Heterophasic Copolymers of Polypropylene: Development, Design Principles, and Future Challenges

Markus Gahleitner, Cornelia Tranninger, Petar Doshev

Borealis Polyolefine GmbH, Innovation Headquarters, Sankt Peterstrasse 25, 4021, Linz, Austria
Correspondence to: M. Gahleitner (E-mail: markus.gahleitner@borealisgroup.com)

ABSTRACT: Initially developed to overcome the limited low-temperature impact resistance of polypropylene (PP) and allow its application in subzero temperatures, the PP/elastomer blends became a very important and industrially relevant material class. Within the last 40 years, a whole range of PP impact copolymers from multireactor processes have been developed that are capable of covering wide application areas. This review summarizes their developmental history and presents options for the in-reactor design of these polymers and their modification by compounding with elastomers and fillers or reinforcements after the polymerization. An overview of the application range is also presented together with a glimpse into the future of this material class. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION: A BRIEF HISTORY OF HIGH-IMPACT POLYPROPYLENE (PP) COPOLYMERS

Soon after the revolutionary discovery of low-pressure polymerization in the early 1950s, the commercial production of high-density polyethylene (HDPE; by Hoechst in Germany) and isotactic polypropylene (iPP; by Montecatini in Italy) were taken up.[1] Although the stiffness and heat resistance of these polymers, which were related to their high crystallinity, were appreciated in the market, questions of toughness and impact resistance appeared soon enough. For HDPE, random copolymerization with higher α-olefins 1-butene or 1-hexene resulted in the desired improvement because the low glass-transition temperature (T_g) of polyethylene (PE) was not limiting the application range. For iPP, a different approach had to be found because the polymer's T_g at about 0°C practically prevented application in subzero environments. The addition of certain amounts of an elastomeric component in a disperse-phase structure turned out to serve the purpose, adding a whole set of new design parameters to the development of iPP.

Compounding, that is, the melt mixing of iPP homopolymers with different amounts of externally produced elastomers, such as ethylene–propylene rubbers (EPRs) or ethylene–propylene–diene elastomers (EPDM) based on vanadium catalysts, were used for this purpose exclusively until the mid-1960s.[2,3] In the third section, the ongoing importance of modifying products after the reactor by compounding are discussed in detail.

Until that time, the use of slurry-type processes with hexane or similar hydrocarbons made the production of propylene-based copolymers with low crystallinities difficult as these would have dissolved at least partly in the reaction mixture.

The next step in terms of both efficiency and performance were products commonly referred to as *block copolymers* from multireactor gas-phase plants, such as the Novolen process,[4] or from bulk/gas-phase combinations, such as the Spheripol[5] or Borstar PP processes. These combine a crystalline PP matrix (produced in the first one or two reactors) with embedded particles of EPR and PE (produced in one or more of the following reactors) defining impact and low-temperature resistance.[6] The correct term for such products is *heterophasic copolymers* (HECOs) or PP impact copolymers; the latter term is used throughout this article.

Decisive for the further development of these products were both the flexible polymerization processes and the continuously improved catalysts. With second-generation Ziegler–Natta (ZN) catalysts still using a combination of solid $TiCl_3$ with $Al(C_2H_5)_2Cl$, it became possible to produce technical copolymers with a moderate EPR content. The commercial introduction of the third generation of ZN catalysts (i.e., $MgCl_2$-supported $TiCl_4$ with ester-type internal donors) at the end of the 1970s, together with the breakthrough of bulk processes for polymerization without solvents finally enabled the synthesis of impact copolymers with very high impact strengths.[7,8] Figure 1 schematically shows the development of polymer particles for
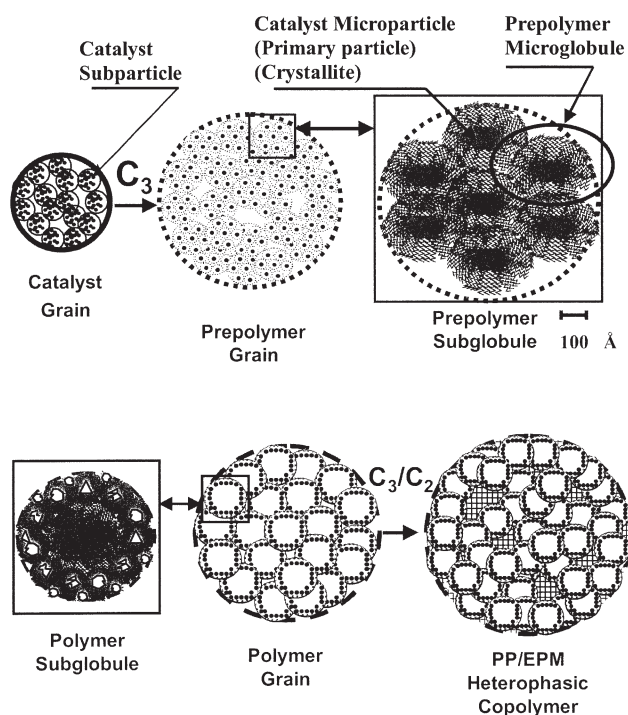
Figure 1. Powder particle growth mechanism for a PP impact copolymer over a spherical MgCl$_2$/TiCl$_4$ catalyst: prepolymerization, matrix polymerization, and ethylene/propylene copolymerization (C3 - propylene, C2 - ethylene). Reprinted with permission from ref. [5]. Copyright 2013 Wiley.

such PP impact copolymers based on the morphology of the catalyst as presented by Cecchin et al.[5] In the second section, the details of this development and the possibilities for polymer design are presented.

