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Polymer Blends: Materials with versatile properties

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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. Especially in the area of engineering thermoplastic materials this approach has led to a significant number of large volume products, like Polyphenyleneether/High Impact Polystyrene-blends (PPE/HIPS), Polycarbonate/Styrenics-blends (PC/ABS), Polycarbonate/Polybutyleneterephthalate-blends (PC/PBT) and Polyamide/Polyphenyleneether-alloys (PA/PPE). 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 in industry[1-3].

There are several reasons for the broad acceptance of the blending technology as tool for the development of new materials. In the area of polymeric materials, usually a combination of properties is needed to fulfill 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 behavior (continuous use temperature, heat distortion temperature), processing properties (melt flow, melt stability), electrical properties, chemical resistance and flame resistance have to be considered.

If the development of a new material starts from new monomers or co-monomers, several properties can be optimized to achieve the anticipated performance. The most important properties are the chemical structure, molecular weight and molecular weight distribution, and the chain topology. For the development of new polymer blends, the already mentioned properties can be changed for each blend component, but additionally, the blend composition and in the case of immiscible polymers, also the morphology can be tuned to obtain the desired set of properties.

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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 (Tab. 1).

Table 1. Advantages of the blending technology for the product development

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

The possibilities of the blending technology have already been recognized in the nineteenth century, when T. Hancock applied for a patent, disclosing mixtures of natural rubber and gutta-percha as materials for the improvement of textiles[4]. The further development of polymer blends was of cause related to the availability of new polymers. The main developments in the field of polymer materials are summarized in table 2[2,5].

Especially in the area of engineering thermoplastic materials this approach has led to a significant number of large volume products, like Polyphenyleneether/High Impact Polystyrene-blends (PPE/HIPS), Polycarbonate/Styrenics-blends (PC/ABS), Polycarbonate/ Polybutyleneterephthalate-blends (PC/PBT), and Polyamide/Polyphenyleneether-alloys

Table 2. History of polymer blends, important developments

Year	Polymer Blend	Properties
1846	Natural Rubber/Guttapercha	stiffness/toughness
1942	PVC / NBR	NBR as plasticizer for PVC
1960	PPE / PS	melt processibility
1969	ABS / PVC	processibility, flame resistance
1976	PET / PBT	dimensional stability
1977	PC / ABS	impact strength
1979	PC / PBT	toughness, chemical resistance
1982	PA / Polyolefin	toughness, barrier properties
1983	PA 6,6 / PPE	high HDT
1984	PA / ABS	flow, toughness
1987	PBT / ASA	dimensional stability
1990	PEI / PC	flow
1996	PC / LCP	dimensional stability
1998	PES / PA	mechanical strength

(PA/PPE). The commercial success of these materials is mainly related to their unique combinations of properties, which enables their use in a multitude of applications. The actual consumption of the most important polymer blends already reached the amount of 300.000 t/a (Tab. 3)[6,7].

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[6].

Table 3: 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 / Styrenics	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

The importance of polymer blends for both industrial and academic laboratories is also reflected by the large number of patent applications and publications related to this topic (Fig. 1)[8].

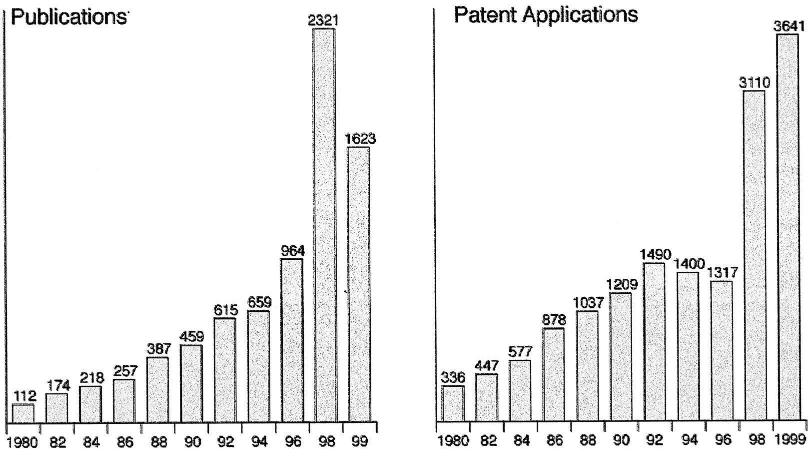

Fig. 1: Number of publications and patent applications related to polymer blends during the period from 1980 to 1999.

