# Compatibilization of a Polyolefin Blend Through Covalent and Ionic Coupling of Grafted Polypropylene and Polyethylene. II. Morphology

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**ABSTRACT:** The morphology of a polypropylene/polyethylene (PP/PE) blend and a maleic anhydride modified PP and PE (PPg/PEg) blend was studied. The initial morphology, at the extruder die, after the melt blending into a twin-screw extruder, was first characterized. Then, the evolution of this initial morphology was followed after a injection molding operation, and during annealing in an oven at 200°C. The influence of the compatibilization of the blend by coupling reactions through covalent (with 1,12-diaminododécane) and ionic reactions (with zinc acetate and sodium hydrogenocarbonate) was also investigated. At the extruder die, the viscosity ratio proved to be a determinant factor governing the dispersed phase diameter of the droplets, and as a second factor, the addition of small amounts of coupling-agents together with (PPg/PEg) to (PP/PE) resulted in a decrease of the diameter of the droplets. The injection molding of these initial blends resulted in important coalescence and in an elongation of the dispersed phase. This was observed for the non compatibilized and also for some of the compatibilized blends. The ionic coupling showed a good stabilization of the morphology. Finally, the morphology of the non compatibilized blends was found to be instable when the material was annealed at 200°C. The average size of the dispersed phase increased. The coupling reactions delayed the occurrence of the coalescence about 5 min and limited its effects. The extent of the coarsening depended strongly on the composition of the blend and on the nature of the coupling. Still, the ionic agents appeared more effective. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2237–2244, 2004

**Key words:** blends; morphology; coalescence; polyolefins; coupling

## INTRODUCTION

In a permanent regime, the morphology of a nonmiscible polymer blend results from an equilibrium between breakup and coalescence of the dispersed phase. This equilibrium is established within a few minutes in an internal mixer[1–6] or just after the first restrictive area in a twin-screw extruder.[7–11]

The diameter of the dispersed phase in a nonmiscible polymer blend is minimum when the matrix to the dispersed phase viscosity ratio is close to 1, the interfacial tension is low, and the shear rate high.[12–18] When a polymer blend is extruded or injection molded, it is submitted to high shear rate and orientation effects; then it is rapidly quenched so that the resulting morphology is out of equilibrium.[7–10,19–21]

Immiscible polymer blends compatibilization generally consists in the addition, or the *in situ* synthesis, of multiphasic copolymers containing one phase miscible with one of the blend constituents, while another phase is miscible with the other blend constituent. A fraction of this copolymer is located at the blend interface and increases the interfacial cohesion, or decreases the interfacial tension. Such compatibilization is expected to enhance the mechanical properties of the blend, to reduce the dimensions of the dispersed phase and stabilize the morphology.[10,11,22–32]

In the first part of this study, small amounts of maleic anhydride grafted PP and PE were added to PP/PE blends together with a chain coupling-agent (covalent coupling: dodecane diamine; ionic coupling: zinc acetate and sodium bicarbonate). In this way, copolymers were *in situ* synthesized with the aim of acting as compatibilizers and coupling of the chains occurred. The effect of coupling on the rheological, thermal, and mechanical properties of the blend have been analyzed.[33,34]

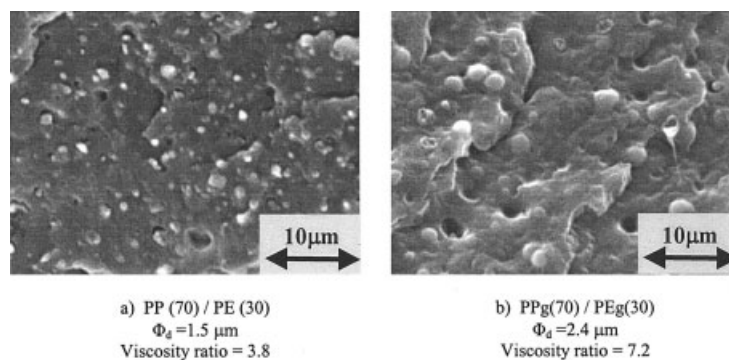*Correspondence to:* F. Fenouillot (Francoise.Fenouillot@insa-lyon.fr).