Over time, PP impact copolymers have conquered a wide range of applications, from seemingly trivial packaging uses to technically complex parts, as the fourth section shows. However, the development never stops, and although future achievements will depend on the availability of new catalyst generations giving better control over the molecular weight distribution and comonomer incorporation, developments in processing technology will further support this advance (see the fifth section).

IN-REACTOR DESIGN

The in-reactor production approach has shown to be more effective for the manufacturing of impact-modified PP. Beyond the evident energy savings due to the elimination of the compounding step, morphology and performance advantages are achieved as well. Indeed, in comparison to mechanical blends, the structure of reactor blends have been shown to be rather complex. In addition to the PP matrix and the amorphous EPR, they can also comprise crystalline copolymers having both PP and PE crystallizable segments and even neat HDPE. The elucidation of this complex structure has been progressing through a combination of cross-fractionation with various thermal, spectroscopy, and chromatography techniques correlating the molecular structure to the performance of these materials.[9–14] The compositional heterogeneity of PP impact copolymers strongly influences the phase behavior and interfacial adhesion

between the matrix and the dispersed phase.[5,15,16] Heterophasic PP copolymers could be regarded as sort of mechanically and physically compatibilized systems rather than simple blends.

The design window of PP impact copolymers from both technological and economic perspectives is defined by the capabilities of the catalyst and the polymerization process that are used.[5,7,17] These can support and compensate each other. The PP and EPR microstructures (tacticity, stereoregularity, comonomer distribution, and molecular weight capability) are mainly defined by the catalyst system. In case of ZN catalysts, this is governed by the catalyst, cocatalyst, internal and external donors, and most importantly, the interaction thereof. The main variables for single-site catalysts (SSCs) are the metallocene (MC) complex and the cocatalyst.

There are well-reported correlations between the degree of matrix isotacticity, degree of crystallinity, and stiffness of iPP.[18,19] The higher molecular weight of both the matrix and the disperse phase results in a higher toughness of the impact PP under plain strain loading.[20–22] Where the comonomer and molecular weight distribution are concerned, copolymers produced by means of ZN catalysts, although homogeneous with regard to the intramolecular sequence distribution, mostly exhibit heterogeneity as far as the intermolecular distribution is concerned.[23] Moreover, the broadening of the molecular weight distribution of the PP matrix has beneficial effects on the stiffness[24] and drawability[25] of the copolymers. The effects were attributed to changes in the nucleation density and the number of tie molecules, respectively.

SSC systems, on the other hand, render homogeneous distribution on both the intermolecular and intramolecular levels; this results in improvements in the purity and optical properties. However, there are hardly any scientific articles describing PP impact copolymers produced by SSCs, and these materials have still limited market penetration (see the fifth section).

A further key feature of the catalyst is its morphology (particle shape, size, distribution, and porosity). In particle-forming polymerization processes, as used for the production of impact PP, the morphology of the produced polymer particles replicates the morphology of the used catalyst particles. Uniform spherical or globular catalyst particles are, therefore, advantageous for the production of free-flowing polymer particles. This is typically achieved by the immobilization of the active catalytic components on an inert support forming a so-called heterogeneous catalyst. For PP catalysts, spherical aggregates of microcrystalline MgCl$_2$ are conventionally used as support materials;[5,7] they offer a porous structure with a large surface area. The maximum amount of elastomer that can be accommodated in the polymer granule without causing stickiness appears to primarily depend on the porosity of the catalyst particle. Existing technologies (Catalloy, Basell) enabled the production of heterophasic ethylene–propylene copolymers with up to 80 wt % EPR; this offered an alternative to plasticized poly(vinyl chloride) (PVC) or thermoplastic elastomers.[26] Figure 2 shows the difference in distribution of the EPR phase between the original reactor powder (defined by the catalyst structure) and the pelletized or processed polymer.
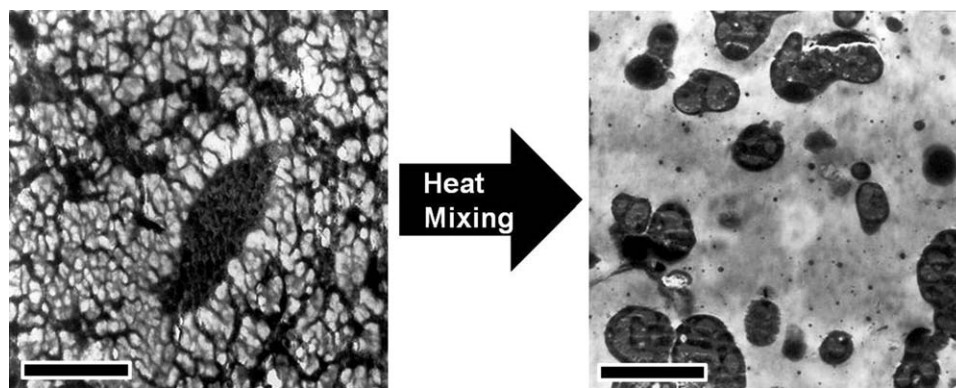
Figure 2. Relation between the powder morphology (left) and granule morphology (right), as shown by RuO$_4$-contrasted transmission electron microscopy. This was a high-impact EP copolymer type with 26 wt % ethylene and 22 wt % elastomer (EPR, xylene-soluble fraction). EPR was dark because of its lower crystallinity, and the PP matrix and PE inclusions in the particles were light (scale bars = 2 μm).

