Macromol. Symp. ***181,*** *189–200 (2002)*

Engineering Polymer Alloys by Reactive Extrusion

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Summary: During the last fifty years blending of dissimilar polymers has been a major path to tailor materials with new properties in industry. Since most of the interesting polymer blends are immiscible, the different compatibilisation strategies have received a lot of attention. In the area of engineering plastics, reactive blending is usually used to compatibilise immiscible polymers. The most important polymer alloys prepared by reactive extrusion [Polycarbonate/Polybutyleneterephthalate-alloys (PC/PBT), Polyamide/Polyphenylene-ether-alloys (PA/PPE), Styrenics/Polyamide-alloys (ABS/PA)] have already reached an interesting sales volume. The commercial success of these materials is mainly related to their unique combinations of properties, which enables their use in a multitude of applications.

Introduction

During the last fifty years blending of dissimilar polymers has been a major path to tailor materials with new properties.[1-4] Especially in the plastics industry, the blending technology has gained a broad acceptance as tool for the development of new materials. In the area of polymeric materials, usually a combination of properties is needed to meet the requirements of a particular application. For applications in different fields, like the automotive and electrical industry, not only mechanical properties like stiffness, strength and toughness are important, but also the thermal behaviour (continuous use temperature, heat distortion temperature), processing properties (melt flow, melt stability), electrical properties, chemical resistance, and flame resistance have to be considered.

In order to adjust the desired properties for a new material, the blend components can be chosen from a large variety of commercially available polymers.

Due to the low contribution of the mixing entropy to the free energy of mixing, a large number of polymer blends are immiscible.[5-7] The whole variety of polymer blends can therefore be distinguished by their phase behaviour (Figure 1). In miscible blends, the chain segments of the different polymers are miscible on a molecular level. These blends show only a single glass transition temperature. The position of the glass temperature is mainly dependent from the composition of the blend. Polyphenyleneether/Polystyrene-

CCC 1022-1360/00/$ 17.50+.50/0

blends are considered to be the most important example for a miscible blend in the field of engineering plastics. Systems that are either partially miscible or completely immiscible, but offer attractive mechanical performance, are often designated as compatible polymer blends. Usually these blends show two glass transition temperatures, which may slightly deviate from the Tg′s of the blend components. Polycarbonate/Styrenics-blends are the most popular representative of these blends.

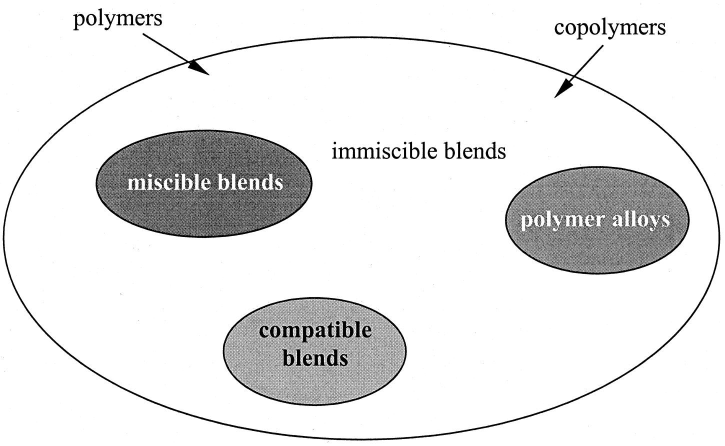

Figure 1. Classification of polymer blends.

The largest group of polymer blends is the immiscible blends. Immiscible polymer blends show a completely phase separated structure. Therefore, the glass transition temperatures of the components in the blends are exactly the same as for the pure components.

The nature of the interface is a main issue for the mechanical performance of polymer blends. The lack of interfacial strength in the immiscible blends leads to adhesive failure and poor mechanical properties.

The morphology of immiscible blends can be modified by the addition of compatibilisers; the compatibilisers act like emulsifiers in oil/water mixtures. In polymer blends the compatibilisers are usually copolymers (block – or graft copolymers) consisting of different segments which are miscible with the respective components of the blend. During the melt mixing procedure the compatibiliser acts as polymeric surfactant, reducing the interfacial tension between the immiscible polymers, which results in a significant size reduction of the dispersed particles (Figure 2). Since the surface of the dispersed particles is covered by the compatibiliser, the coalescence rate of the dispersed particles is tremendously reduced, keeping the morphology of the material stable during the later stage of mixing or subsequent processing steps.[8-10] In the bulk state, the compatibilisers provide a strengthening of the interface, which is an important issue for the toughness of multiphase materials.[11-13] Polymer blends with a modified interface are usually designated as polymer alloys.

