Trends in Industrial Research for Polymer Materials

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Summary

Over the past decades, a paradigm shift has taken place in industrial polymer research for structural materials. Despite excellent properties, only a few new polymers based on new monomer building blocks have been commercialized, mainly because of cost issues. On the other hand, the potential of the “old polymers” is far from exhausted in terms of opportunities for new advances. The main drivers for further development of the “old polymers” are: new low cost raw material routes, more environmentally friendly products, and improved properties at lower costs; some examples from BASF will be given. Additionally, nano technology as a new “mega trend” offers further potential for improvements. Sustainable polymers by biotechnology are the latest challenge to the “old polymers”, however these new polymers also have to compete on a cost basis.

I. Introduction

Polymer consumption still grows faster than gross domestic product as polymers help to improve quality of life. On the other side, the overall economic situation of structural polymers is characterized by: a decrease in margins, growing size of production plants and surplus capacities with the consequence of industry consolidation.

Standard product lines cover more than 80% of the market. New polymers based on new monomers only play a role in niche markets, mainly because of cost reasons. New polymers based on old monomers have been developed during the last years by the progress in catalyst research (polyketones, styrene/ethylene copolymers, syndiotactic polystyrene etc.). Despite cheap monomers, the success of these polymers is still pending.

II. Improved “old polymers”

A question that naturally arises is, whether or not really new polymers are needed. We are convinced that the potential of existing polymers is far from exhausted because we now have an in-depth understanding of structure/property relationships, and there has been great progress in controlled polymer synthesis in recent years.

Improvement of existing polymers, so called “drop in solutions”, is by far easier to implement and commercialize. Many examples can be found within BASF:

Ultramid B® (polyamide 6), as an engineering plastic material, is classically polymerized from caprolactam, which itself is synthesized via several steps from benzene. A new route has been developed, starting from butadiene via adipodinitrile resulting in polyamide 6 by direct polymerization of aminocapronitrile. This new route is based on cheaper raw materials, saves synthesis steps, and allows combination of the polyamide 6 and 6,6 value chains.

Polystyrol (High impact polystyrene, HIPS) for packaging and housing applications is commercially produced by radical polymerization under reaction conditions, that cannot be used for a classical anionic polymerization. The addition of Lewis acids such as aluminum alkyls to conventional anionic initiators, forming an “ate”-complex, enables a slowdown of the anionic polymerization of styrene to the same rates as for radical polymerization. It has been shown by BASF [1,2] that up to 180 °C and in bulk this so called “retarded anionic polymerization” of styrene is still living (**Fig. 1**). This enables us to produce HIPS anionically in existing radical HIPS plants and under the same conditions (drop in solution) to give reduced levels of residual monomers and similar, or even improved, properties. The recent development of a new anionic initiating system (NaH : R_3Al) has allowed us to reach the same production costs as for a radical process.

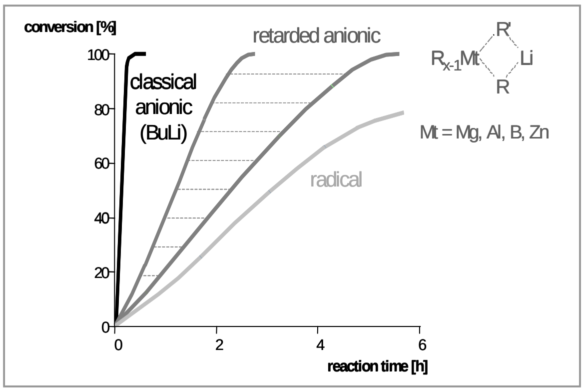

Figure 1. Retarded anionic polymerization: kinetic data and proposed structure of the Na-Al-“ate” complex.

Expandable polystyrene (EPS) is used for packaging and for heat insulation purposes. The addition of microsized graphite leads to a product called Neopor® with better insulation properties than conventional Styropor®. It allows either a reduction in thickness of EPS sheets by 30% at densities between 10 - 15 g/l or a reduction in density of 50% at the same thermal conductivity [3].

The IR radiation, as a main contributor to the heat conductivity, would normally pass through EPS, but in Neopor® it is reflected by the graphite particles (**Fig. 2**).