a) PP (70) / PE (30)
$\Phi_d$ =1.5 $\mu$m
Viscosity ratio = 3.8

b) PPg(70) / PEg(30)
$\Phi_d$ =2.4 $\mu$m
Viscosity ratio = 7.2

**Figure 1** Initial morphology of the binary blends without coupling-agent: a) PP(70)/PE(30), $\Phi_d$ = 1.5 $\mu$m, viscosity ratio = 3.8. b) PPg(70)/PEg(30), $\Phi_d$ = 2.4 $\mu$m, viscosity ratio = 7.2.

In the present work we investigate the stabilization effect of coupling reactions on the morphology after a process, injection molding, that enhances the coalescence and elongation of the dispersed phase of the blends. Moreover, the blends were annealed in a oven so that we can follow the evolution of their structure under quiescent conditions. In both cases, the compatibilization effect of the copolymers prepared by coupling reactions is expected to prevent coalescence of the dispersed phase.

## EXPERIMENTAL

All details on the materials and on the preparation of the blends may be found elsewhere.[33,34] The essential aspects are reviewed below.

### Materials

The pure PE and PP, and the maleic anhydride grafted grades, were supplied by Solvay (Belgium). Three coupling-agents have been employed—dodecane diamine ($C_{12}N_2$); and two metallic salts, zinc acetate (ZnAc) and sodium bicarbonate ($NaHCO_3$). All the reactants were purchased from Sigma Aldrich (France) and used without further purification. These molecules react very fast with the maleic anhydride functions of the grafted polyolefins; hence they are adapted to a use in the extruder.[33]

### Preparation of the blends

The blends were prepared by twin-screw extrusion. The twin-screw extruder was a Clextral BC 21 with a



a) PP/PPg(35) / PE/PEg(15)
$\Phi_d$ =1.2 $\mu$m

b) PP/PPg(17.5) / PE/PEg(7.5)
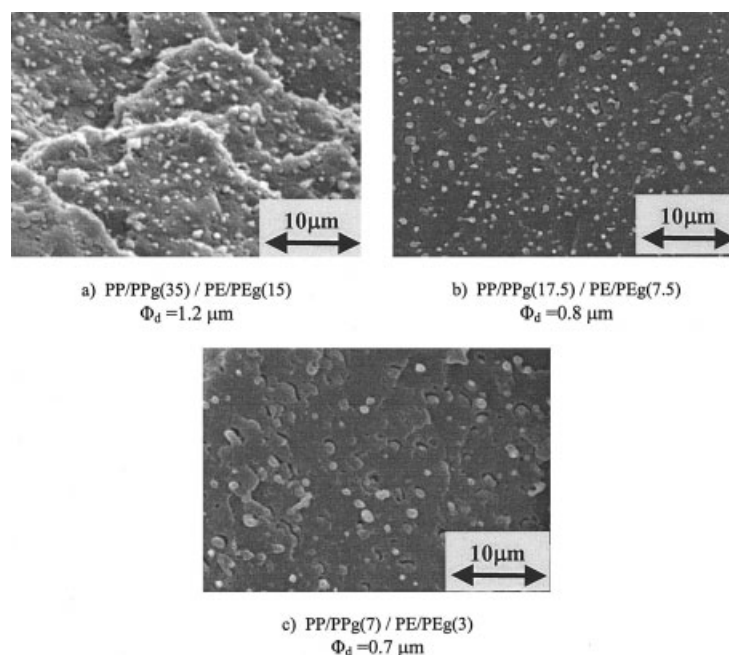$\Phi_d$ =0.8 $\mu$m

