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# Tailor-Made Polymers Through Selective Modification

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**Summary:** Despite being generally regarded as "mass materials" without a high degree of sophistication in public, plastics are revolutionizing our life with new innovations on a day-to-day basis. While stunning developments like self-healing polymers or high-performance nanocomposites are still in a basic phase of their development, recent years have seen "commodity" materials like polyolefins evolving into performance polymers with a variety of technically demanding applications. This has become possible through a selective modification of the material properties on all structural and productional levels: Catalyst and chain structure, copolymerisation and phase morphology, conventional and reactive compounding, processing and crystallinity. A state-of-art review and an outlook on future developments for polyolefins in general, but polypropylene in particular, is given.

## Introduction

In this paper we will try to give a general outline of the many possible ways in which a polymeric material can be adapted to the demands of the application – and the customer. For achieving this far-reaching target, the content will remain predominantly „superficial", i.e. not going into details and rather presenting characteristic examples than a complete picture. Furthermore, it will be a trip through time and space: from the early days of synthetic polymers to the 21st century, and from the molecule to the construction part level.

## What is a "performance material" ?

Quite frequently, the safety of human life will depend on the performance of a material - but not as obviously as in mountain climbing, where it is literally hanging on a rope. Both material scientists and mountaineers will know about the importance of choosing the right combination of fibers to sustain static or dynamic loads. But this area also teaches us a lesson in terms of relativity: While some of the world's highest mountains were conquered in times of hemp or sisal ropes, even modern materials will break if mistreated or wrongly used. For the term "performance material", which is nowadays mostly associated with materials like Kevlar fibers or titanium, this means that not the material itself, but rather the selection of the right means to fullfill the desired purpose

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will define the "performance".

In polymer science, some people had to learn this lesson the hard way: While the mid-70s were full of enthusiastic forecasts for "high performance plastics" (HPPs) like poly(phenylene sulfide) (PPS), poly(ether-etherketone) (PEEK) or liquid crystalline polymers (LCPs)[1], a glimpse at today's plastics application landscape unveils a completely different picture. As Figure 1 shows, the relative share of HPPs has not increased at all, while the share of "engineering thermoplastics" (ETPs) has even declined slightly. In return, polymers considered "commodities" like polyolefins (mainly polyethylene - PE - and polypropylene - PP) and also polystyrene (PS) expanded their market share and entered completely new application areas.

For the time being, there is no sign of a change in this trend, which was induced by two factors: An increased cost pressure making the price-performance relation for construction materials much more important, and a steady expansion of the property range of these commodity plastics[2]. The various ways to adapt materials to the demands of applications (and ultimately customers) will be discussed in detail in the following chapters; these are not necessarily restricted to mechanical performance.

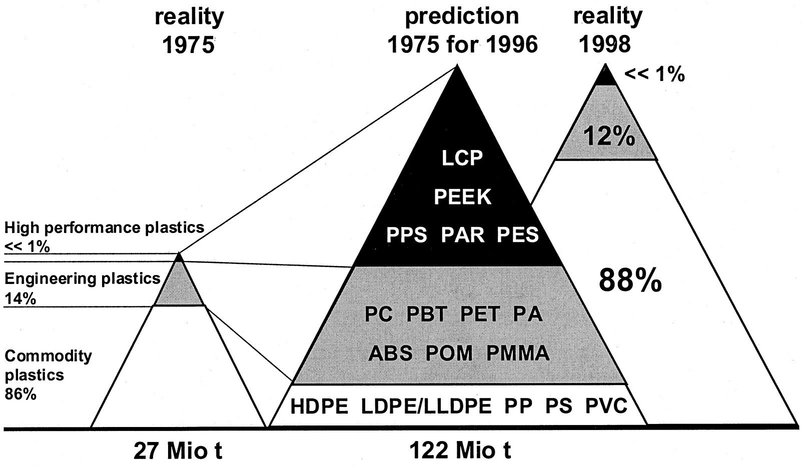


Figure 1. Development of the global market for thermoplastics, projection vs. reality (after ref. [1]).

## From Bakelite to “techno-polymers”

Telephones are a good indicator of technological progress in the past century. For decades, they simply were black. At the same time, they were heavy, sturdy but somewhat brittle, symbols of the material they were made from: Bakelite. This phenolic (PF) resin, developed by Henry Baekeland in 1907[3], was the first fully synthetic polymer to appear on the scene. The fact that it lacked thermoplasticity did not hinder it to stay for a long time, and even today there are households in this world where essential parts of the electrical system are made from PF resins.