Several reasons can be found for the attractiveness of the blending technology. During the last thirty years, extensive know how related to the selection of components, melt mixing, compatibilisation and structure-property relationships in the area of polymer blends has been accomplished, which allows the development of a new material in a short time.

Table 1. Motivation for polymer blending.

Development of new	
Polymers/Copolymers	Polymer Blends
• Synthesis of new monomers, catalysts,... • Development of a new polymerisation process • TSCA*)-approval of monomer/ polymer	• well-known polymers • Development of a formulation
• construction of plants for monomer/polymer production	• melt mixing equipment
=> high investment => long time to market	=> low investment => short time to market

*)TSCA: Toxic Substances Control Act

Since the development of polymer blends usually starts from well known polymers, materials with interesting properties can be obtained with comparatively low investment for product development. If already existing product lines, usually twin screw extruders, are available, flexible production at a competitive cost level is already possible for smaller quantities (Table 1).

The actual consumption of the most important polymer blends in the area of engineering plastics already exceeded the amount of 300.000 t/a (Table 2).[14,15]

Although some of the materials are on the market for more than 25 years, their sales volumes still increases with higher growth rates than the sales of the most engineering thermoplastic materials.[15]

Table 2. Sales volumes and producers of important polymer blends.

Type	Components	Sales in '98	Producer
miscible	PPE/HIPS	305 000	GEP, Asahi, BASF
	PSAN / PMMA / MBS	25 000	Toray, BASF
compatible	PC / Syrenics	320 000	GEP, Bayer, Dow
	PC / Polyester	60 000	GEP, Bayer, BASF
alloy	PPE / PA	25 000	GEP, Sumitomo
	ABS / PA	20 000	BASF, Bayer

Compatibilisation by Reactive Extrusion

For the use in industrial applications, reactive extrusion offers several advantages. For most polymer/polymer-combinations, appropriate block or graft copolymers are not commercially available, the synthesis of such copolymers is sometimes complicated even on the lab scale. On the other hand, several of the commercial polymers like Polyamides or Polyesters offer functional groups, which can be utilised for chemical reactions during the melt mixing process. An excellent survey on the different possible reactions, which can be used, is given by Brown.[16]

As already mentioned, the particle size of the dispersed phase is tremendously reduced by the creation of copolymers during the extrusion process (Figure 2). The in situ copolymer formation can be verified by solvent extraction. This has been extensively studied for Polysulfone/Polyamide-systems, where anhydride-terminated Polysulfone (PSU-PhA) reacted with Polyamide to form PSU-b-PA, which acts as very efficient compatibiliser.[17-19]

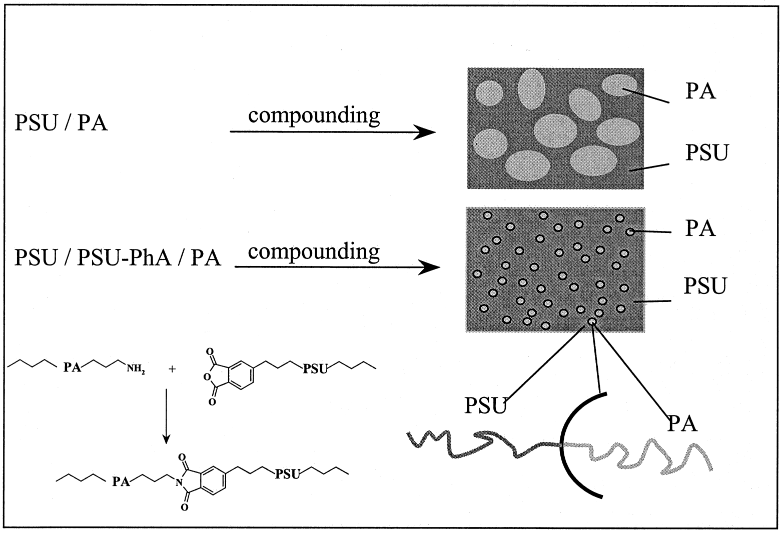

Figure 2. Schematic representation of the compatibilising effect of PSU-b-PA in PSU/PA-alloys.