Recently, a novel approach for the preparation of polymerization catalysts was described.[27,28] In this case, the solid support was formed during the catalyst preparation process as an integral part of the catalyst particle. Such self-supported catalysts are regarded as offering better morphological control and a more uniform distribution of the active species over the catalyst particle.

Similar to heterophasic systems in general, tailoring the morphology of the PP impact copolymers is the key to tailoring the performance. The size, shape, internal structure, and spatial packing of the dispersed domains are critical parameters affecting not only the mechanical performance but also properties such as the surface appearance, transparency, and migration. The morphology is a complex result of the rheological parameters of the single components, the matrix/dispersed-phase compatibility, and the processing conditions. Variation of the EPR composition has been shown to affect all three.[29–32] Propylene-rich EPR, because of its reduced interfacial tension against the PP matrix, gives rise to a fine dispersion.[33,34] Such materials demonstrate very good impact properties at ambient temperatures both under plain strain and plain stress conditions.[35] Moreover, they exhibit a very good transparency, low shrinkage, and high morphology stability during further processing steps. Next to the good chemical affinity between the PP matrix and dispersed phase, the effect is also ascribed to a partial dissolution of a certain amount of the propylene-rich EPR in the amorphous region between the PP lamellae. Parallel to this, a shift in the T_g of the EPR toward higher temperatures and the T_g of the PP toward lower temperatures was observed with increasing propylene content of EPR; there was also a significant effect on the stiffness (modulus and yield stress, see Figure 3).[31] Because of the relatively high T_g, such systems are less suitable for use at very low temperatures (i.e., $< -10°C$).

On the other hand, EP copolymers with an ethylene content above 50 wt % in the EPR comprise a crystalline PE fraction, incorporated as inclusions in the amorphous EPR domains to form core–shell (single inclusion) and salami-like (multiple inclusions) structures.[10,23,31] PP impact copolymers with an ethylene-rich dispersed phase have a very good low-temperature toughness and exhibit benefits in scratch and stress-whitening resistance. The drawback of such EPR is its tendency toward agglomeration[36] and the fairly high brittle-to-ductile transition temperature.

In term of the mechanical properties, the optimum composition rendering an EPR phase sufficiently immiscible with the matrix to maintain phase separation and adequately miscible to assure proper matrix/dispersed-phase adhesion is reported to be 35–45 wt % ethylene.[32,37]

Variations in the viscosity ratio between the dispersed phase and matrix also have a strong influence on the particle size.[22,32] The optimum particle size depends on the dominant deformation mechanism of the matrix, which in turn is influenced by the test conditions, that is, the temperature and deformation
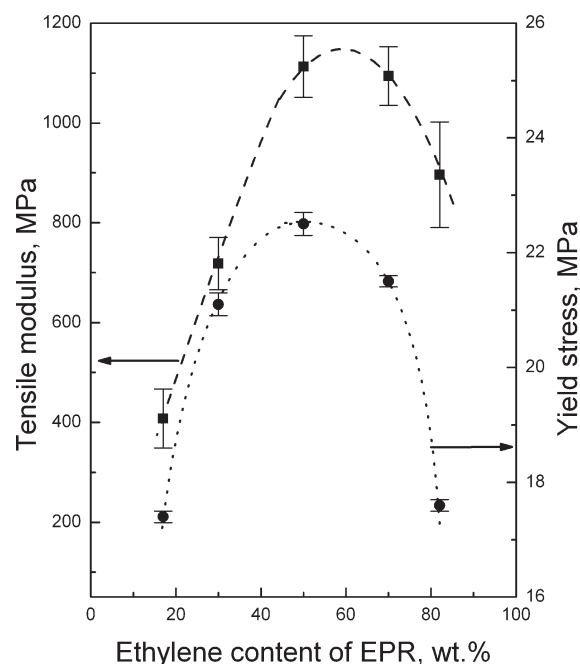

Figure 3. Tensile modulus and yield stress at 23°C as a function of the EPR composition for the PP impact copolymers with a constant matrix and EPR content. Reprinted with permission from ref. [31]. Copyright 2013 Elsevier.