Today's phones are different, the symbol of the last years of the 20th and the first ones of the 21st century is the cellular phone. Light, yet robust, colourful and "handy" due to their size they are definitely also reflecting the capabilities of the polymers they are made from: Polycarbonate (PC), acrylic copolymers like Acrylonitrile-butadiene-styrene terpolymer (ABS) and blends of these with other ETPs. In the time between, polymers have made their way into outer space and back (like carbon-fiber composites originally developed for spacecraft reentry insulation and now used from fishing rods to Formula One racing cars), they have revolutionized war and peace (like polytetrafluoroethylene - PTFE - an accidental development that helped in building the first nuclear bomb and is now covering millions of frying pans worldwide)[4].

And the development continues, despite the fact that no really new mass polymers were introduced on the market in the last 20 years. New structural concepts like nanostructured materials[5] containing natural or even synthetic mineral fillers of well-defined geometry, which will be discussed in detail later, are opening new property combinations (which are not necessarily restricted to mechanical performance). But may be the most stunning innovation of the last year is a self-healing composite material developed at the University of Illinois[6]. This material, targeted at application areas with accessibility problems like outer space and body implants, combines an amorphous polymer matrix with microcapsules containing a liquid monomer. Upon the development of cracks, the resin content can react with catalysts dispersed in the matrix and seal the crack tips, thus stabilising the material.

## Levels of structure and modification

Looking at the various possibilities for polymer modification "from a distance", one will easily recognize an important common factor for all polymeric materials: The possibility to work at different dimensional and structural levels for achieving the desired target[7,8]. As Figure 2 outlines, this covers roughly 9 decades of lengthscale and therefore allows structural reactions to micro- and macro-deformations of the material.

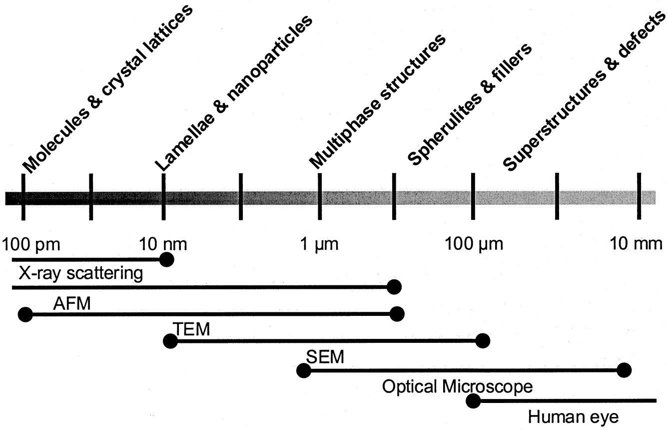


Figure 2. Structural levels and respective dimensions for systematic modification of polymeric materials with appropriate investigation tools for characterization.

Polymer design starts at the level of the molecule, at the chain structure defining the basic characteristics of the material like being crystalline or amorphous. In more detail, variations of crystallinity can be achieved within one polymer type

- by variation of the stereochemistry, where for example PP can be produced in various sterical arrangements between isotactic (iPP) and atactic (aPP) or syndiotactic (sPP)[9]; the property variation is significant here as shown in Table 1
- the copolymerization with structurally different comonomers as in the case of ethylene with higher α-olefins like butene, hexene or octene[10] or propylene with ethylene[11], but also for aromatic polyesters with aliphatic diesters[12]

In all these cases, the chain disturbance leads to reduced crystallisation rate and terminal cristallinity, causing effects on melting temperature (i.e. sealing properties), crystal size (i.e. transparency), modulus (i.e. stiffness) and free volume (i.e. gas and vapor permeability).

Table 1. Comparison of thermal, mechanical and optical properties of iPP- and sPP-homopolymer (representative examples); FM – flexural modulus ISO 178, NIS – Charpy notched impact strength ISO 179 1eA, $S_2$* - normalized small angle light scattering according to internal Borealis standard.

| | **$T_m$ (DSC)** <br> **°C** | **$H_m$ (DSC)** <br> **J/g** | **FM 23°C** <br> **Mpa** | **NIS 23°C** <br> **kJ/m²** | **$S_2$*** <br> **%** |
|---|---|---|---|---|---|
| **sPP** | 114 / 127 | 22 / 27 | 500 | 14 | 8 |
| **iPP** | 164 | 105 | 1400 | 5 | 75 |

Further variations on the molecular structure level are possible by changing the molecular weight distribution (MWD), which decisively affects processability and mechanics for all polymers. The design of special MWDs, especially with a bimodal shape, has been the target of various developments on the catalyst as well as on the process side. Superior mechanics and processability have been found mainly for polyolefins[13], but the question of material homogeneity has to be adressed[14]. Despite this possible problem, conversion processes involving extensional flow components (from film blowing to foaming) are facilitated by the rheological properties offered by such materials and superior performance in terms of optics and mechanics can be reached.

