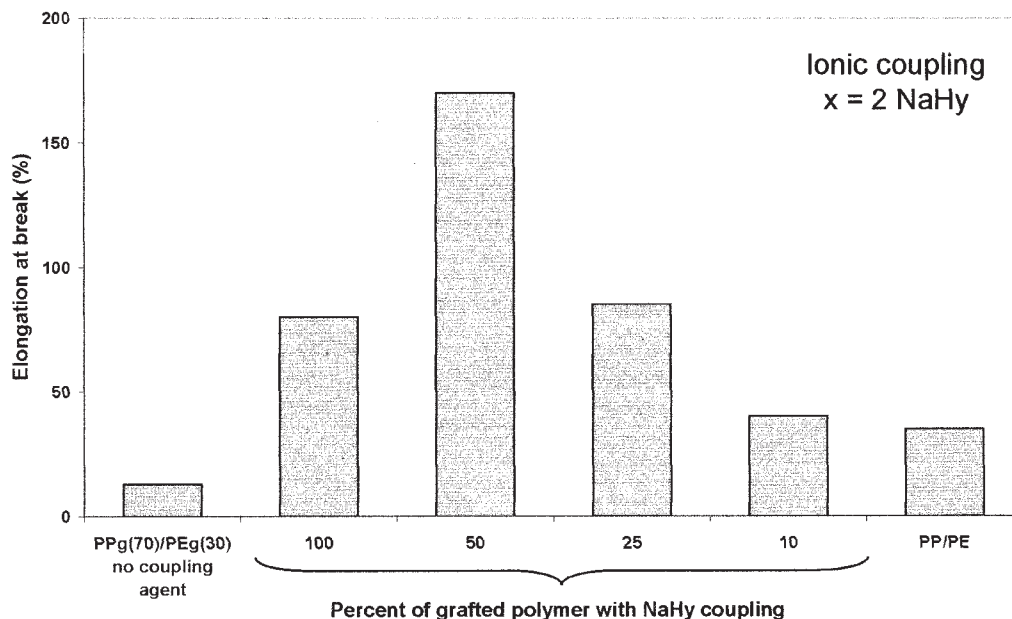


Figure 8 Effect of the proportion of grafted polyolefins on the elongation at break of PP/PPg/PE/PEg coupled with NaHy.

tive phases, this leading to an increase in the molecular weight and, therefore, the viscosity.

Even if the mode of reaction of the coupling agents is not clear, despite the low functionality of the used PPg and PEg, their effects on the morphology, its stability, and the mechanical properties, especially the elongation at break, are significant. The metallic salts have proved to be very efficient for improving the impact strength of the blends. The diamine is better only for obtaining good values of the elongation at break.

One of the objectives of this study was to test a large set of compositions to optimize the formulation, the aim, of course, being to add as low a quantity of the grafted polymer as possible. However, if the mechanical properties are the criteria, a higher proportion of the grafted polymer is needed (30%). The compatibilization effect on the morphological evolution of these blends is the subject of the next article in this series.

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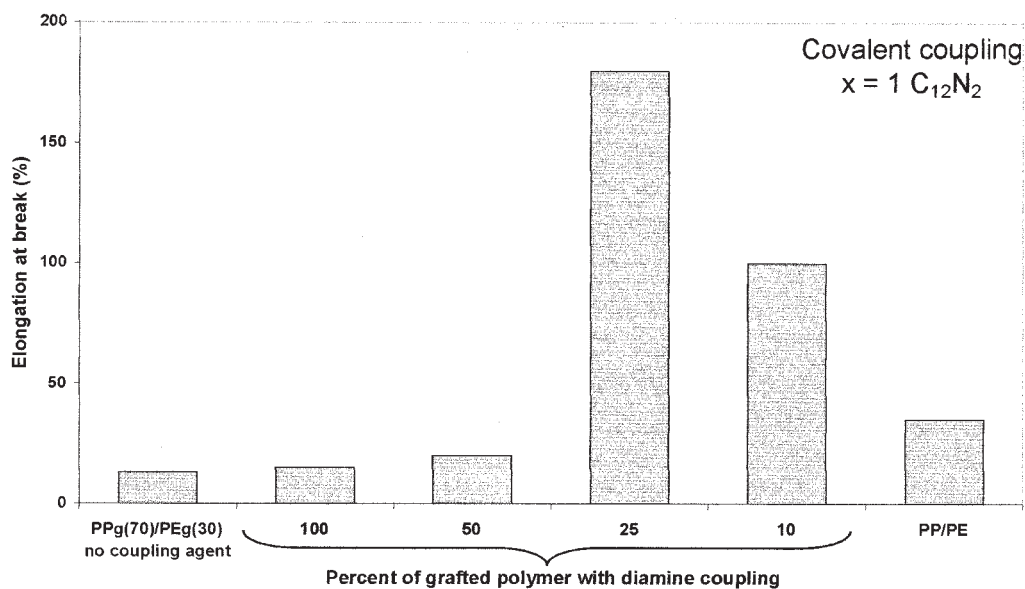


Figure 9 Effect of the proportion of grafted polyolefins on the elongation at break of PP/PPg/PE/PEg coupled with $C_{12}N_2$.

References

1. Utracki, L. *Commercial Polymer Blends*; Chapman & Hall: London, 1998.
2. Teh, J.; Rudin, A.; Keung, J. *Adv Polym Technol* 1994, 13, 1.
3. Greco, R.; Mucciariello, G.; Ragosta, G. *J Mater Sci* 1980, 15, 845.
4. Zhou, X.; Hay, J. *Polymer* 1993, 34, 4710.
5. Schürmann, B.; Niebergall, U.; Severin, N. *Polymer* 1998, 39, 5283.
6. Niebergall, U.; Bohse, J.; Seider, S. *Polym Eng Sci* 1999, 39, 1109.
7. Dumoulin, M.; Farba, C. H.; Utracki, L. *Polym Eng Sci* 1984, 24, 1319.
8. Chaffin, K.; Bates, F.; Brant, P. *J Polym Sci Part B: Polym Phys* 2000, 38, 108.
9. Petrovic, Z.; Budinski-Simendic, J.; Divjakovic, V. *J Appl Polym Sci* 1996, 59, 301.
10. Blom, H.; Teh, J.; Rudin, A. *J Appl Polym Sci* 1996, 60, 1405.
11. Zhu, W.; Zhang, X.; Huang, B. *J Appl Polym Sci* 1995, 58, 515.
12. Yu, D.; Xanthos, M.; Gogos, C. *Polym Mater Eng* 1992, 67, 313.
13. Do, I.; Yoon, L.; Kim, B. *Eur Polym J* 1996, 32, 1387.
14. Colbeaux, A. *Doctoral Thesis, Institut des Sciences Appliquées de Lyon*, 2001.
15. Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley-Interscience: New York, 1989.
16. Greco, R.; Mucciariello, G.; Ragosta, G. *J Mater Sci* 1980, 15, 845.
17. Zhou, X.; Hay, J. *Polymer* 1993, 34, 4710.
18. Schürmann, B.; Niebergall, U.; Severin, N. *Polymer* 1998, 39, 5283.
19. Blom, H.; Teh, J.; Rudin, A. *J Appl Polym Sci* 1995, 58, 995.
20. Chodak, I.; Repin, H.; Bruls, W. *Macromol Symp* 1996, 112, 159.
21. Chodak, I.; Janigova, I.; Romanov, A. *Makromol Chem* 1991, 192, 2791.
22. Hetteema, R.; Van Tol, J.; Janssen, L. P. B. M. *Polym Eng Sci* 1999, 39, 1628.