rate (see Figure 4). In PP, both the crazing and shear yielding have been observed to depend on the test temperature and deformation rate. A significant advantage of the PP impact copolymers over mechanical blends is that an intimate mixing of the components can be obtained over a wide range of molecular weights. Indeed, a relatively fine dispersion (weight average particle diameter, $D_w = 0.9–2.0$ μm) was observed in these copolymers at phase viscosity ratios between 3 and 25.[22]

Increasing the EPR weight fraction in PP impact copolymers is another approach for improving the toughness by reducing the interparticle distance and increasing the energy absorption capacity. Indeed, a stepwise brittle-to-tough transition is observed as a function of the EPR concentration, combined with a linear reduction of the tensile modulus.[38–40] Figure 5 presents the respective correlation for the material series of Starke et al.[38] The blend concentration where this transition occurs is determined by the chemical composition of the matrix and the dispersed phase and their viscosity ratio, but it should be noted that this concentration still depends on the geometry and test conditions. For the PP/EPR blends, the phase transition and the respective development of the mechanical performance was comprehensively discussed by Kotter et al.[40]

A trend in the latest decade has been the development of PP systems containing more than two dispersed phases. The design concept of such blends is to choose the minor components in such a way that the advantages of the one to compensate the deficiencies of the other. The benefits of the use of two different elastomers as impact modifiers have also been pointed out in the literature.[29,41] A synergistic toughening of glassy polymers by the combination of two elastomer phases has been reported as well;[42] this was attributed to both the interfacial adhesion and particle size effects. For toughened semicrystalline polymers, the particle size bimodality is expected to have an even stronger influence because of the dependence of the main deformation mechanism on the temperature. As the optimum particle size for the toughening of PP decreases with increasing
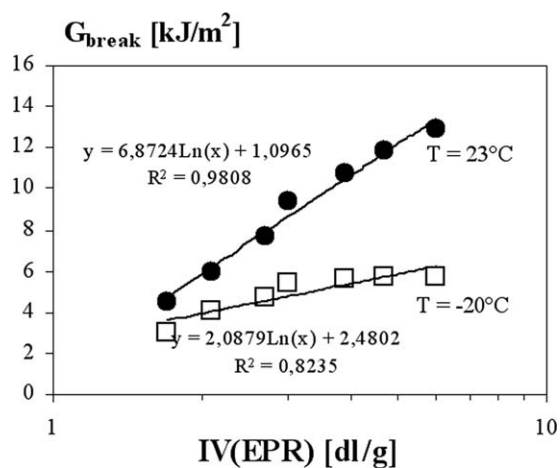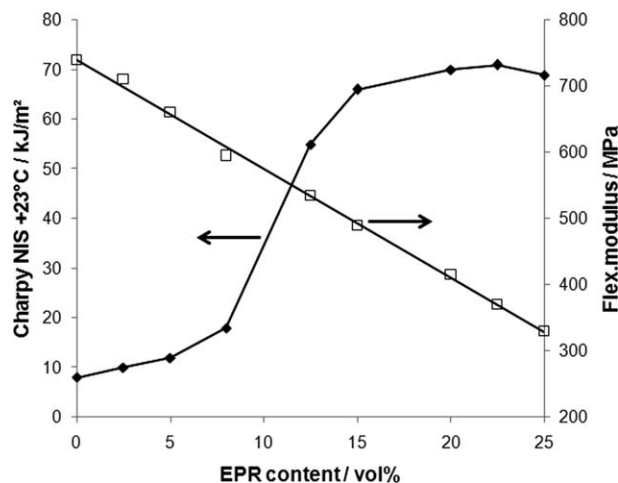

Figure 5. EPR concentration effect on the stiffness (flexural modulus, ISO 178) and toughness (Charpy notched impact strength (NIS), ISO 179 1eA) at 23°C for a series of random HECOs with a constant matrix and EPR composition (data from ref. [38]).

temperature, a bimodality of the dispersed phase size could be a promising approach to ensure toughness over a wide temperature range. Indeed, toughness optimization has been quoted for a combination of PP with EPR and a MC-based plastomer.[43,44]

The advantages of PP-based reactor blends with a bimodal particle size distribution have been suggested in several articles[5,41] and many patents.[45–48] Such materials can be produced directly in a reactor cascade composed of at least three reactors, such as the Borstar or the Spheripol processes. In this way, two EPR phases can be incorporated into a PP matrix differing in composition (EPR_1 and EPR_2) (ethylene/propylene ratio) and/or molecular weight. In accordance with the theory,[49,50] three main types of morphology have been proposed for $PP/EPR_1/EPR_2$ materials (see Figure 6). When the chemical composition of the two EPRs is similar, they are suggested to be mutually miscible and to interpenetrate each other to give a rise to common dispersed domains, with the morphology (Type I) resembling conventional HECOs [Figure 6(a)]. Increasing the gradients in the composition and molecular weight between the two EPRs deteriorates the compatibility and results in two separate disperse phases. In compliance with refs. [49] and [50], two limiting types of phase morphology can be expected: (1) EPR_1 encapsulates EPR_2 and acts as a compatibilizing agent [type II morphology, Figure 6(b)]. The dispersed domains will be smaller than for conventional HECOs with ethylene-rich EPR while they retain their internal structure. (2) Both EPR phases disperse in discrete domains [type III, Figure 6(c)], with one dispersing in significantly smaller domains without internal structure and the other one dispersing as larger core–shell or salami-like particles. A broader or a bimodal particle size distribution is anticipated in case of types II and III morphology.