c) PP/PPg(7) / PE/PEg(3)
$\Phi_d$ =0.7 $\mu$m

**Figure 2** Initial morphology of the quaternary blends without coupling-agent: a) PP/PPg(35)/PE/PEg(15), $\Phi_d$ = 1.2 $\mu$m. b) PP/PPg(17.5)/PE/PEg(17.5), $\Phi_d$ = 0.8 $\mu$m. c) PP/PPg(7)/PE/PEg(3), $\Phi_d$ = 0.7 $\mu$m.
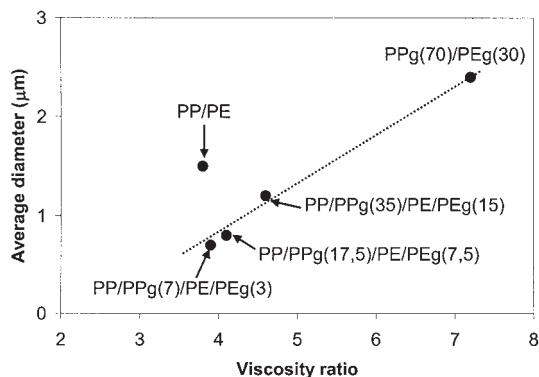
**Figure 3** Average diameter of the dispersed PE as a function of the viscosity ratio of the blend. Binary and quaternary blends without coupling-agent.

length to diameter ratio of 36 and a screw diameter of 25 mm. The screw configuration, temperature profile, and experimental conditions are detailed elsewhere.

## Composition of the blends

The studied blends were always composed of 70 wt % of PP/PPg and 30 wt % of PE/PEg.

Two types of blends were prepared:

- Binary blends: PP/PE or PPg/PEg—70/30.
- "Quaternary" blends: PP/PPg(a)/PE/PEg(b) with 10 to 50% of the total weight being grafted polyolefins.

a and b are the proportions of PPg and PEg, respectively.

The blends were prepared with or without a coupling-agent.

The stoichiometric ratio, x, is defined as the number of amine functions per anhydride function. For the salts, the stoichiometric ratio, x, is the number of moles of cations per mole of carboxylic acid. For instance, x = 1 corresponds to one $Zn^{2+}$ for one carboxylate. In this case, the system is not at electronic neutrality.

The following blend, for instance, PP/PPg(35)/PE/PEg(25)/2 $C_{12}N_2$, contains the diamine coupling-agent with a stoichiometry of 2 relative to the anhydride functions.

## Injection molding

Tensile test specimens (ISO 1/2) were injection molded with a 12 tons injection molding machine. The set temperature of the plasticating unit was 200°C, and the mold temperature was 35°C.

## Annealing of the blends

Samples of the blend were packed in a aluminum mold to avoid a change of shape at high temperature. They were placed in an oven at a set temperature of 200°C, removed at the desired intervals of time, and then quenched.

**TABLE I**
**Average Diameter of the Dispersed Phase Before and After Injection Molding**
**for the Non Compatibilized and Compatibilized Blends**

