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The Effect of the Compatibilization Route of PA/PO Blends on the Physico-chemical Phenomena Developing Along a Twin-screw Extruder

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Summary: The effect of the compatibilization method (ex-situ, in-situ, cross linking) on the chemical conversion, morphological and rheological evolution of polyamide/polyolefin blends along a twin screw extruder is investigated. For this purpose, samples were quickly collected from the extruder at specific barrel locations, quenched and subsequently characterized off-line. While significant changes occur very quickly in the melting zone for the ex-situ and in-situ routes, changes of the cross linking system could be detected along all the extruder. Correlations between chemical conversion, particle size and linear viscoelastic response could be established.

Keywords: blends; compatibilization; particle size distribution; reactive extrusion; rheology

Introduction

Although it is currently normal practice to prepare new materials with innovative properties by blending existing polymers, rather than by searching for new monomers, this route faces practical difficulties as most promising polymer pairs are thermodynamically immiscible. The incorporation of a compatibilizer (also known as interfacial agent, or emulsifier), usually a graft or block copolymer, is therefore necessary to reduce the interfacial tension, enhance the adhesion at the interface, facilitate the dispersion of one phase in the other and stabilize the morphology [1–3].

Compatibilization can be achieved (a) *ex-situ*, by addition of a pre-synthesized copolymer to the components, b) *in-situ*, by creating a copolymer during blend preparation which is located at the interface between the two components and c) by stabilizing the dispersed phase via dynamic vulcanization, or cross linking. Ex-situ compatibilization provides the opportunity for controlling more easily the molecular architecture of the copolymer. However, not only it requires specific chemical routes and reaction conditions (when possible), but when the compatibilizer is added to the blend components it is difficult to ensure that most of it actually goes to their interface. In-situ (or reactive) compatibilization requires that both polymers have reactive groups at the interface. For example, terminal amine groups of PA6 can react with maleic anhydride groups of a modified polyolefin. Since the reaction takes place at the interface, the process is very effective, although it is difficult to control the rate of formation, as well as the amount and molecular architecture of the compatibiliser. Finally, cross linking of a given material during mixing (dynamic vulcanization) determines the dispersed phase and guarantees stable size and shape during subsequent thermomechanical cycles [1,3].

All above methods have been widely used to obtain compatibilized immiscible

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polymer blends using co-rotating twin-screw extruders [4–6]. Polyamide/polyolefin blends, which combine the tenacity, rigidity, thermal and chemical resistance of the former with the dimensional stability, constancy in mechanical and electrical properties of the latter have been thoroughly investigated, given their industrial interest, particularly in what concerns their performances [7–10]. However, little is still known about the effect of the compatibilization method on the nature and rate of evolution of the physico-chemical phenomena developing along the extruder during blend preparation. Since the availability of such data would be useful to optimize industrial blending, the aim of this paper is to monitor chemical conversion, morphological and rheological evolution during preparation of polyamide/polyolefin blends using different compatibilization routes in a twin screw extruder, and investigate whether interrelationships exist between those responses.

Experimental

Materials

Commercial injection-type low viscosity PA6, PP and PE were used in the experiments. PE bearing maleic anhydride species was used as the compatibilizer for the *in situ* route. A PA6 grafted PP copolymer was used as the compatibilizer for the *ex situ* route [11]. For the cross linking route, a co-reactive blend of PE bearing maleic anhydride species and PE bearing epoxy groups was used. The composition of the blends is such that a PA6 matrix with PO nodules is always ensured.