On the next structural level one finds the creation of multiphase structures through blending or sequential copolymerisation. This is based on the principle finding that practically any polymer can be made tougher by the addition of a small amount of „rubbery“ material[8,15], leading to a change in the failure behavior from brittle to ductile failure. While details like the internal structure – homogeneous or core-shell – and the particle shape will depend strongly on the material in question, there are some common dominating factors[16]:

- the modulus ratio between the matrix and the dispersed particles should be much greater than 1
- the particle size and/or the interparticle distance should be below a certain critical value

Various examples can be named for which the effects of these and other factors have been studied in detail. Apart from pure toughness increase, the questions of processability effects and processing sensitivity, optical properties and temperature dependence of the performance have been adressed. Most roughly, one can distinguish between the impact modification of

- amorphous polymers like PS, PC or PMMA[17], where transparency of the resulting structures is of great importance because of the high clarity of the original polymers; an important system in this category is also ABS, for which the effects of size and modulus of the elastomer particles have been studied extensively[18]
- crystalline polymers like polyamide (PA) or PP[19,20], where the impact strength improvement below the glass transition temperature of the matrix polymer is most important; for a defined particle size and structure, the effect of elastomer concentration (particle density) can be seen in Figure 3

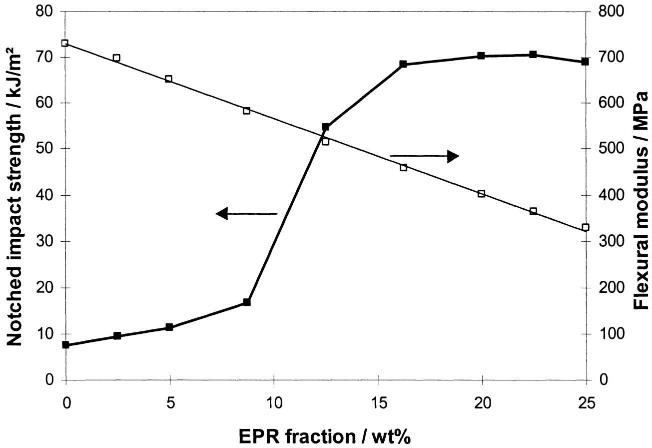


Figure 3. Variation of mechanical properties (Charpy notched impact strength ISO 179 1eA and flexural modulus ISO 178) with the concentration of EPR particles in a heterophasic ethylene-propylene copolymer with random copolymer matrix (RAHECO), materials as in ref. [20].

In principle, high-impact materials of heterophasic structure can be equally well produced in serial polymerization (reactor blends) and by compounding the selected components (extruder blends). While the former method is more economical for high-volume applications and allows better phase compatibility, the latter can be used to tailor materials for special and low-volume applications. In any case, the stability of the created phase structure against flow effects in processing, which can lead to particle orientation and agglomeration, needs to be considered[21]. Optimised viscosity ratio between the phases and good chemical compatibility are key factors for this stability.

Partially overlapping with blend structures in terms of dimension are filled and reinforced polymers[22] resulting from an important area of post-polymerization modification. Both natural mineral fillers and glass, mineral or carbon fibers an be used to significantly improve the mechanical performance, mainly stiffness (modulus) and heat deflection temperature (HDT), possibly in combination with barrier properties and cost reduction (see Figure 4).

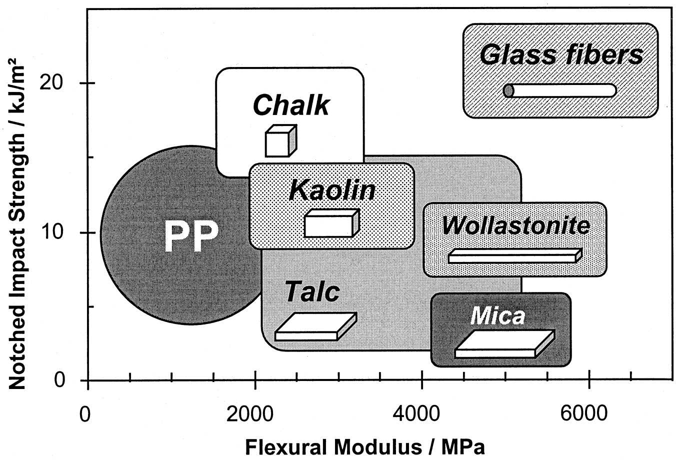


Figure 4. Effect of various fillers or reinforcements on the mechanical performance of polypropylene (after ref. [23]).