The most important engineering polymer alloys, which are produced by reactive extrusion, will be discussed in the following chapters.

Important Engineering Polymer Alloys

Polycarbonate/Polybutyleneterephthalate-Alloys (PC/PBT/MBS)

Polycarbonate/Polybutyleneterephthalate-blends are a combination of an amorphous and a semi-crystalline material. The excellent toughness and dimensional stability of PC is combined with the good flow and the high solvent resistance of PBT. In order to boost the impact toughness, these alloys furthermore contain Methylmethacrylate-Butadiene-Styrene (MBS) core-shell type rubbers. Both polymers are immiscible, but since PBT contains traces of titanium-catalysts from the polycondensation reaction, transesterification reactions between the two polymers lead to the formation of Polyestercarbonates during the melt mixing process.[20-22] This can be seen from TMA-curves of PBT/PC-alloys (Figure 3), where the shift of the Tg of both phases, compared to the Tg's of the pure components, can be clearly seen. In a recent paper, the different pathways for the transesterification reactions leading to Polyestercarbonates, but as well to products with reduced molecular weight, are discussed.[23] The in situ formed Polyestercarbonates improve the compatibility between both polymers, but the formation of

Polyestercarbonates has to be controlled by the addition of scavengers for the titanium-species, to avoid further reactions during compounding and processing, which finally would lead to almost amorphous materials with undesirable properties.

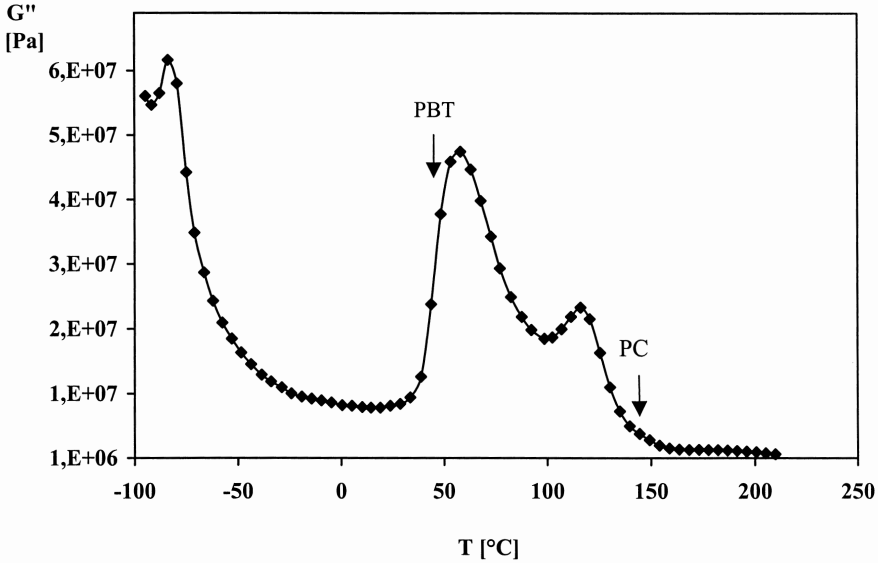

Figure 3. TMA-curve of a PBT/PC/MBS-alloy, the arrows indicate the peak position of pure PBT and PC.

Therefore, the control of the transesterification process during compounding and processing of PC/PBT-materials is a critical issue. Usually Phosphites or Phosphates are used as transesterification inhibitors.[24,25]

The influence of the transesterification inhibitors can be seen from DSC-measurements and TEM-images (Figures 4 and 5). In Figure 4 the DSC-traces of a PC/PBT/MBS-alloy with and without a transesterification inhibitor after three heating cycles from 30 to 290°C are depicted. It can be easily seen that the sample without transesterification inhibitor has a very broad melting peak for the PBT-phase compared to the sample with Tetrakis- (2,4-di-tert.butylphenyl) -4,4′-diphenylenediphosphonite as transesterification inhibitor.