Preparation of the Blends

The blends were prepared in a laboratory modular Leistritz LSM 30.34 intermeshing co-rotating twin-screw extruder and subsequently pelletized using the corresponding downstream equipment. The configuration of the screws, which contained three mixing zones with staggered kneading disks and a left hand element that ensured sealing for devolatilization purposes, is depicted in Figure 1. The extruder was fitted with a number of sampling collecting devices, whose location is also shown in the Figure. These are used to detour material from the extruder and collect it quickly for subsequent characterization (see, e.g. [12] for a more complete description of this tool). Material samples were thus made available where the blend was subjected to intensive mixing and significant changes in morphology and/or chemistry would be anticipated. Immediately after collection, the samples were quenched in liquid nitrogen in order

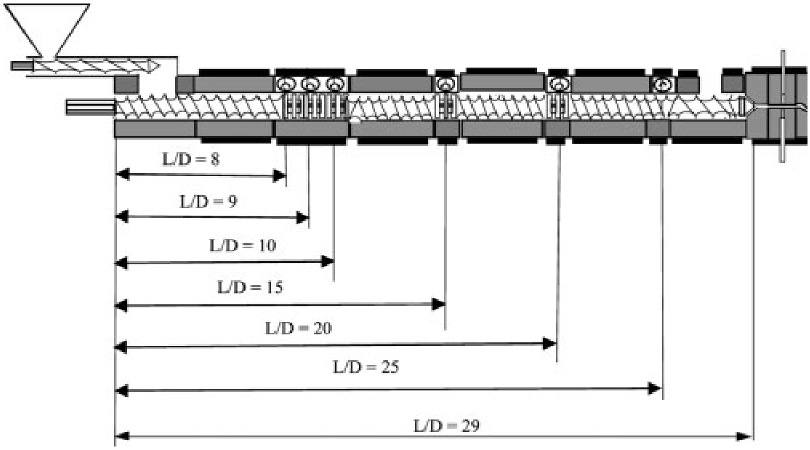

Figure 1.
Extruder layout.

to prevent further reaction or morphological changes.

All experiments were performed with the screws rotating at 300 rpm and all temperature zones set at 260 °C, with a mass output of 15 kg/h prescribed by a gravimetric feeder.

Material Characterization

The overall experimental procedure is summarized in Figure 2 and is described below in more detail.

Samples obtained from in-situ compatibilization were milled and dried overnight, followed by hydrolyzation with hydrochloric acid for 6 hours and subsequent filtering, washing with water and drying for one hour at 180 °C, in order to convert dicarboxylic acid back to anhydride [13]. Thin films were prepared by compression-moulding and characterized by FT-IR (Perkin Elmer 1600 spectrometer). The anhydride carbonyl peak at 1785 cm^{-1} together with an IR calibration rule determined with a set of references, allowed the quantitative determination of the residual MA content.

Results and Discussion

Direct observation of the samples removed from the extruder showed that, in all cases, melting was far from complete at L/D = 8 (see Figure 1), pellets of PA 6 being visible, but one L/D downstream a more or less homogeneous melt had already developed. Such observations are well in line with previous studies [12,13] and confirm that melting in a co-rotating extruder is a very fast process, involving efficient dispersion mechanisms. It also means that any rheological data on samples from location L/D = 8 cannot be directly compared with the remaining (and thus it will not be included in the discussion).

Chemical Evolution

Figure 3 shows the evolution along the extruder of the residual MA content (in-situ copolymer formation) and the cross linking rate (cross linking method), presented in terms of percentage.

Imidation is a very fast reaction, developing mainly in the melting zone (first kneading block) and proceeding slowly