Especially during the last five years a tremendous increase in the number of publications as well as the number of patent applications could be observed.

Classification of polymer blends

The multitude of existing polymer blends can be distinguished by their phase behavior. The thermodynamics of polymer-polymer-mixtures can be treated by a simple lattice model$^{9,10)}$. This treatment illustrates the small contribution of the mixing entropy to the free energy of mixing in polymer-polymer-mixtures. Therefore, the enthalpy of mixing is mainly responsible for the miscibility of polymer mixtures. The miscibility behavior of different polymers is subsequently related to interactions between the components, which could be of different nature, for example dipole-dipole-interactions, ionic-interactions or hydrogen bonding$^{11)}$.

Table 4: Classification of polymer blends

blend type	**systems**
miscible	PPE/PS, PVC/PBT
compatible	PC/SAN; PBT/SAN, PES/PC
immiscible	PS/PB; PA/SAN; PA/PPE; PA/PP; PS/PE
alloy	PPE/PA; PA/ABS; PC/PBT

The whole number of polymer blends can therefore be divided in four groups (Table 4).

The first group that has to be mentioned are the miscible blends, where the chain segments of the different chains are miscible on a molecular level. Such kinds of blends have only a single glass transition temperature (Tg), which mainly depends on the composition (Fig. 2a). PPE/PS (Polyphenyleneether/Polystyrene)-blends are considered to be the most important example for the group of miscible blends.

Systems that are either partially miscible or completely immiscible, but offer attractive performance are often designated as compatible polymer blends. These blends usually have two glass transition temperatures, which may slightly deviate from the Tg´s of the blend components (Fig. 2b). The deviation of the glass transition temperatures from the Tg´s of the blend components might be different and depend on the partial miscibility of each component in the other. On a microscopic scale these polymer blends have a phase separated structure (morphology) which could be of different nature, depending on the composition of the blends. Usually the major component forms the matrix phase, wherein particles of the minor phase are dispersed. In the area of the 1/1-mixture, a bi-continuous morphology may exist.

The size of the dispersed particles is related to the interfacial tension and the viscosity ratio between the matrix and the dispersed phase12). Usually the particle size of the dispersed phase is in the range of 1 to 5µm. The most popular system belonging to this group are PC/Styrenics-blends.

The largest group are the immiscible blends, having 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 (Fig. 2c). Immiscible polymer blends usually have a coarse morphology with particles of a size up to several microns.

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

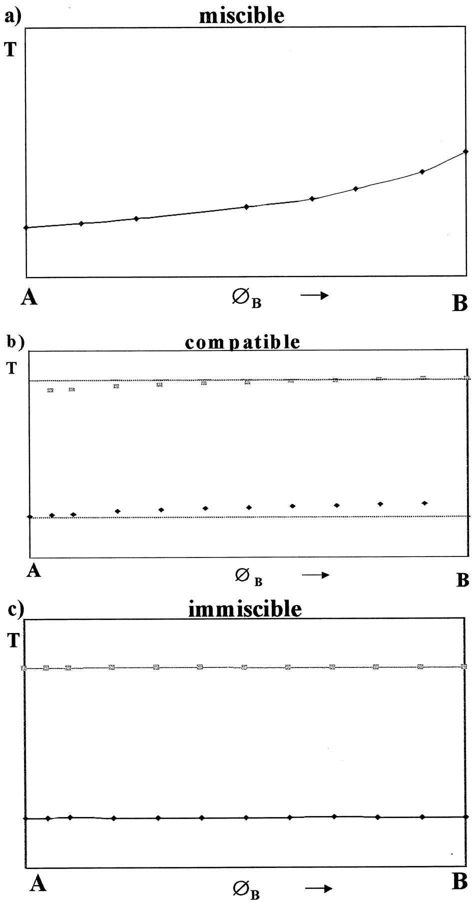

Fig. 2: Tg/composition-relationship for miscible, compatible and immiscible polymer blends

The morphology of immiscible blends can be modified by the addition of compatibilizers, which act like emulsifiers in oil/water mixtures. In polymer blends the compatibilizers 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 compatibilizer acts as polymeric surfactant, reducing the interfacial tension between the immiscible polymers, which results in a significant size reduction of the dispersed particles (Fig. 3). Since the surface of the dispersed particles is covered by the compatibilizer, 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[13-15].