Indeed, the addition of a second ethylene-rich EPR_2 to an impact PP already containing propylene-rich EPR_1 can be detected by dynamic mechanical thermal analysis, where the presence of EPR_2 is indicated by the development of a second T_g peak at low temperatures; this indicates the presence of two discrete dispersed phases (see Figure 7). In compliance with

Figure 4. Charpy notched impact strength (23 and −20°C) as a function of the EPR molecular weight for a constant matrix and EPR content (IV - intrinsic viscosity, T - temperature, G_{break} - fracture energy). Reprinted with permission from ref. [22]. Copyright 2013 Wiley.
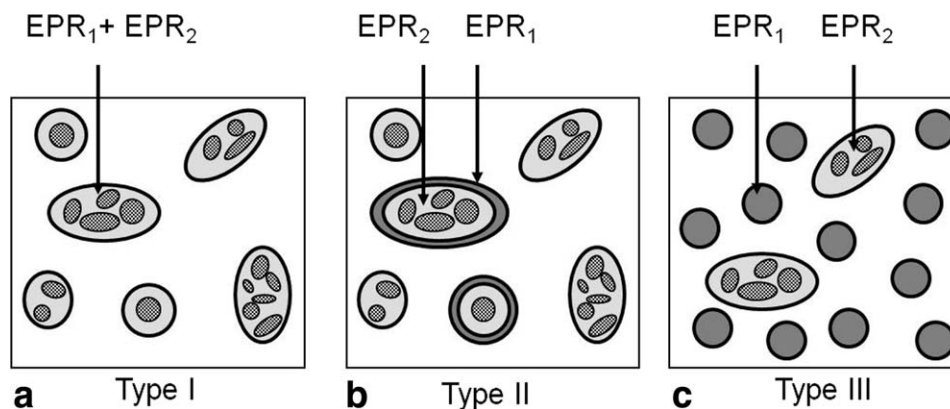
Figure 6. Proposed morphology types of HECOs containing two EPR phases: (a) type I (EPR_1 and EPR_2 interpenetrated each other), (b) type II (EPR_1 encapsulated EPR_2), and (c) type III (discrete dispersion of EPR_1 and EPR_2).

this, bimodal particle size distribution (type III) was also observed by AFM. In addition to the advantages in the mechanical properties, the incorporation of two dispersed phases has been shown to be advantageous for the surface characteristics, such as the transparency, scratch resistance, and gloss of impact-modified PP.[45–48] To characterize such complex systems, recently, a novel 3D mapping of tan δ was presented.[51]

POSTREACTOR MODIFICATION

The addition of external elastomers/plastomers and PE to high-impact PP is a widely known technique, particularly for improving the impact behavior of these materials. Historically, the blending of PP with various impact modifiers, such as EPR, EPDM, or polystyrene-*block*-poly(ethylene-*co*-but-1-ene)-*block*-

Figure 7. Dynamic mechanical thermal analysis curves [storage modulus G' and tan(δ)] of the two different EP impact copolymers: monomodal EPR with xylene solubles (XS) $\approx$ 25 wt % and C2 (XS) $\approx$ 17 wt %, bimodal EPR with (XS) $\approx$ 25 wt % and C2 (EPR_1) $\approx$ 17 wt %, and C2 ($EPR2$) $\approx$ 70 wt % and EPR_1/EPR_2 ratio $\approx$ 80/20.

polystyrene (SEBS), was used to produce impact-modified PP.[23,52,53] Although the development of new polymerization hardware and catalysts allowed the *in situ* preparation of these materials, the resulting heterophasic systems were quite complex in structure; this required advanced analyses to establish the structure–property relationships.[9,10] An alternative approach for analyzing these relations and developing new copolymers is the use of melt-blended model compounds; this would allow the production of heterophasic systems at lower cost and in small quantities.[54–56]

In blends of heterophasic PP with polymeric modifiers, the end-use properties such as the mechanical performance and optical properties strongly depend on the formed phase structure; this depends on structural factors (as for reactor-based systems) and on the processing respectively the compounding step.[57] Commonly used factors to describe these parameters are the viscosity ratio between the dispersed phase and the matrix, the phase compatibility, and the deformation history in processing. The compatibility of polymer blends can be described by the interfacial tension of the components, which can be determined by means of rheology for PP-based systems.[58–60] From rheological investigations of both the components and the compounds, information about partial miscibility[54] and a prediction for the formed core–shell structures can be gathered;[53] the latter study, however, already showed the stability problems of these blends in the form of processing effects (see Figure 7). A partial miscibility of the propylene–ethylene copolymers in the melt was also found by Kamdar et al.,[61] doing small-angle neutron scattering measurements. The higher the compatibility of the components is, the smaller the formed inclusions are; this results in a higher impact strength at room temperature. The effect of PE addition to EPR on the mechanical properties was investigated by Petrović et al.;[62] they observed an increase in the impact strength related to the special particle morphology formed in these materials but also in general to the increased particle fraction (especially when tested above the matrix T_g) as discussed by Kotter et al.[40]