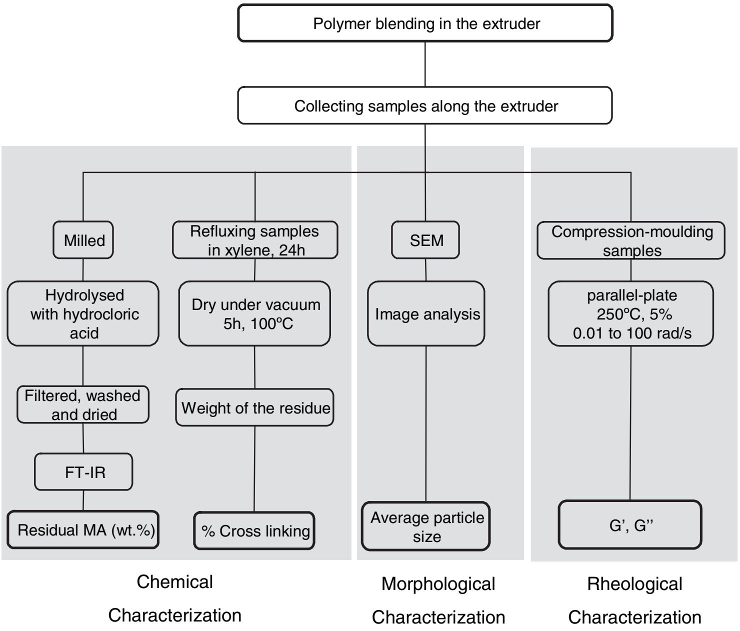

Figure 2.
Experimental procedure.

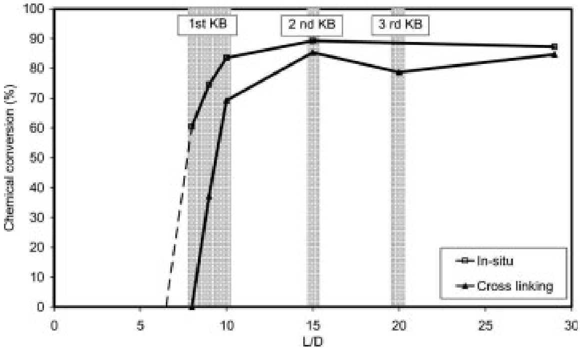

Figure 3.
Chemical conversion of the reactive blends along the extruder.

further on. This could be related to the intense generation of interfacial area provided by the kneading disks. However, at the tip of the screws the amount of reacted MA reaches circa 90% and the figure indicates that, in practical terms, the reaction may be taken as completed. One possible explanation for this behaviour could be that some of the initial MA groups remain inside the polyolefin particles and thus not available to react with the amine groups of PA-6 [13]. Yin et al [14] and Hu et al [15] put forward an alternative explanation, arguing that when the interface is covered by the copolymer already formed, reactive groups cannot diffuse through it, i.e., an interfacial screen effect develops [15].

The cross linking reaction seems to initiate later, but then the rate is equally high during the first kneading block. A less intense increase in conversion seems to occur until L/D = 15, no further reaction being detected downstream. Differences in reaction rate between the two systems can be explained by the different reactivity of the functional pairs [16].

Morphology Evolution

Observation of Figure 4, which quantifies the morphologies presented in Figure 5, shows that ex-situ compatibilization (addition of a pre-synthesized copolymer) yields the blend with the largest particle size and particle size distribution. This seems to signify that addition of a copolymer versus its formation in situ may affect the dispersion mechanisms in the extruder due to the distinct rheologies of the various compo-

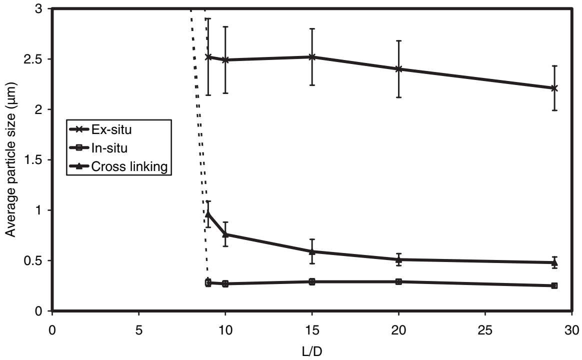

Figure 4.
Evolution along the extruder of the average particle size (and size distribution, as error bars) of the dispersed phase.