In the TEM-image of the PBT/PC/MBS-alloy without transesterification inhibitor (Figure 5, right hand side) no distinct PC-phase is visible after the thermal treatment. This is further evidence for the formation of Polyestercarbonates. As can be seen from Figure 5, the MBS-rubber in PC/PBT/MBS-alloys is exclusively located in the PC-phase. The MBS-rubber mainly boosts the low temperature impact performance of these compounds.

Due to the excellent balance of properties like high toughness, good dimensional stability, high heat distortion temperature and good flow properties, PC/PBT/MBS-alloys are used for large exterior parts in the automotive industry. In the electrical industry PC/PBT/MBS-alloys are mainly used for sockets and housings.[26]

New developments in this area are compounds with high rubber loading, in order to ensure ductile failure mode at low temperatures even for painted parts, and mineral filled grades with reduced coefficient of linear thermal expansion (CLTE).[27]

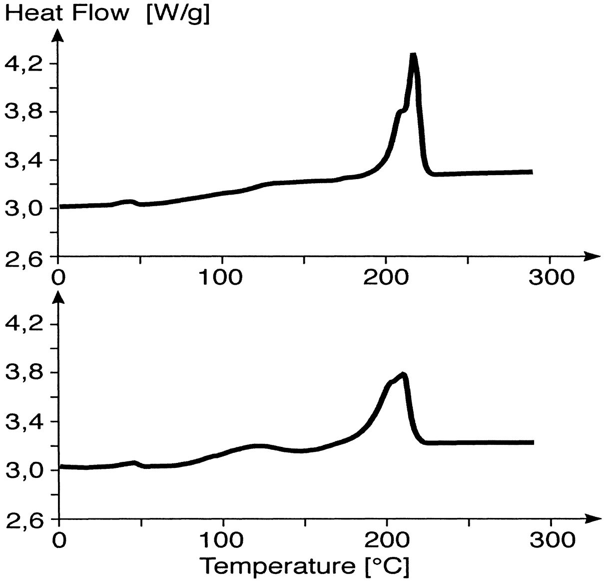

Figure 4. DSC-traces of PC/PBT/MBS 48/42/10-alloys after three heating cycles from 30°C to 290°C with a heating rate of 20 K/min; lower picture: without transesterification inhibitor; upper picture: with 0,5 wt.-% of Tetrakis-(2,4-di-tert.butylphenyl)-4,4′-diphenylenediphosphonite.

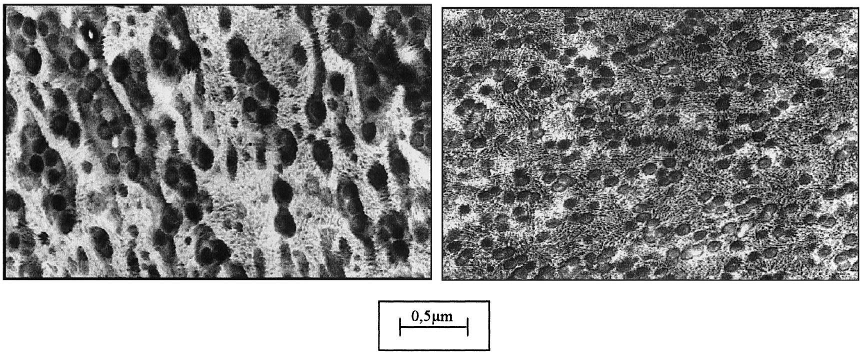

Figure 5. TEM-images of PC/PBT/MBS 48/42/10-alloys after three heating cycles from 30°C to 290°C with a heating rate of 20 K/min; right side: without transesterification inhibitor; left side: with 0,5 wt.-% of Tetrakis-(2,4-di-tert.butylphenyl)-4,4′diphenylenediphosphonite.

Polyphenyleneether/Polyamide-Alloys

Another interesting combination of an amorphous and a semi-crystalline polymer are the Polyphenyleneether/Polyamide-alloys (PPE/PA). PPE offers several interesting properties like high glass transition temperature (215°C), low moisture up-take, high dimensional stability, and low density. On the other hand, this material has low chemical resistance and bad processibility. Therefore, a combination with a polymer like Polyamide 6,6, which has good chemical resistance, excellent melt processibility, and good toughness could offer interesting properties.[28]

Binary blends of PPE and PA 6,6 are completely immiscible and have very unsatisfactory mechanical properties. The main issue in this system was to find an appropriate compatibiliser. Several different ways to compatibilise PPE and PA 6,6 are described in the literature.[29-32] The most appropriate ways are schematically presented in Figure 6.