By matching the density of the polymer matrix and inclusions, good optical properties can be achieved, as reported for ternary blends with two types of elastomers by Grein et al.[44] Dependent
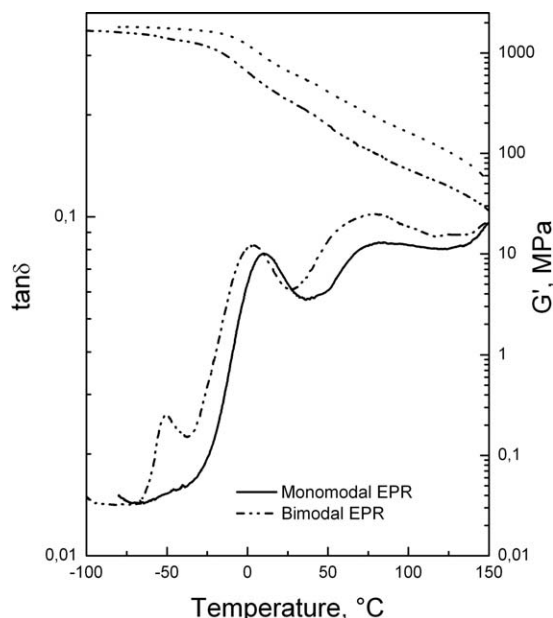
on the amount of disperse phase, the resulting structure can be described as a continuous matrix with distinct modifier inclusions or a cocontinuous structure in which both phases are interconnected. Although the former systems show a balanced mechanical performance, cocontinuous systems exhibit a strong increase in the toughness combined with a major loss in stiffness and might also lead to a decrease in the thermal expansion of the materials.[63,64]

Another possibility is the chemical modification and/or degradation of a reactor grade by the use of peroxides. Depending on the temperature during the radical reaction and the presence of co-agents, grafted PP, branched PP, or degraded PP can be obtained.[65] The peroxide-induced degradation is often used to increase the flow properties of PP. For heterophasic PP, the influence of the EPR design and PE addition on the visbreaking reaction was studied by Sheng et al.[66] They analyzed the effect of the molecular weight of an ethylene-*block-co*-PP on the crystallization behavior, morphology, and fracture behavior after peroxide-induced degradation, whereas a combination of radical modification and recombination in the presence of a coupling agent led to a high-melt-strength PP with long-chain branching when a PP homopolymer was used as the base material. This reaction led to the so-called reactive-modified copolymers when a heterophasic PP was the base material.[65,67] The addition of a free-radical initiator and a co-agent such as a diene causes the formation of ethylene–propylene grafted to PP. This grafted copolymer is thought to strengthen the interface between the PP matrix and the EPR particles and thus reduces the tendency of the particles to agglomerate. These materials show a refined morphology and a strongly increased impact strength.[67]

The use of inorganic fillers in heterophasic PP has been further used to expand the property profile of the materials but also to reduce the formulation cost. Among the most used inorganic fillers for PP are calcium carbonate ($CaCO_3$), talc, and kaolin, whereas wollastonite is used if a high dimensional stability of the compound is required. However, it is not the chemical type or composition of the filler determining the end-use properties of a compound; it is the filler's particle shape and surface area that define the reinforcement quality. The best properties are generally achievable for anisotropic particles of fine particle size equally distributed in the polymer.

$CaCO_3$ is a very cheap filler and leads to only a minimal increase in the polymers' strength, but the compounds generally show a higher impact strength.[68] With kaolin, the reinforcing effect on the stiffness is much stronger, but actually talc is the most commonly used inorganic filler for PP impact copolymers. The compounds exhibit a balanced property profile, including an increased modulus, a higher heat-deflection temperature, and a better dimensional stability.[69] The high reinforcing effect of talc is also caused by the strong nucleation effect.[70] PP–talc compounds may contain up to 50% filler, but the mineral's water absorption can cause surface appearance problems. Additionally, the impact strength decreases with increasing filler content because of the anisotropic nature of the filler.[68] To combine the advantages of different filler types, hybrid composites containing two or more filler types have also been

described in the literature.[71,72] Many attempts have been made to enhance the compatibility of the nonpolar PP with different inorganic filler types, mostly with silane and titanate coupling agents.[72] Also, the use of maleic anhydride grafted polypropylene (PP-*g*-MA)[73] was discussed in the literature.