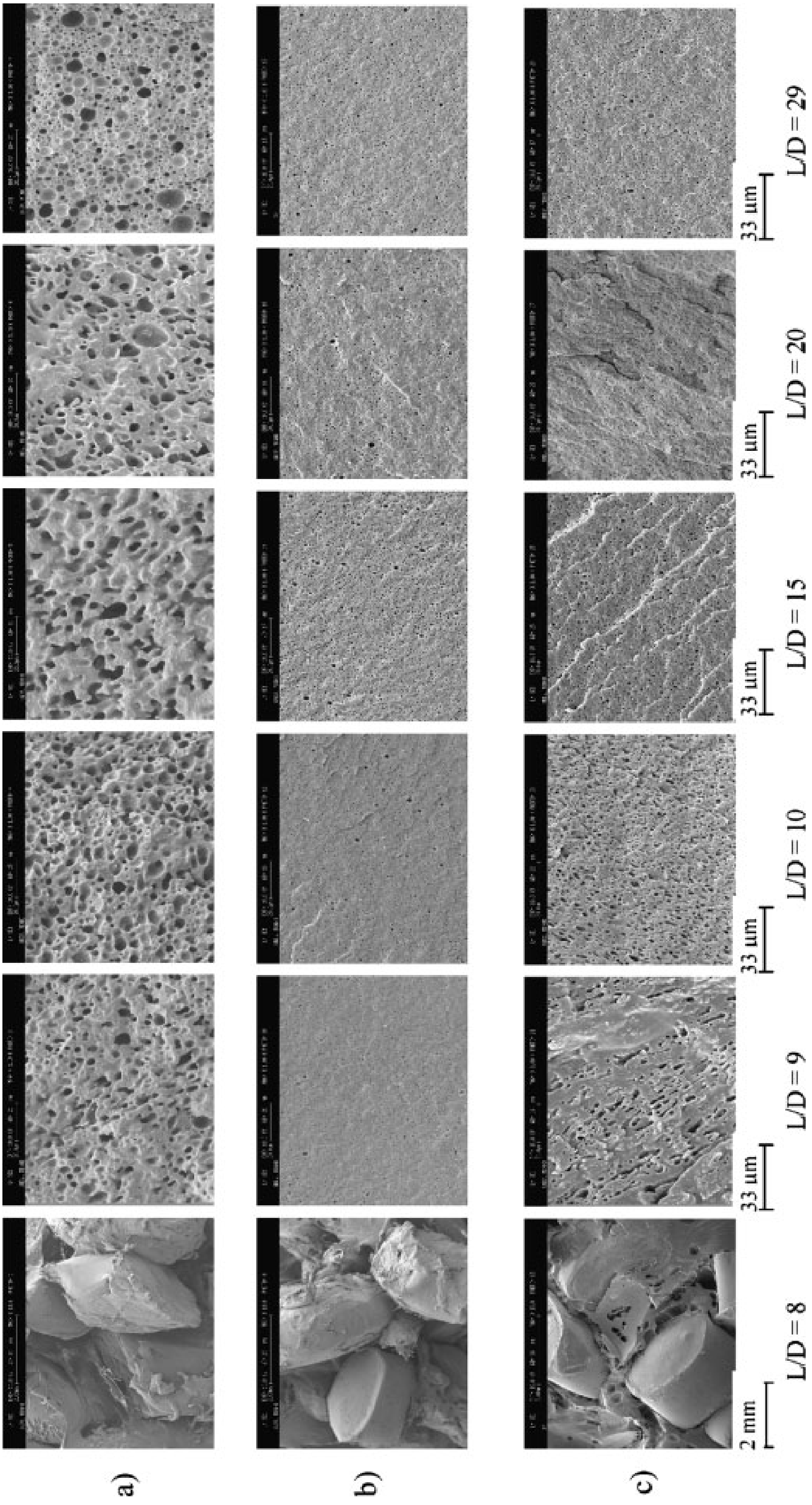

Figure 5.
SEM micrographs of the different blends along the extruder: a) ex-situ, b) in-situ, c) cross linking.

nents, as well as the rate of arrival and/or amount of copolymer present at the interface that can stabilize the morphology.

Apart from this difference, in all cases there are dramatic changes in morphology from L/D = 8 to L/D = 9 and the final blend exhibits a high level of distributive mixing.