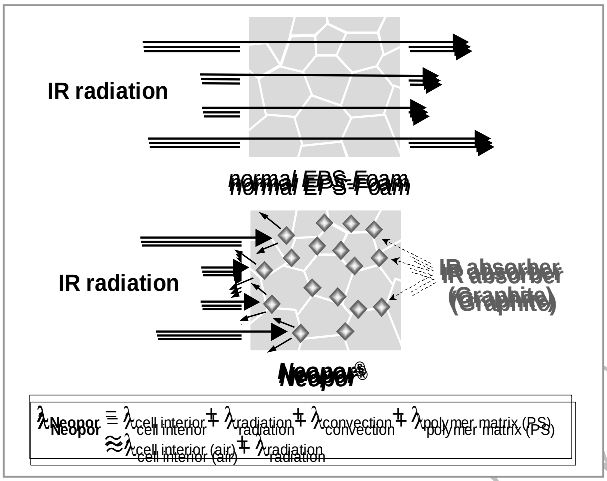

Figure 2. How Neopor® cellular foam works.

Integrated system solutions also allow for new applications and growth potential for known polymers. High off-line coating costs and/or expensive polymer blends for on-line coating have so far limited the usage of plastic panels in automotive applications. BASF is developing a new concept of Paintless Film Molding (PFM) to significantly reduce costs [4]: A three layer coextruded and pigmented SAN/ASA foil is backed by injection molding of glass reinforced ABS. The key is that the materials exhibit good compatibility to result in good adhesion to each other.

As biodegradability does not depend on the origin of a material but only on the chemical structure, BASF was able to develop a low cost biodegradable polymer based on old polymers/monomers (Ecoflex®).

Market requirements of an LDPE-like material for packaging applications could be best met by modifying PBT (polybutylene terephthalate). The partial replacement of terephthalic acid by the aliphatic adipic acid leads to a 100% biodegradable polymer. The properties for film applications can be tailor made by branching and chain extension [5].

III. Mega trend nano Technology

Nano technology as a cross disciplinary technology offers a new toolbox for product improvements in a broad range from surface to bulk properties. This confirms even more our hypothesis that the potential of the so called "old polymers" is by far not yet exhausted. Some examples are given that are close to commercial application:

Nature, and here especially the Lotus plant, has taught us how micro and nano structuring in combination with water repellant chemical compounds can generate super hydrophobic surfaces. On such surfaces water droplets do not adhere but keep their spherical form and roll off the slightest slope removing simultaneously particles of dirt. This so called Lotus effect can be used for easy to clean applications.

The use of nano fillers offers new potentials for polymers based on well-known monomers. Block copolymers, e.g. Styrolux® made of styrene and butadiene show a unique combination of stiffness, toughness and transparency due to their nano-structuring.

The dotted line in **Fig. 3** shows the dependency between elongation at break and elastic module of conventional Styrolux® and Styrolux® / polystyrene blend.

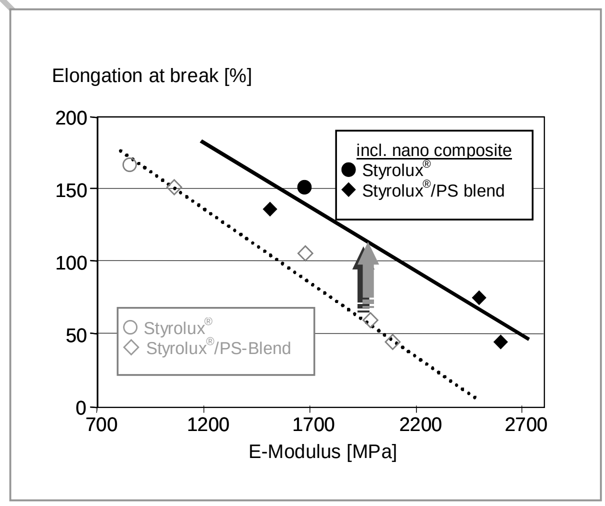

Figure 3. Mechanical Properties of Styrolux® and Styrolux® nanocomposites.

By the dispersion of organically modified clay minerals, within the nanometer range, in Styrolux® and its blends with polystyrene, a nano composite could be obtained with a so far unmatched toughness/stiffness level at same transparency (drawn through line of **Fig. 3**).