| Type of blend | Blend | Average diameter after extrusion ($\mu$m) | Average diameter after injection-molding ($\mu$m) |
|---|---|---|---|
| Binary non compatibilized blends | PP/PE | 1.5 | 5.6 |
| | PPg(70)/PEg(30) | 2.4 | 8.3 |
| Binary compatibilized blends | PPg(70)/PEg(30)/0.5 ZnAc | 1 | |
| | PPg(70)/PEg(30)/1 ZnAc | 0.7 | 1.5 |
| | PPg(70)/PEg(30)/2 ZnAc | 0.7 | 1.5 |
| | PPg(70)/PEg(30)/0.5 NaHCO$_3$ | 2.0 | |
| | PPg(70)/PEg(30)/1 NaHCO$_3$ | 1.2 | |
| | PPg(70)/PEg(30)/2 NaHCO$_3$ | 0.7 | 1 |
| | PPg(70)/PEg(30)/1 C$_{12}$N$_2$ | 1.9 | |
| | PPg(70)/PEg(30)/2 C$_{12}$N$_2$ | 1.9 | |
| | PPg(70)/PEg(30)/3 C$_{12}$N$_2$ | 1.6 | 3.5 |
| | PPg(70)/PEg(30)/4 C$_{12}$N$_2$ | 1.3 | |
| Quaternary blends | PP/PPg(7)/PE/PEg(3) | 0.7 | 3.5 |
| | PP/PPg(7)/PE/PEg(3)/2 NaHCO$_3$ | 0.8 | 2.5 |
| | PP/PPg(7)/PE/PEg(3)/2 C$_{12}$N$_2$ | 0.8 | |
| | PP/PPg(35)/PE/PEg(15) | 1.2 | 6.3 |
| | PP/PPg(35)/PE/PEg(15)/2 ZnAc | 0.9 | 2.6 |
| | PP/PPg(35)/PE/PEg(15)/2 NaHCO$_3$ | 0.6 | 0.8 |
| | PP/PPg(35)/PE/PEg(15)/2 C$_{12}$N$_2$ | 1.2 | 3.1 |
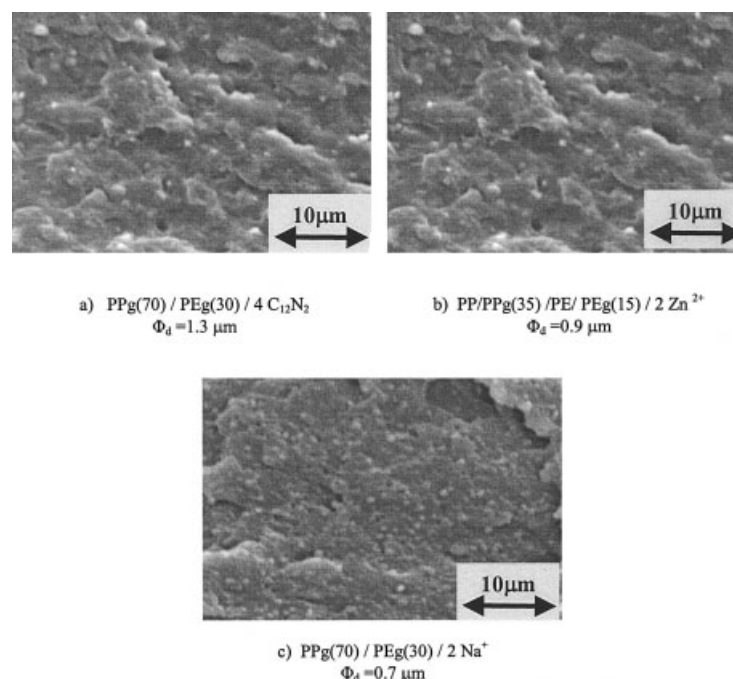
**Figure 4** Initial morphology of binary blends with different coupling agents: a) PPg(70)/PEg(30)/4 $C_{12}N_2$, $\Phi_d = 1.3$ $\mu$m. b) PP/PPg(35)/PE/PEg(15)/2 $Zn^{2+}$, $\Phi_d = 0.9$ $\mu$m. c) PPg(70)/PEg(30)/2 $Na^+$, $\Phi_d = 0.7$ $\mu$m.

## Blend morphology

The structure of the blends was analyzed by scanning electron microscopy (SEM) using a XL 20 microscope (FEI Company, Eindhoven, The Netherlands). The samples were cryofractured and gold plated prior to analysis.

## RESULTS AND DISCUSSION

We call "initial morphology," the structure of the blends after the extrusion stage.
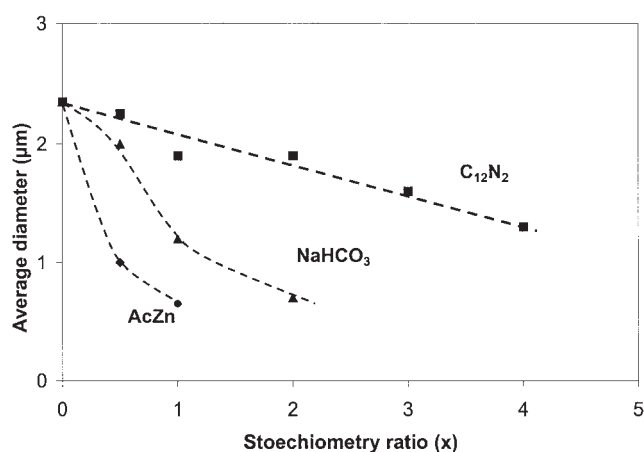


**Figure 5** PPg(70)/PEg(30) binary blends. Average diameter of the dispersed phase after extrusion, as a function of the stoichiometry ratio of different coupling-agents.