Morphology development of the in-situ blend along the extruder is particularly fast, changes being only perceived up to L/D = 9. In the case of the other compatibilization routes the initial developments in the first kneading block are also similarly quick, but a regular evolution along the barrel seems to be noticeable. In other words, in these cases continuing shear may provide an improvement in terms of morphological features, whereas in situ compatibilization yields very quickly a fine and stable morphology.

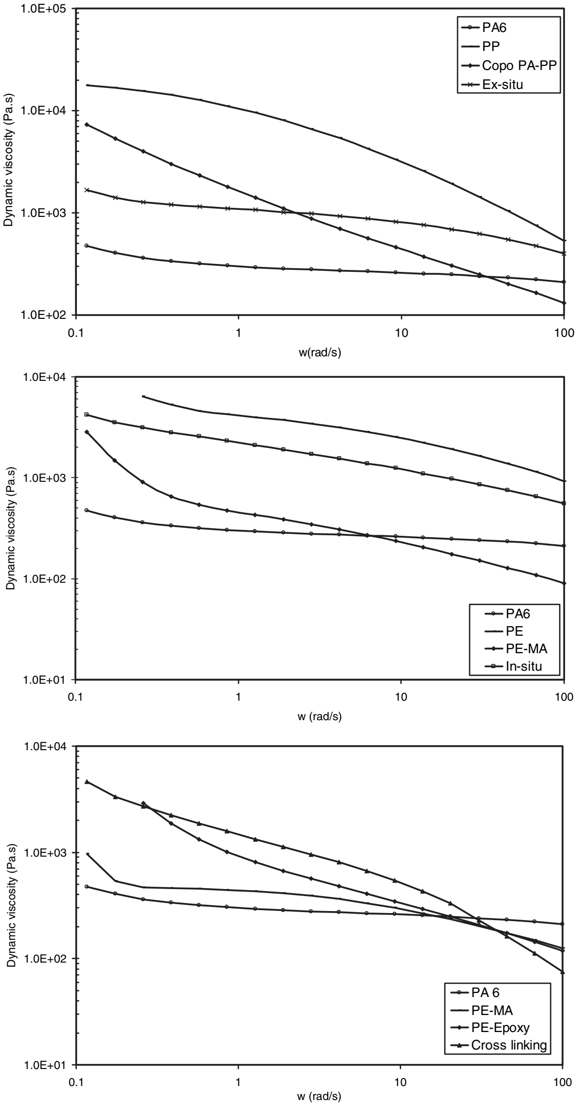

Figure 6.
Rheological behaviour of the ex-situ (top), in-situ (middle) and cross linking (bottom) compatibilized blends.

Rheological Evolution

Figure 6 presents the dynamic viscosity of all blends (extrudates) and their components. The rheological behaviour of the blends is quite distinct (but direct comparisons are meaningless as the components are also different).

In the case of the ex-situ blend, PP is much more viscous than the polyamide in the considered shear rate range and the copolymer has an intermediate behaviour, although much more non-newtonian. The viscosity of the blend mirrors that of PA 6, but shifted to higher viscosities.

In the case of in situ compatibilization, PE is one order of magnitude more viscous than PA 6 in the considered shear rate range (and less viscous than PP), but maleated PE has similar values to those of PA. The viscosity of the blend is similar to that of PE, but shifted to lower viscosities. In other words, deviation from the rule of mixtures in the latter case is much more significant than for the ex-situ blend. This could be explained not only by a stronger interaction between phases, but also because at constant incorporation ratio smaller particles have a higher effect on increasing viscosity than fewer bigger particles.

Finally, as expected, the blend obtained using the cross linking route is more viscous than its initial components (maleated PE and PA 6 have similar rheology, PE functionalized with epoxy groups is slighty more viscous).