In the bulk state, the compatibilizers provide a strengthening of the interface, which is an important issue for the toughness of multiphase materials[16-18].

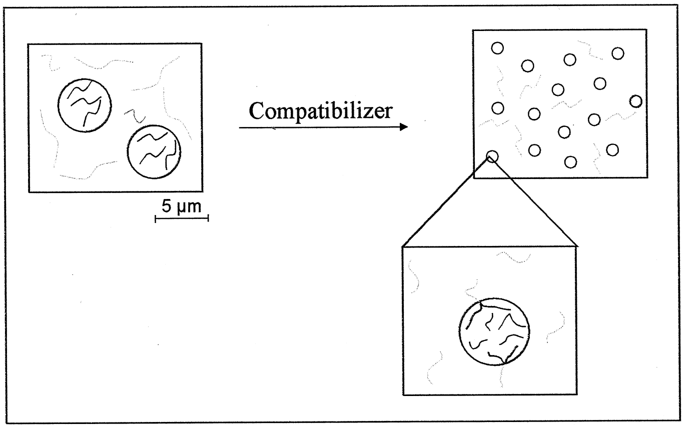

Fig. 3: Schematic representation of the compatibilizing effect of graft copolymers

Important Engineering Polymer Blends and Alloys

Polyphenyleneether/High Impact Polystyrene-Blends (PPE/HIPS-Blends)

Since 1960 it was known, that Polyphenyleneether and Polystyrene form homogeneous polymer mixtures[19]. By the addition of Polystyrene it was possible to improve the processibility of Polyphenyleneether and use these mixtures as thermoplastic materials[20,21]. Already in 1965 PPE/PS and PPE/HIPS-blends were commercialized by General Electric Plastics (Noryl®).

All PPE/PS-mixtures have a single glass transition temperature, which depends on the blend composition[22]. This behavior allows the adjustment of the heat distortion temperature of PPE/HIPS-blends by the simple variation of the blend composition. Therefore, one of the major disadvantages of Polystyrene, the low heat distortion temperature of approximately 90°C, can be significantly improved by the addition of PPE. Actually, some of the available PPE/PS-blends offer heat distortion temperatures of up to 190°C.

In order to improve the ductility and solvent resistance of PPE/PS-blends usually HIPS is used as blend component in commercial products. Therefore TEM-images of PPE/HIPS-blends mainly reveal the structure of the rubber particles (Fig. 4) of the HIPS-component. The further addition of Styrene-Butadiene-block copolymers (SB, SBS) or hydrogenated block copolymers (SEBS) is another tool to improve the toughness of these materials.

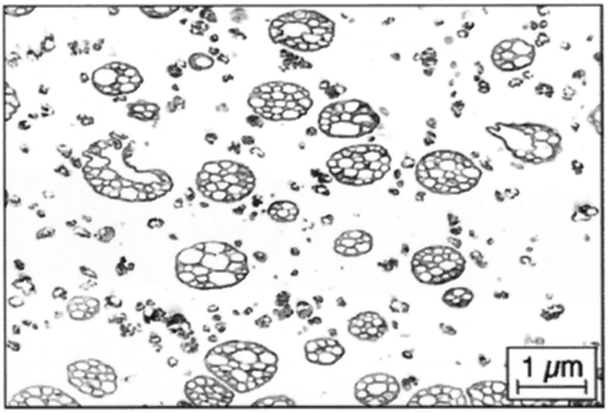

Fig. 4: TEM-image of a PPE/HIPS-blend stained with OsO_4

One of the major advantages of Polyphenyleneether is the low flammability. This property is maintained in the PPE/HIPS-blends to a large extent, therefore the addition of just 5 to 10 wt.-% of phosphate esters allows the production of materials with low flammability. These formulations fulfill the Underwriter Laboratories burning tests (UL 94) without the further addition of halogenated additives. This property is a prerequisite for the use of PPE/HIPS-blends in electrical and electronics applications.