Nano technology also offers the vision for the next generation of foams. In a nano cellular foam the cellular size is so small that only one or no gas molecule can fit into the foam pores (“Knudsen effect”). As a consequence, thermal conductivity of the cellular gas molecules by collision is prevented. Such foams exhibit without evacuation insulation properties similar to vacuum panels. Consequently, the foam thickness can be reduced by 70% compared to conventional foams.

The improvement of flow of thermoplastic materials without sacrificing mechanical properties is of high commercial interest.
Newly designed nanoscopic flow additives for PBT (polybutylene terephthalate) allowed for lowering the injection molding temperature by 30-40°C resulting in a reduction of cycle time by at least 20% (**Fig. 4**).

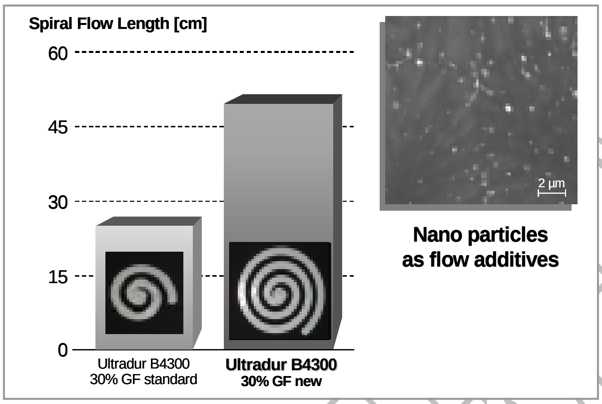

Figure 4. Nano particles for high flow PBT.

IV. Sustainable Polymers

Limited crude oil resources and the commitment to responsible care have initiated the development of sustainable polymers. Starch as a cheap natural polymer can be processed like a thermoplastic material by adding plasticizers.

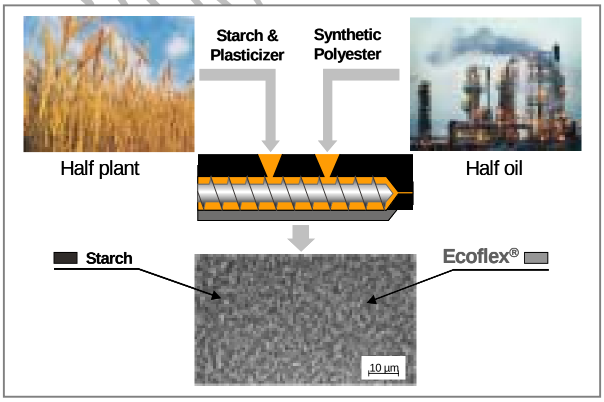

Figure 5. Ecoflex® starch blends.

However, because of its hydrophilic properties, much better performance can be achieved by blends with synthetic biodegradable polyesters like Ecoflex® (**Fig. 5**).

PHB (polyhydroxybutyric acid) is a biodegradable natural polymer, produced by a fermentation process with genetically engineered bacteria from sugar or palm oil. PHB has a wide property range covering injection molding and extrusion applications. Property wise it can be best compared with conventional polymers like PP (**Fig. 6**).

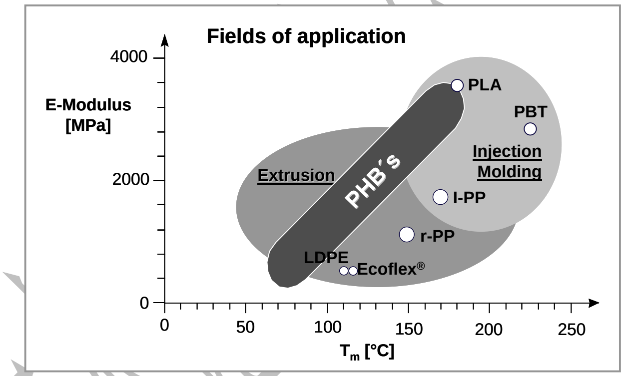

Figure 6. PHB: “The Biodegradable PP”

V. Outlook

These examples demonstrated innovative solutions to further expand the potential of the “old polymers”. We are steadily improving properties to fulfill customer’s needs while lowering the costs that is the key factor for further growth.

Literature

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