The actual evolution of the rheological response of the various blends along the extruder is depicted in Figure 7, in terms of dynamic viscosity at constant frequency (1 rad/s). The figure also shows the viscosities of the initial components for each case. It is worth noting that direct comparison of rheological data can only be carried for fully molten samples, which implies considering only those located beyond L/D = 8 (otherwise, data for filled and homogenous materials would have to be confronted, this being quite difficult as it would require consideration of uniform particle sizes). Unfortunately, this limits the potential of using oscillatory rheology as a tool for monitoring the physico-chemical phenomena taking place along the extruder: most of the evolution has already been consumed when rheological measurements become possible.

Anyway, Figure 7 demonstrates that the viscosity of the ex-situ and in-situ blends is quite stable as soon as their components melt, whereas a noticeable decrease in viscosity is observed for the cross linking route, after the important increase (relative to the initial components) achieved upon

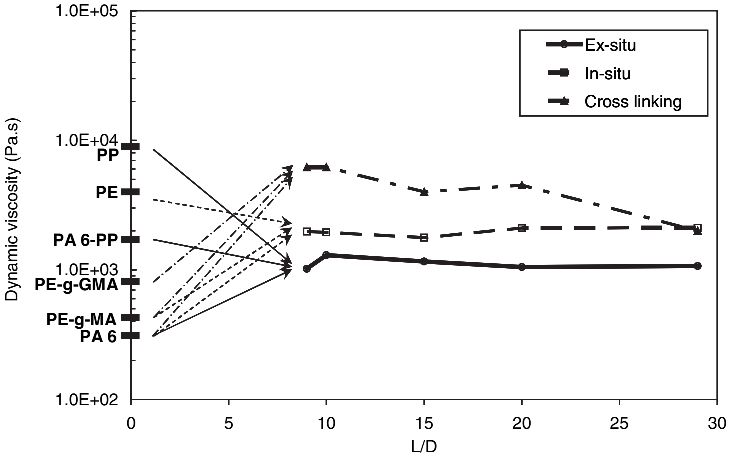

Figure 7.
Rheological behaviour of the blends along the extruder (w=1 rad/s).

cross linking. Such a decrease could be explained by the progressive degradation of the dispersed phase network exposed to heat and mechanical stresses.

Morphology-Chemical Conversion-Rheology Correlations

Although the initial stages of the process are currently a matter of debate [17], it is well known that chemical reactions and morphology evolution are inter-related, chemical conversion leading to finer morphologies. It has also been demonstrated that the linear viscoelastic response of a blend is sensitive to changes in its morphology [18]. Therefore, it makes sense to speculate whether correlations exist between these three variables.

Figure 8 illustrates 3D representations of chemical conversion versus particle size versus dynamic viscosity for the in situ and cross linking blends. Since there is no reaction during ex situ compatibilization, a 2D representation was performed. In this case, and as discussed above, the rheological data was not sensitive to the small changes in particle size (2.2 to 2.5 μm range) that occurred during the section of the extruder where a molten blend was being processed.

Despite the small number of points (each one corresponds to a measurement along the extruder's barrel) and the associated experimental errors (in the case of particle size, the ''error'' contains the effect of size distribution), satisfactory correlations seem to exist for the other blends, particularly for the cross linking route. As the gel content increases, the viscosity and particle size decrease, the former due to probably degradation of the dispersed phase, the latter due to the formation of a more stable morphology. Finally, chemical conversion of the in-situ blend yields a finer morphology (the rate of evolution being higher at low conversions), viscosity playing again a minor role.