## Initial morphology of the blends without coupling-agents

The structure of binary and quaternary blends without the addition of coupling-agents is depicted in Figures 1 and 2. Note that even for non compatibilized blends, the diameter of the polyethylene particles, $\phi_d$, is relatively small (1.5 $\mu$m for the PP/PE blend). Polyethylene and polypropylene are immiscible polymers; but the similarities of their chemical structures, and their solubility parameters close to each other (respectively, 16.8 and 17 $(J/cm^3)^{0.5}$ for PP and PE), could explain that a relatively fine dispersion is observed. For instance, polyethylene associated with a polar polymer like poly(ethylene terephthalate) would give a much coarser structure.

Moreover, the viscosity ratio is not favorable. It is equal to 3.8 for the PP/PE blend, while it is equal to 7.2 for the PPg/PEg blend (from measurements at T = 200°C and 100 rad $s^{-1}$). The structure of the blends is different, with an average diameter of 1.5 $\mu$m for PP(70)/PE(30) and 2.4 $\mu$m for PPg(70)/PEg(30) (Fig. 1). It is clear from the difference of the dispersed phase size that the viscosity ratio is a determinant factor for the quality of the morphology.

The addition of grafted polymers improves the morphology of the PP/PE blend even when no coupling-agent is used (Fig. 2). The viscosity ratio changes with the blend composition and becomes more favorable to finer dispersion for the "noncompatibilized" quaternary blends. All the observed blends show a finer dispersion
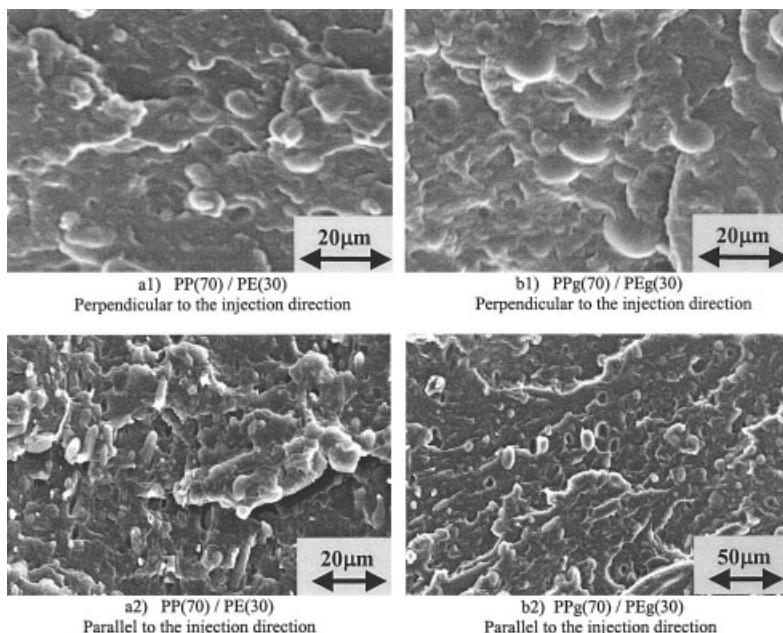
**Figure 6** Morphology of the PP/PE and PPg(70)/PEg(30) binary blends after injection molding: a1) PP(70)/PE(30) perpendicular to the injection direction. b1) PPg(70)/PEg(30) perpendicular to the injection direction. a2) PP(70)/PE(30) parallel to the injection direction. b2) PPg(70)/PEg(30) parallel to the injection direction.