The most common way is the use of modified PPE, which is obtained by grafting functionalized species like Maleic anhydride[29] or Fumaric acid[33] onto the PPE-chain in the melt. The modified PPE can subsequently react with PA 6,6 during the compounding procedure in order to form graft copolymers, composed of a PPE-backbone with PA 6,6-grafts.

The same kind of copolymers can be obtained by grafting PPE with Glycidylmethacrylate.[34] The epoxy-group of this compound can react with the terminal carboxyl-groups of the PA 6,6.

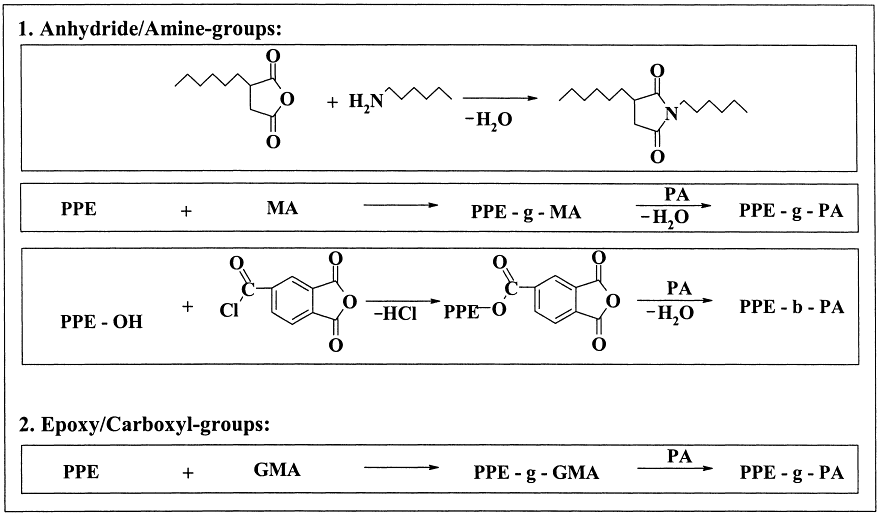

Figure 6. Possible pathways for the compatibilisation of PA and PPE.

A pathway to PPE-b-PA copolymers has also been disclosed in the patent literature.[35,36] The OH-groups of PPE can be reacted with Trimellitic acid chloride anhydride (TMA) in solution. In the first step, primarily the acid chloride function reacts, and a PPE with anhydride endgroups is formed. During melt mixing, this compound can form PPE-b-PA.

The in situ creation of graft or block copolymers lead to a significant decrease of the particle size of the dispersed PPE-particles as can be seen from Figure 7. Usually PA 6,6 (appears bright in TEM-image) forms the matrix phase whereas PPE forms the dispersed phase (grey particles). The average particle size of the dispersed phase is below 1 μm, which is a prerequisite to achieve an appropriate toughness level. In order to enhance the toughness of the system, these alloys furthermore contain hydrogenated Styrene-Butadiene-Styrene-block copolymers. As a consequence of the present Styrene-blocks, these impact modifiers are located exclusively in the dispersed PPE-particles (Figure 7).

The first PPE/PA-alloy on the marked was the so-called Noryl®GTX. This product was introduced to the market in 1986.

Due to the high Tg of the PPE-phase and the semi-crystalline nature of polyamide 6,6, these alloys have a high heat distortion temperature of up to 190°C, which allows the direct painting of parts moulded from this alloy at temperatures up to 170°C in usual paint lines used for steel parts (on-line painting). Therefore PA/PPE-alloys are widely used as material for large exterior parts in the automotive industry.[27]

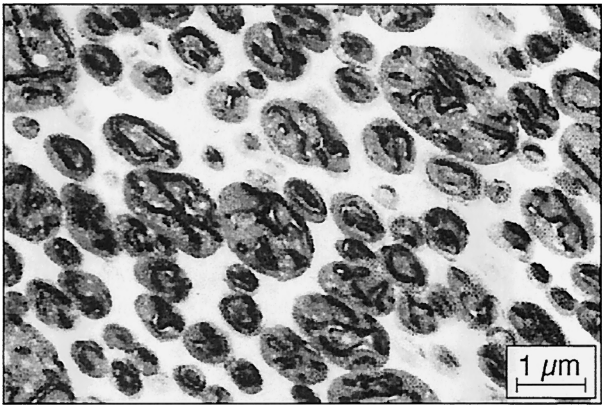

Figure 7. TEM-image of a PA 6,6/PPE/SEBS-alloy stained with RuO_4.

