Miroslav Raab, Jiří Kotek
Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic

The contribution of polymer physics to commodity plastics with added value

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Summary

Polymeric materials find applications in a number of fields and in variety forms. Nowadays, synthetic polymers are important pillars of our civilization. From the 1930's polymer physics has emerged as an important and respected part of polymer science and followed the development of polymer chemistry. The understanding of the relations between structural hierarchy and macroscopic behaviour, brought about by polymer physics, led to important modifications of existing polymers and the development of new polymeric materials with added value.

KEYWORDS
commodity plastics
new polymeric materials
polymer physic
polymeric technology

KLJUČNE RIJEČI
fizika polimera
novi polimerni materijali
širokoprimjenjiva plastika
polimerijska tehnologija

Doprinos fizike polimera širokoprimjenjivoj plastici poboljšanih svojstava

Sažetak

Polimerni materijali široko se primjenjuju u raznim područjima pa su sintetski polimeri postali važan čimbenik suvremene civilizacije. Već tridesetih godina prošloga stoljeća fizika polimera postala je cijenjen i važan dio polimerijske znanosti, posljedica čega je intenzivan razvoj polimerijske kemije. Razumijevanje odnosa strukture polimera i njihova makroskopskog ponašanja, što objašnjava fizika polimera, omogućilo je modifikacije postojećih, osobito široko primjenjivih plastomera te razvoj novih polimernih materijala poboljšanih svojstava.

Birth of polymer physics

The year 2005 was declared the world year of physics in recognition of the 100th anniversary of the publication of three important papers by Albert Einstein (1879-1955).[1] His papers published in the *miraculous year* 1905 were devoted to photoelectric effect, Brownian motion and special relativity. Since that time, the application of physics has become the basis of many of contemporary technologies. Incidentally, in the year 2005 we also celebrated 70 years of the physics of polymers. In 1935, Wallace H. Carothers (1896–1937) prepared polyamide 6,6 (Nylon 6,6).[2] Cold drawing of nylon fibres became an important part of Carother's patents, because the molecular orientation imposed in the solid state increases the fiber strength considerably. Thus, a purely physical method contributed to the enhancement of end-use properties and opened a wide market for nylon fibres. Therefore, we can consider the year 1935 as the year of birth of polymer physics. From that time on, the impact of polymer physics to polymer processing technologies and polymer materials science steadily increased. The understanding of the relations between structure and macroscopic properties led to the development of new polymeric materials with added value. The aim of this article is to show some important contributions of polymer physics to the modification of structure and resulting properties of commodity polymeric materials. Special attention will be devoted to the multiscale approach to polymer structure and to controlling strength and toughness by structural transformations.

Materials and society

Human civilization is supported by several pillars (Figure 1). There is no doubt, that materials represent one of the most important preconditions of the quality of life of human society.[3,4] Indeed, historians use some typical materials for the characterization of the technological level. They distinguish the stone age, followed by the periods of bronze and iron. Simultaneously with the development of materials technology, some attempts were made to understand the nature of the world of materials. In the early time, the technology and science developed independently (Figure 2). As we now know it, the first theories explaining material properties were naïve and in fact it was good luck that the unrealistic theoretical ideas did not affect the technology. Later, especially in the nineteenth and twentieth centuries, scientific knowledge began to positively influence technological development. This was particularly the case in metallurgy and later on in polymer technology. Even if iron, or more precisely steel, are still very important for today's world, various classes of polymeric materials that emerged in the twentieth century brought about revolutionary changes not only in industry but also in our everyday life.

The individual discoveries and milestones that subsequently contributed to the present situation. A wide spectrum of polymeric materials are listed in Table 1. It should be noted that some polymeric materials of natural origin were used also in the distant past. Indeed, Christopher Columbus imported samples of natural rubber to Europe from his second voyage to America in 1496. The first man-made plastic, called *Parkesine*, was an organic material derived from cellulose by treatment with nitric acid. It was prepared by the British inventor Alexander Parkes in 1862. Six years later, John W. Hyatt invented the first thermoplastic - celluloid. The first completely synthetic man-made substance was discovered in 1909, when Leo Baekeland developed phenolic resin, which he named *Bakelite*. However, the most dramatic growth of production and consumption of polymeric materials started in the thirties of the last century. In just 40 years most of the important polymers were successfully synthetized by polymer chemists. These new materials, including polyvinylchloride, polyethylenes, isotactic polypropylene and polystyrene, have maintained their importance through today. As already mentioned, the discovery of nylon 6,6, is closely connected with the emergence of polymer physics. The table also illustrates the time that elapsed between the invention of a particular material and its introduction on an industrial scale. Indeed, it took more than 20 years for metallocene catalysts to begin to applied commercially.