than those presented in Figure 1. The viscosity ratio of the nonmodified and grafted polyolefins blends were measured, and the viscosity ratio of the other blends was approximated by considering that the viscosity of the PP/PPg and of the PE/PEg phases followed a proportionality law. Figure 3 presents the average diameter of the PE droplets as a function of the viscosity ratio. For all the blends containing graft maleic anhydride, a linear evolution of the average diameter of the dispersed phase was obtained. However, the average diameter of the PP/PE blend is almost twice higher than the one expected by analogy with the other studied blends and considering only the viscosity ratio. This signifies that the viscosity ratio is not the only parameter governing the morphology of these blends. The decrease of the size of the PE/PEg phase is also attributed to favorable interactions at the PPg rich and PEg rich interface as a consequence of the presence of anhydride functions.
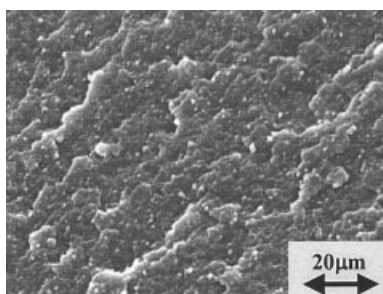
### Initial morphology of the blends with coupling-agents

When coupling-agents are employed during the preparation of PPg/PEg blends, the dispersed phase diameter ($\Phi_d$) decreased significantly (Table I and Figs. 4 and 5). The decrease of the particle size of the dispersed phase is attributed mainly to the presence of compatibilizing copolymer at the interface between PPg and PEg. It can also be partly due to a change of the viscosity ratio due to coupling reactions inside of the phases. The addition of small quantities of zinc acetate, 0.5 $Zn^{2+}$ per carboxylic acid function in PPg
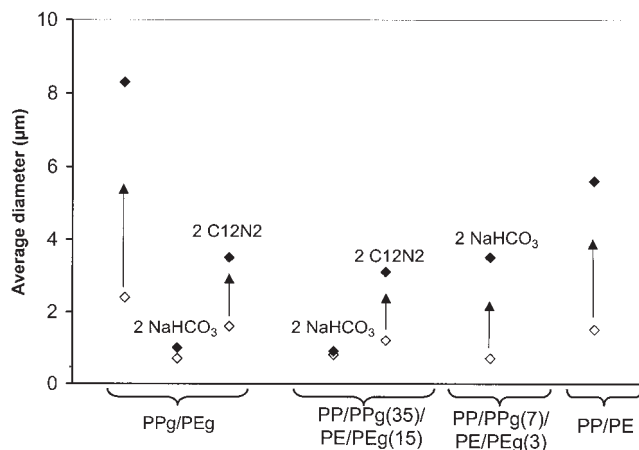


**Figure 7** Morphology of the PPg(70)/PEg(30) with x = 2 NaHCO$_3$ after injection molding.



**Figure 8** Average diameter of the PE phase before ($\diamond$) and after ($\blacklozenge$) injection molding for binary and quaternary blends with and without coupling agent.
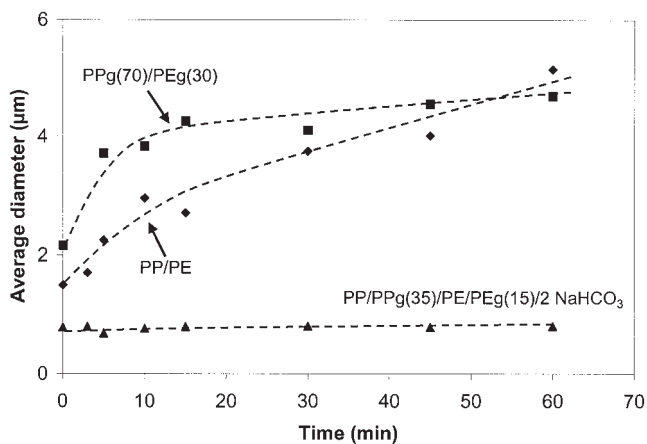
**Figure 9** Evolution of the diameter of the PE phase during annealing at 200°C for the binary non compatibilized blends (◆, ■) and for the PP/PPg(35)PE/PEg(15)/2 NaHCO₃ quaternary blend (▲).