As completely amorphous materials PPE/HIPS-blends also offer high dimensional stability, which allows the use up to temperatures near the glass transition temperature of the particular product without significant dimensional changes. Other advantages of PPE/HIPS-blends are the low moisture uptake and the good hydrolytical stability.

Due to this interesting combination of properties, PPE/HIPS-blends are excellent materials for a broad range of applications. The initial properties can be further diversified by the addition of fibers or fillers to enhance the stiffness and strength, or by the incorporation of other additives (anti-static agents etc.). Main fields of applications are any kind of housings in the electrical industry, automotive interior (dash board, radiator grills), machinery (pumps parts etc.).

Polycarbonate/Styrene-Copolymer-Blends (PC/Styrenics-Blends)

Although Polycarbonate (PC) and Poly(styrene-co-acrylonitrile) (PSAN) are immiscible or only partially miscible, the mechanical properties of appropriate rubber toughened blends are excellent and exceed some of the properties of the blend components to a certain extend5).

PC/ABS-blends were first commercialized (Cycloy®) in 1967. Compared to Polycarbonate, PC/ABS-Blends offer improved processibility, chemical resistance and toughness. On the other hand, the heat distortion temperature as well as the toughness of the ABS is substantially improved by the addition of Polycarbonate5).

Different interpretations for the phase behavior of PC/PSAN-blends can be found in the literature. By DSC-measurements, usually a small reduction of the PC glass transition temperature and a small increase of the PSAN Tg can be detected for PC/PSAN-mixtures. While some authors count this behavior as an indication for partial miscibility23,24), other publications discuss about the influence of low molecular PSAN and PC for this result25,26).

The phase behavior is also influenced to a certain extend by the AN-content of the PSAN. The best phase adhesion between PSAN and PC is observed with PSAN having an AN-content of about 25 wt.-%25).

Due to the phase separated structure of PC/PSAN-blends there is no linear relationship between the heat distortion temperature and the composition of the materials. The heat distortion temperatures of the blends are determined by the nature of the matrix phase. If the PC-content exceeds 55 - 60 wt.-%, PC forms the matrix phase (Fig. 5, grey) wherein the ABS-particles are dispersed. In the dispersed ABS-phase the PSAN-matrix and the rubber particles (dark spherical particles) can be distinguished (Fig. 5). Most commercial products have this kind of morphology, which also gives rise to the high impact strength of these blends5).

As PPE/HIPS-blends, PC/ABS-blends also offer low flammability. In order to pass the UL-94 burning tests, Phosphate esters (Triphenylphosphate, Resorcinoldiphenyldiphosphate, etc.) are applied as flame retardants with loadings up to 15 wt.-%. Since these compounds are miscible with PC as well as ABS, the Tg's of both phases are significantly suppressed, leading to a reduced heat distortion temperature. For certain applications a high heat distortion temperature (> 125°C) is necessary, therefore also products with halogenated flame retardants are available on the market. As halogenated flame-retardants brominated Polycarbonates or Polyhydroxyethers are used.

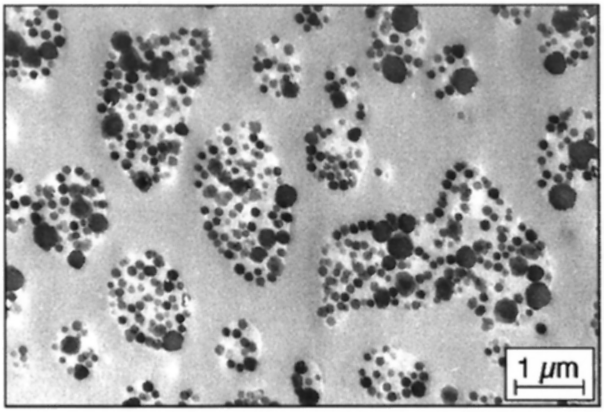

Fig. 5: TEM-image of a PC/ABS 60/40-blend stained with RuO_4

Due to the high ductility of PC/ABS-blends, these materials are widely used for automotive applications like automotive interior, mirror housings, panels, spoilers.