Styrenics/Polyamide-Alloys

The combination of Polyamide 6 (PA 6) and preferably Acrylonitrile-Butadiene-Styrene-Copolymers (ABS) to polymer alloys gives materials with excellent ductility, high chemical resistance and good flow behaviour.[37] Since SAN (matrix of ABS) and PA 6 are completely immiscible, compatibilisation is as well the main issue in these alloys. Also in this system, the compatibiliser can be created in situ, by adding terpolymers consisting of Styrene, Acrylonitrile and Maleic anhydride (MA) to the main components. During the compounding step, the amino end-groups of PA 6 react with the anhydride units of the terpolymer and form graft copolymers consisting of PA 6 grafts and the terpolymer as backbone. Since the amount of MA in the terpolymer is in the area of 1 wt.-%, the terpolymer is completely miscible with the PSAN-phase of the ABS. The optimum performance in terms of ductility is obtained, if a terpolymer with 1 wt.-% of MA is used to create the compatibiliser.[38]

Another prerequisite for the desired combination of toughness and chemical resistance is the bi-continuous morphology of the blends. The TEM-images depicted in Figure 8 show the dark stained Rubber-particles in a grey appearing PSAN-phase and the co-continuous dark grey stained PA 6-phase. To reach this morphology, the amount of PA 6 has to be in the range from 38 to 60 %. These TEM-images also reveal the influence of the terpolymer. The size of the co-continuous structure is significantly reduced by the addition of the terpolymer.

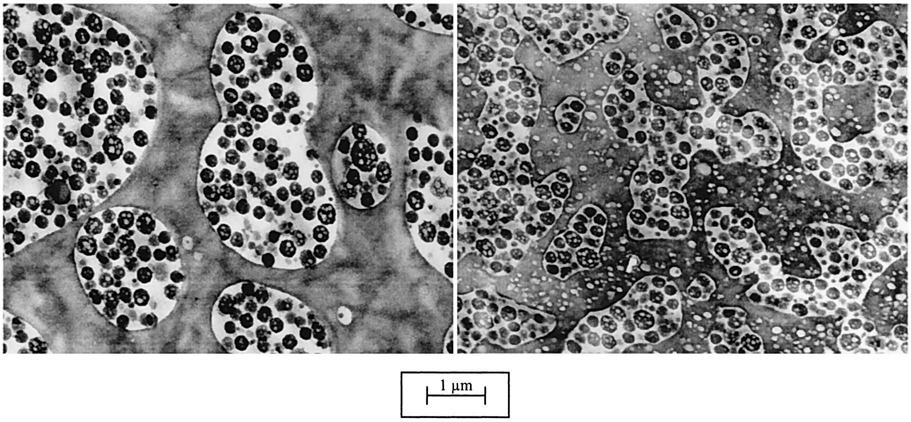

Figure 8. TEM-images of a) ABS/PA 6-blend (left side); b) ABS/PA 6-alloy (right side), staining: OsO_4/PTA (Phosphotungstic Acid).

The already mentioned properties allow the use of ABS/PA 6-alloys for automotive interior applications as well as for bumpers.[37] Further applications can be found in the electrical industry.

Conclusions

Due to the tremendous advantages regarding the investment for product development and production, the blending technology is still used extensively for the development of new materials both in industrial and academic laboratories. Reactive extrusion is already widely used to compatibilise immiscible polymers, several products like PBT/PC/MBS, PPE/PA, and ABS/PA have gained broad acceptance in the plastics industry. As documented by the huge number of appearing patents and articles, the importance of reactive extrusion as economic tool to compatibilise immiscible polymer blends will grow in the future.

Acknowledgements

The contributions of Dr. W. Heckmann and Dr. I. Hennig are acknowledged. The author also wishes to thank B. Cunningham for her technical assistance.

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