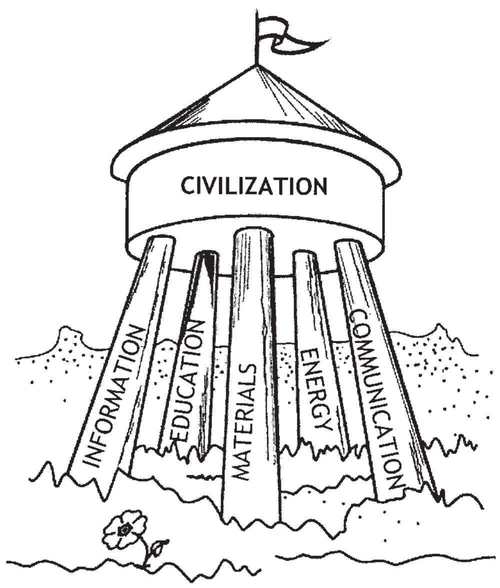

FIGURE 1. Important supports of civilization

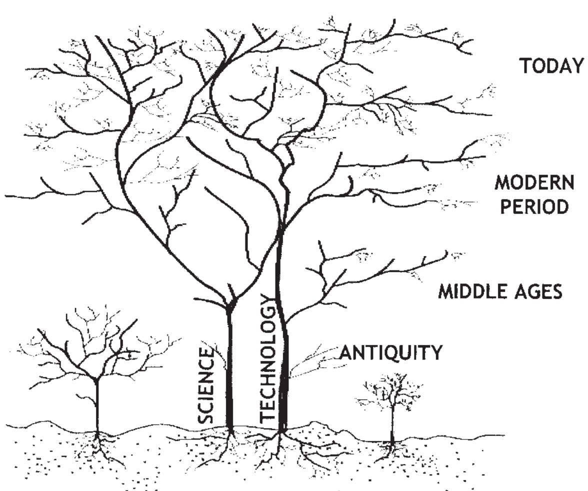

FIGURE 2. Relations between science and technology in history

TABLE 1. Discoveries and milestones in polymeric materials

1496	Rubber balls appeared in Europe (C. Columbus)
1748	Natural rubber imported to Paris (C.-M. de la Condamine)
1832	Term polymer introduced (J. Berzelius)
1844	Sulphur vulcanization of rubber (C. Goodyear)
1862	First man-made plastic, Parkesine (A. Parkes)
1868	Celluloid (J. W. Hyatt)
1878	Light-induced polymerization of vinyl chloride (E. Baumann)
1909	Phenol-formaldehyde resin, Bakelite (J. H. Baekeland)
1913	Polymerization of vinyl chloride with organic peroxides (F. Klatte)
1924	Polymer chain suggested (H. Staudinger)
1926	Plasticized PVC (W. Semon)
1935	Polyamide 6,6 (W. H. Carothers)
1935	Cold drawing - birth of polymer physics
1938	Polyamide 6, Epoxy resins (P. Schlack)
1938	Low-density polyethylene (R. Gibson, E. Fawcet)
1941	Polyethylene terephtalate (J. R. Whinfield, J. T. Dickinson)
1943	Theory of polymer networks (P. J. Flory)
1952/53	High-density polyethylene, isotactic polypropylene (K. Ziegler, G. Natta)
1953	Polycarbonates (G. Schnell)
1961	Soft contact lenses from hydrogels (O. Wichterle)
1967	Aromatic polyamides (DuPont)
1976	Metallocene catalysts reveiled
1976	Gel-spun UHMW polyethylene fibres, future Dyneema (P. Smith, P. J. Lemstra)
1990	Industrial production of Dyneema (DSM in Geelen)
1997	Production of metallocene polyolefins