A major drawback of PC/ABS-blends is their low weatherability, which is of course due to the presence of Polybutadiene rubber. To improve this deficiency, other kinds of PC/Styrenics-blends were developed. In these blends, rubbers without olefinic double bonds (Acrylate-rubber: ASA, Ethylene-propylene-rubber: AES) are used as impact modifier. Especially the PC/ASA-blends have excellent weatherability and can be used for out-door applications.

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

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. Both polymers are immiscible, but since PBT contains traces of titanium-catalysts from the polycondensation process, transesterification reactions between the two polymers lead to the formation of

Polyestercarbonates during the melt mixing process[27-29]. The 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.

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[30,31].

The influence of the transesterification inhibitors can be seen from DSC measurements and TEM-images (Fig. 6 and 7). In figure 6 the DSC-traces of a PC/PBT/MBS-blend 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-blend without transesterification inhibitor (Fig. 7, 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 7, the MBS-rubber in PC/PBT/MBS-blends is exclusively located in the PC-phase. The MBS-rubber mainly boosts the low temperature impact performance of these blends.

Due to the excellent balance of properties like high toughness, good dimensional stability, high heat distortion temperature and good flow properties, PC/PBT/MBS-blends are used for large exterior parts in the automotive industry.

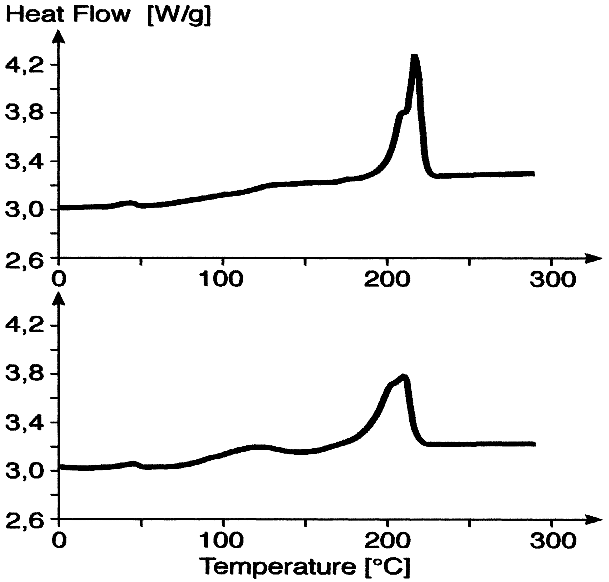

Fig. 6: DSC-traces of PC/PBT/MBS 48/42/10-blends after three heating cycles from 30°C to 290°C with a heating rate of 20 k/min; lower picture) without transesterification inhibitor, upper picture) with 0,5 wt.-% of Tetrakis-(2,4-di-tert.butylphenyl)-4,4′-diphenylenediphosphonite

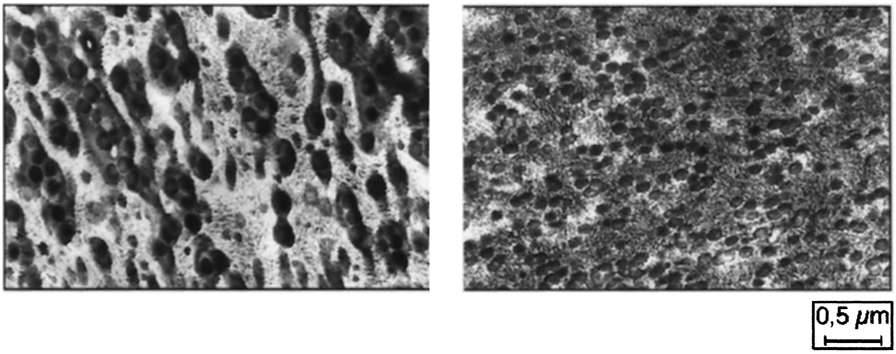

Fig. 7: TEM-images of PC/PBT/MBS 48/42/10-blends after three heating cycles from 30°C to 290°C with a heating rate of 20 k/min; right side) without transesterification inhibitor, left side) with 0,5 wt.-% of Tetrakis-(2,4-di-tert.butylphenyl)-4,4′-diphenylenediphosphonite

Polyphenyleneether/Polyamide-Alloys

Another combination of amorphous and semi-crystalline polymers are the Polyphenyleneether/Polyamide-alloys (PPE/PA). As already discussed previously, PPE offers several interesting properties like high glass transition temperature, low moisture uptake, and high dimensional stability. 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.