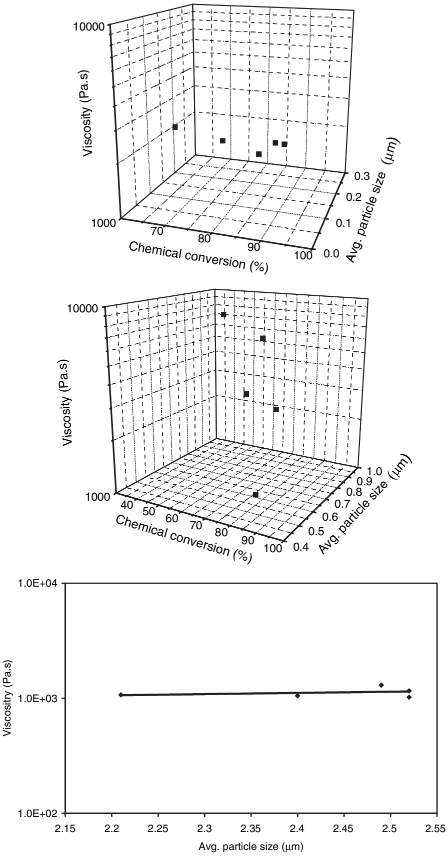

Figure 8.
3D representations of chemical conversion *vs* particle size *vs* viscosity of in-situ (top) and cross linking (middle) compatibilization; 2D correlation for the ex-situ (bottom).

Conclusion

The available sampling device allowed the nearly real-time investigation of the processes occurring inside a twin screw extruder during blending. In this study, the chemical, morphological and rheological evolution along the extruder of different PA/PO blends, which differ by their method of compatibilization, were performed.

Morphological changes could be detected along the extruder in the case of ex-situ compatibilization.

For the in-situ compatibilization method, the major changes (in chemical conversion, morphological development and rheological behaviour) occur quickly, upon melting. In the case of the cross linking of one phase, the evolution extend along the extruder (more particularly up to the second kneading block zone). In all cases, this study highlights the strong correlation existing between chemistry, morphology and rheology. When the chemical conversion reaches a maximum a regular morphology (structure and particle size) is obtained and a change in morphology induces a change in rheological behaviour.

[1] S. Datta and D. Lohse, *Polymeric Compatibilizers*, Hanser Publishers, 1996.

[2] L. A. Utracki, *Encyclopaedic Dictionary of Commercial Polymer Blends*, ChemTec Publishing, 1994.

[3] S. Datta and D.J. Lohse, "Polymeric Compatibilizers, Uses and Benefits in Polymer Blends", Hanser Publishers, Munich, 1996.

[4] M. van Duin, M. Aussems and R. J. M. Borggreve, *J. Polym. Sci.: Part A: Polym. Chem.* **1998**, *36*, 179.

[5] H. Cartier and G.H. Hu, *J. Polym. Eng. Sci.* **1999**, *39*, 996.

[6] K. Dedecker and G. Groeninckx, *Macromolecules*, **1999**, *32*, 2472–2476.

[7] B. Brulé, J.J. Flat, Fracture mechanism in rubber toughened PA6/HDPE alloys, Congress France – Chine, Nancy, 2004.

[8] Ph. Blondel, B. Brulé, J.J. Flat, Benefit of alloy technology in term of control of surface properties of materials, European Polymer Blends Conference, Lyon, 2002.

[9] B. Brulé, Benefit of alloy technology in term of permeability properties, European Polymer Blends Conference, Lyon, **2002**.

[10] B. Brulé, Permeability of polymer alloys, Kunstoffe **2004**, 4, 102.

[11] Patent DE 3909273

[12] A.V Machado et al, *J. Appl. Polym. Sci.* **1999**, 71, 135.

[13] A.V Machado, J.A. Covas, M. Van Duin, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, 37, 1311.

[14] Yin , Z., Koulic , C., Jeon , H.K., Pagnoulle , C., Macosko , C.W., Jérôme , R., *Macromolecules* **2002**, 35, 8917.

[15] G. Hu, M. Lambla, chap.6, in H. E. H. Meijer (ed.) *Volume 18 - Processing of Polymers* of R.W. Cahn, P. Haasen, E.J. Kramer (eds.), *Materials Science and Technology - A Comprehensive Treatment*, Wiley-VCH, Weinheim, **1997**.

[16] Orr et al, *Polymer* **2001**, 42, 8171.

[17] C.W. Macosko, H.K. Jeon, T. R. Hoye, *Prog. Polym. Sci.* **2005**, 30, 939.

[18] C. Lacroix, M. Gramela, P. J. Carreau, *J. Rheol.* **1998**, 42, 41.