The general process of application of a scientific discovery on an industrial scale is shown in Figure 3. Even if the diagram seems simple, the commercial application of a scientific idea is not easy. Industrial experts estimate that only about one out of 3 000 promising bright ideas will witness practical application. Obviously not only scientific and technological problems, but also economic aspects play an important role in the transfer of scientific ideas to industrial production. In any case, polymer science initiated the development of several major industrial branches, including:
– production and processing of plastics
– rubber and tire industry
– production of films and packaging
– production of synthetic fibers and textiles
– production of synthetic resins, paints and adhesives
– prodution of polymer composites

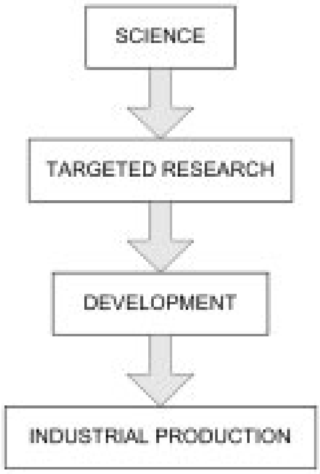

FIGURE 3. The way from the basic ideas to industrial products

Plastics affect all of our lives – from providing improved packaging to cutting edge technologies in cars, computers and communication. Finally, plastics in medicine enable people to live more productive and longer lives. So, plastics made it possible for us to continue to enjoy the quality of life that we have today.

All important plastics can be arranged into a schematic pyramid (Figure 4). The pyramid consists of three layers, representing commodity, engineering and special polymers. While the volume of production increases from top to bottom, price and performance (such us strength, toughness or temperature resistance) increase in the opposite direction. During the last decades, some overlapping of the layers occurred. Polymers considered as commodity plastics have expanded their market share and entered into completely new application areas. Isotactic polypropylene represents here a typical example. The reason is the possibility to modify its properties in very wide intervals by copolymerization, nucleation, blending and reinforcement. On the other hand, the application of polyethyleneterephthalate for beverage bottles and other packaging caused a substantial increase in production and decrease in price of this polymer. This development can be characterized as *commoditization*.

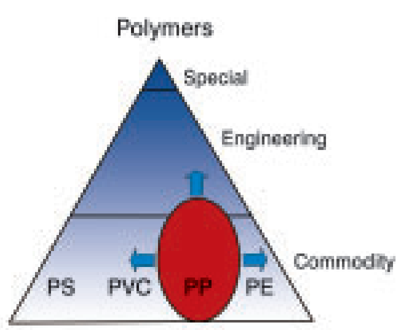

FIGURE 4. Pyramid of polymer classes

Hierachical structure

Looking at the possibilities of property modification by structural transformations, we can easily recognize that the structural modifications can be done at individual levels of structural hierarchy. The design of structure starts at the molecular level established already during the polymerization process. Crystalline structure of semicrystalline polymers represents the next level of the hierarchy. This level, however, depends on the molecular structure. Crystalline lamellae form more complex structures, spherulites, and many spherulites create the spherulitic structure. In polymer blends and composites an even higher level of hierarchical structure can be recognized. It is important to note that mutual interrelation exists between individual structural levels.

For example, the isotacticity of the polypropylene chain is crucial for its ability to crystallize. The supermolecular levels of the polypropylene structure can further be controlled by various post-reactor modifications. The resulting morphology is very sensitive to the conditions of solidification from a melt and also subsequent thermal history of the materials in the solid state. Nucleation is also an efficient way of controlling the supermolecular structure of isotactic polypropylene.

Controlling polymer morphology

The methods developed by polymer physics for the characterization of polymer structure led to the tailoring of individual levels of hierarchical structure. In particular, morphology, i.e. the structure visible by conventional microscopic techniques, can be intentionally controlled by several physical methods:
- thermal history
- mixing conditions and compatibilization (blends)
- nucleation
- shear fields and temperature gradients during solidification
- orientation processes

These effects influence the supermolecular structure of final parts of thermoplastic polymers prepared by injection moulding, compression moulding, blowing, extrusion, etc. The understanding of the physical phenomena during processing allowed for important modification of traditional techniques and enhancement of product properties.