In contrast to the previously described fillers, the use of high-performance fillers, such as glass fibers (GFs), nanoclays (organically modified layered silicates), or carbon nanotubes, increases the formulation cost of PP compounds. Thus, they are only used when the needed performance levels are not accessible otherwise. When these two classes are compared, it has to be said that PP-based nanocomposites are hardly used commercially because of their high cost and problems in reproducing scientific results on a commercial scale. If nanometer-sized particles are obtained by dispersion, these systems will show improved mechanical, thermal, optical, and physicochemical properties.[74–76] Nevertheless, it is still hard to fully exfoliate nanoparticles, although various methods to increase the affinity and dispersion of nanofillers and PP have been reported.[76–81]

Heterophasic PP copolymers reinforced with GFs are industrially used in the automotive and other technically challenging areas to replace polycarbonate, polyamide, or acrylonitrile–butadiene–styrene terpolymers. Because of the high aspect ratio of GFs, the reinforcing effect is much stronger than with talc. Generally, a higher modulus and heat-deflection temperature but also an increased strength can be realized by this type of filler.[82] However, coupling agents to increase the adhesion between the fiber and the polymer are needed, as well as fiber coating to avoid fiber breakage and further promote the adhesion.[83,84]

Next to standard types, sustainable filler systems, such as wood fibers, flax, or other cellulose-based fibers, become more and more important.[85] Their low cost and low density combined with high specific properties provide advantages over conventional reinforcement materials. The biggest drawback results from their hydrophilic nature, which stands in contrast to the hydrophobic character of PP; this results in incompatibility, a tendency to agglomerate, and poor moisture resistance. Various efforts have been undertaken to develop compatibilization methods for these fibers, where one can distinguish between fiber- and matrix-based compatibilization techniques.[86] Among the fiber-based strategies are fiber treatments with silanes, maleated polyolefins applied to the fibers, mercerization, and acetylization.[87,88] Matrix-based strategies are based on the use of coupling agents that are added during the compounding step. Most of these coupling agents are functionalized polyolefins such as PP-*g*-MA[89] or combinations with MA-grafted SEBS.[90] These compatibilization methods generally lead to a strong increase in the strength (tensile and or flexural) of the compound and no effect or a slight increase in the moduli.[88,91] The relatively low impact strength of these compounds has to be seen as the main weak point of these compounds. Possible solutions were presented by Wu et al.[87] through the use of an SEBS-*g*-MA copolymer as a compatibilizer combined with fiber pretreatment and by Yeh et al.[90] via a synergistic effect of SEBS-*g*-MA and PP-*g*-MA.

APPLICATIONS

Because of the flexibility of the product design in multistage reactors and the possibilities of postreactor modification, heterophasic PP copolymers serve the demands of various application segments, such as in packaging, automotive, or infrastructure. Additionally, heterophasic PP can be converted by various processes, such as injection molding or extrusion, which can lead to a wide range of products. However, it is of great importance to choose the material and the conversion process carefully because the final properties of the product are in a large part determined by the material morphology, which is in turn is strongly affected by the conversion process.[92,93]

In the packaging sector, injection molding and cast or blown film processes are of high importance. The combination of a high impact strength and rigidity allows the packaging solution to withstand transportation and storage unscathed, and it protects the contents. The development of heterophasic PP, which shows high transparency and gloss also after sterilization, has allowed the use of such materials for flexible packaging solutions such as stand-up pouches.[94] The development of high-purity PP and the debate concerning the adverse effects of plasticizers in plasticized poly(vinyl chloride) (PVC) increased the use of very soft heterophasic PP copolymers in health care applications, such as in medical infusion bags and in packaging for medical instruments.

Heterophasic PP offers, because of its property profile, many advantages over traditional wastewater pipe materials, such as concrete, cast iron, or stoneware, and is thus a widely used material for wastewater and drainage systems. Its morphology allows the material to accommodate extensive deformation without rupture. Additionally, PP pipes are characterized by their high level of abrasion and chemical resistance.[95]