and PEg, decreased the mean diameter of the PEg rich phase from 2.4 $\mu$m to 1 $\mu$m. Doubling the $Zn^{2+}$ lead to PEg rich phases ($\Phi_d$) of 0.7 $\mu$m. Equivalent results were also obtained with the use of $NaHCO_3$. However, the $NaHCO_3$ to carboxylic acid functions stoichiometry must be twice the stoichiometry of the equivalent blend with $Zn^{2+}$ to obtain PEg rich phase domains of 0.7 $\mu$m. The covalent coupling seems to be less efficient than the ionic coupling. Even with an amine to carboxlic acid functions stoichiometric ratio of 4, the obtained PEg domains size was only 1.3 $\mu$m.

For the quaternary blends containing PPg + PEg up to 25 wt %, no effect on $\Phi_d$ was observed with the used coupling-agents. It was necessary to add 50 wt % of grafted chains to observe a decrease of $\Phi_d$. Here also, the ionic coupling-agents decreased $\Phi_d$ considerably while the $C_{12}N_2$ did not (Table I).

In the next parts, the necessity of addition of PPg +PEg for the compatibilization of the quaternary reactive blends will be verified.

### Evolution of the morphology of the blends after injection molding

The stability of the morphology of blends prepared by reactive extrusion is not studied very often. However, most of the time, the formulated material will undergo a second step of processing, generally a second extrusion or an injection molding, before obtaining the final product. Injection molding generates very high shear rates; hence, it is a particularly severe test to check the stability of the structure of the blend.

The specimens prepared by injection molding were cryofractured perpendicularly or parallel to the injection flow direction, then analyzed by SEM.

The morphology of the non compatibilized binary blends has clearly evolved after this second process step, the dispersed phase, was subjected to coalescence and elongation (Table I and Fig. 6). For the PE/PP and PEg/PPg blend, the analysis of the specimens fractured parallel to the flow direction shows also that the dispersed phase was elongated, this elongation being more important for the PE/PP blend.

However, the addition of a coupling-agent stabilizes at least partially the morphology. For the PPg(70)/ PEg(30) coupled with a stoichiometry of 2 AcZn and 3 $C_{12}N_2$, the apparent $\Phi_d$ has only coubled after injection molding. With the use of $NaHCO_3$, the structure is almost stable.

For the quaternary blends, the use of 10 wt % of grafted polymer in the blend is not enough to suppress the coalescence of the drops during injection molding (Table I). As for the compatibilization of these blends by extrusion, it is necessary to add 50 wt % of graft copolymers to stabilize the morphology of the quaternary blends during injection molding. In addition, one should note that only for the PP/PPg(35)/ PE/PEg(15)/2 $NaHCO_3$ blend, the $\Phi_d$ remained unchanged after injection molding (Figs. 7 and 8). These results are in concordance with those described in the preceding paragraph. Figure 8 summarizes the main results.

### Evolution of the morphology in quiescent conditions

In the preceding section, the effect of compatibilization on the dispersion quality and on the blend evolution during injection molding was highlighted. It was shown that some of the studied blends have stable morphologies under dynamic solicitation. The study of the stability of the morphology of these
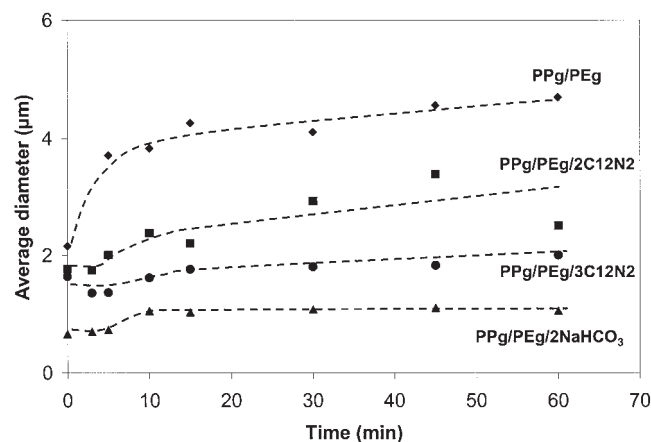