Generally, the performance of mineral- or fiber-filled compounds will depend on matrix properties, particle size and shape, volume fraction of the filler and, finally, the dispersion quality. Apart from PP, also PA, poly(butyleneterephthalate) (PBT), PC and PVC are frequently modified this way. The applied compounding equipment plays a major role in defining the product quality, and side effects of the fillers have to be considered. These may include additive adsorption or general promotion of degradation processes as well as significant changes in the rheological behavior[24].

External nucleation, which will act on various structural levels from lamellae to superstructures, can be applied for two reasons: if there is no or very little crystallisation without nucleation as in the case of poly(ethyleneterephthalate) (PET), or to optimise property combinations for specific applications as for PP. Apart from the two thermoplastics already mentioned here, nucleation is mainly relevant for various polyamides (PA-6, PA-66) and other polyesters like PBT[25].

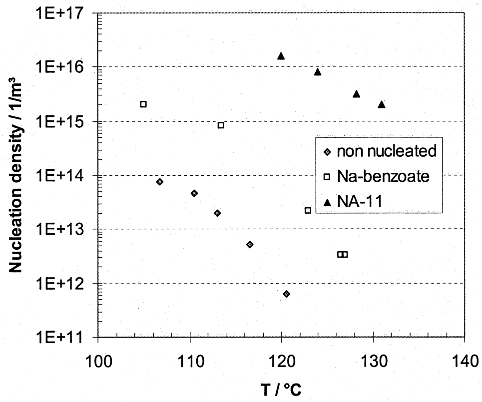


Figure 5. Effect of different nucleating agents (NA 11 - organophosphate) on the nucleation density of a PP homopolymer (MFR 8, reactor grade).

To be effective, a nucleating agent must be able to increase the nucleation density by more than a factor of 10 (see Figure 5). For this, a good matching of the crystalline lattice structure between nucleant and polymer is required as well as a certain adhesion to the polymer matrix in molten state to allow fine dispersion. Different nucleating agents will also produce a significantly different combination of external properties (shrinkage, anisotropy, mechanics, optics), but the reasons of these variations are not always well-known. At least for PP, the formed morphology and crystalline superstructures (shear-induced layers) can be related to the differences between optical and mechanical effects of the nucleation process. Depending on the application in question and the desired property improvements, "ideal" combinations of nucleant and polymer will have to be found[26].

A similarly wide range of structural levels from the molecular to the phase-structure scale can be controlled through reactive modification processes. While the general principle, namely the reactive addition of low molecular weight substances to polymers through radical or ionic reactions, is the same for this wide range of processes, both the reaction method (e.g. reactive extrusion or solid-state grafting) and the targeted material properties can be very different[27]. Practically applied examples include:

- addition of special functionality like polarity or dyeability to polymers
- production of reactive blends from non-compatible polymers
- creating adhesion to fillers or fibers
- improving the melt strength of polyolefins by creating long-chain branched structures (LCBs)[28]
- selective crosslinking of multiphase structure to improve e.g. the processing stability of high-impact materials

Finally, the effects of the processing step need to be considered. While density fluctuations and residual stresses on an „optical" scale can also be found in amorphous polymers like PMMA or PC, the variation is strongest for crystalline polymers again. A look at Figure 6 clearly shows the limited usage of the theoretical mechanical capacities of such „simple" polymers like PE or PA-6,6. Various attempts have been made to come closer to the theoretical limits while keeping the flexibility and geometric variability of standard thermoplastics processing. May be the best-known process in this respect is SCORIM (shear-controlled orientation injection moulding) developed at Brunel University in the UK[29], which is able to increase the modulus of injection-molded PP parts by 50-70%.