The need of the automotive market for lightweight solutions and safety for passengers and pedestrians can be met with heterophasic PP compounds. Fenders, bumpers, and many automotive interior parts are already being made from these commodity polymers, whereas for automotive exterior parts, a good balance of impact and stiffness combined with paintability is required. Materials used in the interiors of cars must meet additional requirements with respect to surface aesthetics (soft touch, high scratch resistance, and low surface tack) and purity.[96,97] With PP compounds for car body parts, the overall vehicle weight can be reduced significantly, whereas the material is also fully recyclable and facilitates cost-effective production. An example is the innovative Smart Fortwo (see Figure 8), where the originally selected polycarbonate/poly(butylene
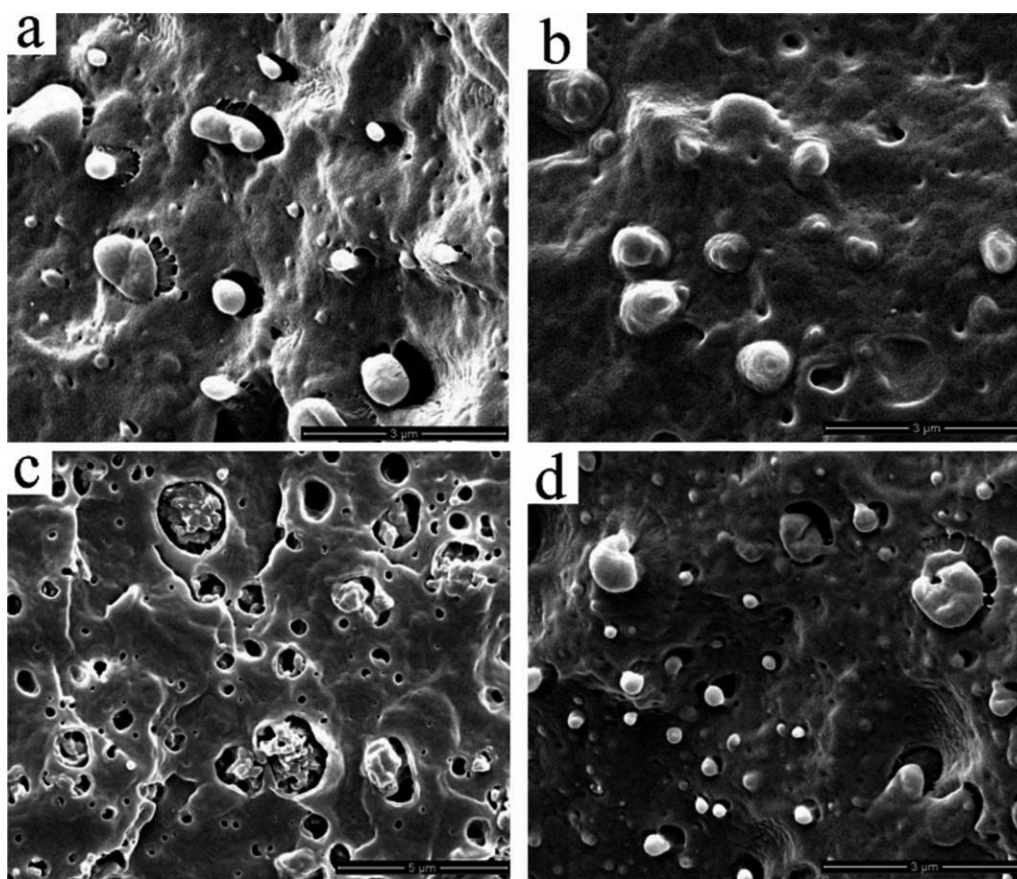

Figure 8. Morphologies of the binary and ternary blends: (a) 90/10 PP/HDPE blend prepared by direct extrusion, (b) 70/20/10 PP/EPDM/HDPE blend prepared by direct extrusion, (c) 70/20/10 PP/EPDM/HDPE blend with EPDM etched by xylene, and (d) 70/20/10 PP/EPDM/HDPE blend prepared by lateral injection molding. Reprinted with permission from ref. [52]. Copyright 2013 Elsevier.

Figure 9. Smart Fortwo, a passenger car with in-color body panels molded from a composite based on a high-impact PP copolymer. Reprinted with permission from Borealis Co (copyright Borealis AG, 2008).

terephthalate) blend, Xenoy from GE Plastics, was replaced by a PP compound some years after market introduction.

FUTURE TRENDS

Although the main goal of incorporating one or more disperse phases into PP is the enhancement of toughness, for end use, it is the property balance that counts. The mutual advancement of different properties, including stiffness, toughness, transparency, and processability, still has to be seen as a challenge. New technical and legal requirements require a steady expansion of the design window and will trigger the development of novel polymer designs that will often require new catalyst systems and/or process modifications.

On the catalyst side, SSC, or specifically MC catalysts, have been used already early in their development to produce PP impact copolymers,[98] but scientific literature in this area is scarce. Although numerous articles have dealt with the impact modification of PP by SSC-based elastomers or linear low-density polyethylene,[44,61,63,91,99] in none of the studies dealing with reactor-based PP impact copolymers involving an MC system is this catalyst used alone. Instead, hybrid catalyst systems with a combination of ZN and MC catalysts have been tested by a number of authors,[100,101] with the main advantage seen in the possibility of using higher α-olefins such as 1-octene[101] for polymer design. A significant expansion of the property window of PP impact copolymers with specific advantages in processability (high melt flow rate (MFR)), emissions, and extractables, can be expected from such approaches in the future.

The development of traditional ZN catalysts is also moving forward, both on the support side[102] and in the area of internal and external donors.[103] For the former, the legal requirements for developing largely phthalate-free catalyst systems will change the scene very soon and will probably also cause major product adaptation needs. However, this could be only one of several challenges to be imposed by stricter environmental regulations, with emissions and extractables being already dealt with for some time.[96]

Creating multimodality in both molecular weight and comonomer distribution becomes more and more a key polymer design

tool. This is practically done by the operation of the series of polymerization reactors under different conditions to expand the product window on both sides of the stiffness/impact curve. Multireactor processes are one option here, but the opportunities by special constructions such as the Spherizone process[104] still remain to be seen, and hybrid catalyst systems could also be an option in the future.

In the area of solid-particle modification, the development of an efficient process for nanoparticle dispersion is an ongoing challenge. Even the *in situ* synthesis of nanocomposites by supporting catalyst components on reinforcing nanoparticles such as carbon nanotubes[105] remains so far without practical application. Although they give far better particle dispersion than melt compounding, the high productivity of modern catalysts is counterproductive here. For reasonable amounts of nanofillers in the final polymer (0.5–2.0 wt %), alternative concepts for catalyst and particle feeding to the reactor would need to be developed, as present residual catalyst amounts in the polymer are less than 0.1 wt %.

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