**Figure 10** Evolution of the diameter of the PE phase during annealing at 200°C for the binary compatibilized blends.

blends, when melted in an oven, allows their analysis under static coalescence conditions. Coalescence is not balanced here by breakup so that the phase size depends on interfacial tension and attraction forces between the droplets; it depends also on the shape relaxation of the dispersed domains.

For the binary PP/PE blend placed at 200°C in an oven, the mean diameter of the dispersed phase increased with time. The morphology of this blend is not stable, and the dispersed domains coalesce rapidly as a result of the incompatibility of the blend constituents. In the PPg/PEg blend, coalescence is only observed during the first 5 min, then the increase of the diameter of the droplets is slower. After one hour in the oven, the $\Phi_d$ of the PPg/PEg blend is lower than the $\Phi_d$ in the PP/PE blend. This shows clearly that, even if the viscosity ratio is more favorable for the PP/PE blend, the interfacial tension decreases, due to the fact that grafted functions in the PPg/PEg blend have a limited but visible effect preventing coalescence (Fig. 9).

The addition of a coupling-agent to PPg/PEg considerably stabilizes these blend morphologies; when annealed in an oven at 200°C (Fig. 10), the $\Phi_d$ increase is relatively limited. The PPg/PEg/2NaHCO$_3$ is particularly stable. For the PPg/PEg/2C$_{12}$N$_2$, $\Phi_d$ regularly increased, and it is necessary to add more coupling-agent to have a correct stabilization and prevent coalescence (PPg/PEg/3C$_{12}$N$_2$).

For the quaternary blends containing less than 50% of grafted polyolefins, the morphology is not stable under quiescent conditions. During the first 10 min, the $\Phi d$ increased rapidly and then coalescence is slower.

It is necessary to add much higher quantities of grafted polymers and coupling agents to obtain a reasonable stabilization (Fig. 9). Here also, the ionic coupling-agent is particularly efficient in stabilizing the blend morphology; almost no coalescence was obtained in this case.

In preceding studies we showed that under the used conditions, covalent or ionic coupling reactions certainly occurred. These reactions can either take place between PPg and PPg, PEg and PEg, or PPg and PEg. The first two reactions lead to branched polymers; only the reaction between PPg and PEg leads to a graft copolymer. This copolymer is supposed to compatibilize the PP/PE blends. The fact that high quantities of PPg and PEg are necessary to compatibilize PP/PE blends means that most reactions were between PPg and PPg or PEg and PEg. The issued branched copolymers are probably situated inside the PP rich and PE rich phases. Only a few reactions were made between PPg and PEg; the issued copolymer is probably at the interface and is responsible for the compatibilization of the blend. It is important to take also into account

this part of the study to define a strategy for PE/PP blend preparation.

## CONCLUSION

The functions grafted on PPg and PEg result in a limited compatibilization of the binary and quaternary blends consequently to polar attractions. Coupling reactions lead to a finer dispersion; and in stabilization of the blends preventing coalescence under dynamic and static conditions, sodium bicarbonate was more efficient than zinc acetate and 1,12-diaminododécane. Some of the coupling reactions are supposed to occur between PPg and PPg or PEg and PEg leading to branched chains. Only a few reactions were made between PPg and PEg, with the issued copolymer being responsible for the compatibilization of the blend. This study shows that a reasonable strategy for PE/PP compatibilized blend preparation by coupling reactions can be a direct reaction of maleic anhydride with PP and PE in the first section of a twin-screw extruder; in the second section, the coupling agent should be added. However, we have shown that for our particular blend, a proportion of 50 wt % of grafted chains is needed to obtain a good stability of the morphology after injection.

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