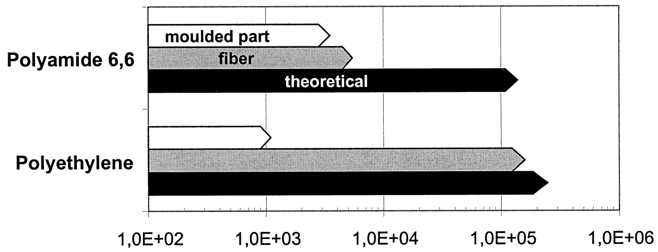
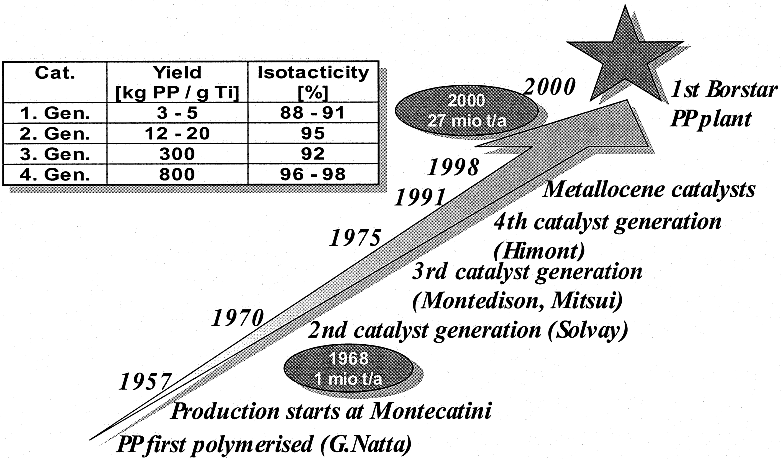


Figure 6. Elastic modulus of crystalline polymers as affected by crystallinity and crystal orientation (after ref. [1]).

## Polypropylene – yesterday, today and tomorrow

Since the first stereospecific polymerization of propylene in 1954, PP has made a series of evolutionary and revolutionary development steps connected to progress on the catalyst side as well as on the polymerization technology side (see Figure 7). Within less than half a century, it developed from a strange mixture of tacticities and crystalline phases to a wide range of well-defined materials. On the molecular level, it can be selectively produced in isotactic, syndiotactic and atactic varietes as well as some combinations of these[9]; further structural modifications are possible at higher levels through copolymerization and post-polymerization processes[30]. Most of these possibilities have already been outlined in the previous chapters as well as in earlier papers[23,31]. This development has produced a set of PP grades with optimised properties in a wide range of stiffness, which are covering literally thousands of applications.



| Cat. | Yield [kg PP / g Ti] | Isotacticity [%] |
|---|---|---|
| 1. Gen. | 3 - 5 | 88 - 91 |
| 2. Gen. | 12 - 20 | 95 |
| 3. Gen. | 300 | 92 |
| 4. Gen. | 800 | 96 - 98 |

Figure 7. Schematic summary of the history of PP as determined by continuous technological progress.

The obvious question now is: What comes next? A basic requirement for following future trends in the polymer industry is to understand the principles of market growth. For the case of polyolefins, more than 75% of the volume growth results from intermaterial substitution, still more than 50% from inter-polymer substitution. Planning future material developments will require consideration of this fact as well as the lesson from Figure 1; also in years to come the demand for high-priced polymers with outstanding performance will remain limited. Technological progress like the introduction of new polymerization technologies[32] therefore need not focus on expanded product variation possibilities alone, but equally on economical performance expressed by factors like catalyst yield.

Nevertheless, the development of nanocomposites combining mineral and polymeric material characteristics on a very fine structural level[5] is definitely one of the most interesting perspectives for PP as well[33,34]. Limiting development targets of these systems to mechanical performance would be a grave mistake, as they can offer far-reaching perspectives in terms of processability, surface functionality and barrier properties as well, giving access to completely new application areas for PP.

Another very interesting area for the future of polyolefins, and again mainly for PP, is the development of extremely soft and transparent materials, which could be used as alternatives for plasticized poly(vinylchloride) (PVC-P) as well as other „high-end“ elastomers with similar properties like styrene-butadiene-elastomers (SBE) or thermoplastic poly(urethanes) (TPU). Especially in „sensitive“ applications like infusion systems (or medical applications in general) and toys for small children, PVC-P has come under pressure repeatedly for alleged health problems related to leaching of phthalate plasticizers from the material[35]. The healthcare industry has partially reacted to this by introducing PVC-free systems based on rather expensive co-extrusion or compounding solutions, especially for the infusion segment.

As a response to these and other requirements, the development of „supersoft“ PP grades has been going on for some time[36]. The possibility to achieve very low modulus and Shore hardness values with low isotacticity materials (homo- or copolymers) has been demonstrated, but the practical requirements on production and application side make a close control of stereostructure and molecular weight distribution necessary. The best chances are presently seen with single-site catalysts[9,37], where several companies worldwide are active in development.

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