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 compatibilizer. Several different ways to compatibilize PPE and PA 6,6 are described in the literature[32-35)]. The most interesting way is the use of modified PPE, which is obtained by grafting of functionalized species like Maleic anhydride or Fumaric acid 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. This process leads to a significant decrease of the particle size of the dispersed PPE-particles as can be seen from figure 8. 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 boost the toughness of the system, these alloys furthermore contain hydrogenated Styrene-Butadiene-Styrene-block copolymers. Due to the presence of the Styrene-blocks, these impact modifiers are located exclusively in the dispersed PPE-particles (Fig. 8).

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 molded 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[5,36)].

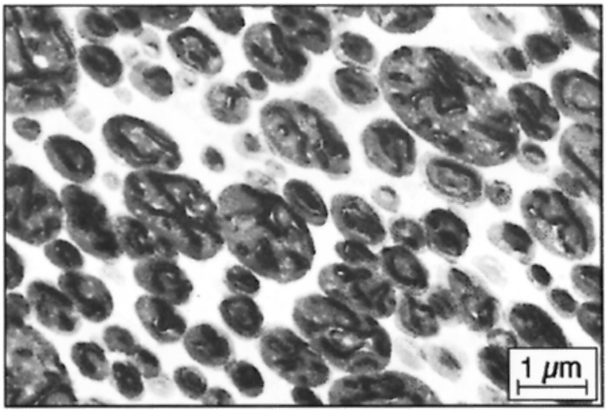

Fig. 8: TEM-image of a PA 6,6/PPE/SEBS-alloy stained with RuO_4

New Developments

During the last years several new polymer blends appeared on the market. As examples PC/LCP-, PES/PA- and PEI/PET-blends will be discussed briefly.

The combination of Polycarbonate and a thermotropic liquid crystalline Polyester (LCP) yields materials with excellent dimensional stability and good flow. Due to these properties, PC/LCP-blends can be used as materials for connectors, where requirements regarding to dimensional accuracy, heat distortion, and melt flow have to be fulfilled37).

Fiber reinforced blends of Polyethersulfone (PES) and Polyamide offer excellent mechanical strength and high melt flow. The good heat resistance of PES is still maintained in these products. Compared to PES, PES/PA-blends offer a significantly improved performance/price-ratio. Fiber reinforced PES/PA-blends are appropriate for under the hood-applications in the automotive industry38).

Mixtures of the high performance polymer Polyetherimide (PEI) and Polyethylene-terephthalate are marketed under the tradename Ultem ATX. Compared to pure PEI, this material offers improved chemical resistance, higher melt flow and of course a significant cost reduction39).

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. In the area of engineering thermoplastic materials several products (PPE/HIPS, PC/ABS, PC/PBT/MBS, PA/PPE) have already reached large sales volumes, but most of these products still grow faster than the usual engineering plastics. This is of cause due to their unique combinations of properties and the large number of possibilities to fine tune the overall performance.

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References

1. D.R. Paul, S. Newman, *Polymer Blends*, Academic Press, New York 1978
2. L.A. Utracki, *Polymer Alloys and Blends*, Hanser, München, Wien, New York 1989
3. L.A. Utracki, *Encyclopaedic Dictionary Of Commercial Polymer Blends* ChemTec Publishing, Toronto 1994
4. Engl. Pat. 11,147, (1846) T. Hancock
5. L. Bottenbruch, *Technische Polymer-Blends,* Kunststoff-Handbuch 3/2, G.W. Becker, D. Braun (Eds.), Hanser, München, Wien 1993
6. H. Warth, D. Wittmann, *Kunststoffe* 10/**89**, 126 (1999)
7. J. Braat, J. Liska, *Kunststoffe* 10/**89**, 118 (1999)
8. Literature survey with CAS, M. Wijnands, BASF, March 2000
9. M.L. Huggins, *J. Chem. Phys.* **9**, 440 (1941)
10. P.J. Flory, *J. Chem. Phys.* **9**, 660 (1941)
11. O. Olabisi, L.M. Robeson, M.T. Shaw, *Polymer-Polymer-Miscibility* Academic Press, New York 1979
12. S. Wu, *Polym. Eng. Sci.* **27**, 335 (1987)
13. C.E. Scott, C.W. Macosko, *J.Polym. Sci., Part B* **32**, 205 (1992)
14. C.E. Scott, C.W. Macosko, *Polymer* **35**, 5422 (1994)

15. A. Nakayama, T. Inoue, A. Hirao, P. Guegan, P. Khandpur, C.W. Macosko, *Polym. Prepr.* **34**(2), 840 (1993)
16. H.R. Brown, *Macromolecules* **24**, 2752 (1991)
17. C. Creton, E.J. Kramer, G. Hadziioannou, *Macromolecules* **24**, 1846 (1991)
18. J. Washiyama, C. Creton, E.J. Kramer, *Macromolecules* **26**, 2928 (1993)
19. US 3,063,851 (1962), General Electric, E.M. Boldebuck
20. F. E. Karasz, W.J. MacKnight, J. Stoelting, *Polym. Prepr. Chem. Soc. Div. Polym. Chem.* **14**, 357 (1970)
21. W.J. MacKnight, J. Stoelting, F.E. Karasz, *Adv. Chem. Ser.* **99**, 29 (1971)
22. W.M. Prest, R.S. Porter, *J. Polym. Sci. Polym. Phys. Ed.* **10**,1639 (1972)
23. J.D. Keitz, J.W. Barlow, D.R. Paul, *J. Appl. Polym. Sci.* **29**, 3131 (1984)
24. R.A Mendelson, *J. Polym. Sci., Polym. Phys. Ed.* **23,** 1975 (1985)
25. T.A. Callaghan, K. Takakuwa, D.R. Paul, A.R. Padwa, *Polymer* **34**, 3796 (1993)
26. M.J. Guest, J.H. Daly, *Eur. Polym. J.* **25**, 985 (1989)
27. J. Devaux, P. Godard, J.P. Mercier, *J.Polym.Sci., Polym. Phys. Ed.* **20**, 1875 (1982)
28. J. Devaux, P. Godard, J.P. Mercier, *J.Polym.Sci., Polym. Phys. Ed.* **20**, 1895 (1982)
29. A.N. Wilkinson, S.B. Tattum, A.J. Ryan, *Polymer* **38**, 1923 (1997)
30. A. Golovoy, M.-F. Cheung, K.R. Carduner, M.J. Rokosz, *Polym. Eng. Sci.* **29**, 1226 (1989)
31. EP 683 200 (1995) General Electric, R.C. Crosby, L.I. Flowers, R.R. Odle, J.L. De Rudder, Y.-G. Lin
32. US 4,315,086 (1982), Sumitomo Chemical Company Ltd., K. Ueno, T. Maruyama
33. US 4,338,412 (1982), Sumitomo Chemical Company Ltd., K. Ueno, T. Maruyama
34. EP 129 825 (1985), General Electric, V. Abolins, J.E. Betts, F.F. Holub
35. US 5,357,003 (1994), General Electric, H.J.E. Smits, R. van der Meer, A.H.L. Groothius
36. C. Verpy, J.L. Gacougnolle, A. Dragon, A. Vanlerberghe, A. Chesneau, F. Cozette, *Progr. Organic Coatings* **24**, 115 (1994)
37. M. Roemer, A. Neupauer, *Kunststoffe* **86**, 1310 (1996)
38. M. Weber, U. Eichenauer, J. Queisser, *Kunststoffe* **88**, 1472 (1998)
39. M.Huff, *Polymer News* **22**, 290 (1997)