Impact of polymer physics to plastics technology

Thanks to polymer physicist polymeric materials originally synthetized by polymer chemists, have developed new properties and added value. Basically physical processing methods allow for tailoring the properties. Thus, polymer physics helps in developing sophisticated processing methods enhancing strength and toughness considerably. Typical example are advanced processing methods developed by Allan and Bevis. They introduced shear controlled orientation technology called *SCORTEC*.[5] It has been applied both to injection moulding (*SCORIM*) and extrusion (*SCOREX*). The *SCORIM* method operates on the principle that after the mold is filled and before the polymer is allowed to solidify, subsequent shearing steps are applied. The structural background of these processes is the formation of shish-kebab crystalline structures imparting high strength and toughness to the product.

High-performance fibres from flexible chain polymers represent another new class of materials. Having originated from fundamental academic research in polymer physics, they are now attracting the interest of large industrial companies and have a significant potential impact on our everyday lives. Efforts to convert cheap commodity plastics into valuable specialized products have been particularly successful in the case of ultra-high-molecular-weight polyethylene. Extremely strong and lightweight polyethylene fibres developed by Smith and Lemstra is now finding applications ranging from marine ropes and bullet proof jackets to composite materials.[6]

Einstein's contributions to polymer composites

The incorporation of rigid particles into the polymer matrix is a traditional way of adjusting stiffness, strength and toughness. At the same time, it can also decrease the price of the final material. The physical theory of particulate composites starts with an equation for the viscosity η of a suspension of rigid spherical particles (with volume fraction ϕ_2) immersed in a liquid with viscosity η_1:

$$\eta = \eta_1 \left(1 + k_E \phi_2\right)$$

Incidentally, this equation was derived by Albert Einstein and k_E is called the Einstein coefficient. Basically the same equation, only substituting modulus for viscosity, can also predict the behaviour of particulate polymer composites. The subsequent *hydrodynamic* theories of filled polymers were based on Einstein's original concept. Polymer physics was later devoted to molecular interactions of the polymer matrix and solid reinforcement; it studied the molecular structure of the interphase layer, immobilized polymer molecules in the vicinity of the filler surface. Recently, this approach was also applied to various classes of nanocomposites.

Nanocomposites are a new class of particle-filled polymers in which at least one dimension of the dispersed particles is in the nanometer range. The most common nanocomposites are composed of polymers and layered silicates. The layered silicates consist of a sheet-like structure where the dimensions in two directions far exceed the particle thickness. The thickness of the layers (platelets) is of the order of 1 nm and their aspect ratio is above 200. Individual layers are stacked together to form tactoids and aggregates with platelet structure. Uniform dispersion of the layers leads to a much greater specific contact area with a polymer matrix than for an equivalent volume fraction of a conventional filler. In fact, in this case a substantial portion of the matrix is the interphase containing immobilized molecules. As a result, significant property improvements are observed at very low loading levels of only about 5 wt.%. Properties that undergo substantial improvements include: stiffness, strength, heat distortion temperature, thermal stability, barrier properties, dimensional stability, surface hardness, and barrier properties. Again, smart polymer physics allowed for the development and characterization of these new and promising classes of polymeric materials.

Conclusions and future trends

The introduction of fully synthetic polymeric materials based on new monomers started in the 1920's and passed through a maximum in the period of the 1950's.[7] After that, only few new polymers were introduced and even fewer were successful in the market (Figure 5). Today it is unlikely that any new polymer with a volume production potential will be introduced industrially. However, exactly in this period new polymeric materials with tailored properties and added value were created by the physical modifications of originally commodity polymers.

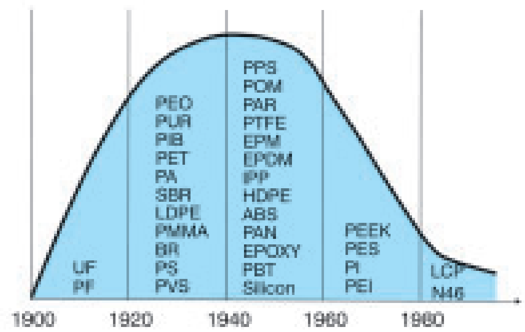

Figure 5. Emergence of new polymers from new monomers during the 1920's

At the same time, there occured a *commoditization* of more advanced thermoplastics such as polyesters and polycarbonate. These trends caused the overlapping of commodity and engineering plastics. From this point of view, we can return to the problem of prediction of future developments in the market. Even if the production and consumption of many polymer has become mature, some increase can still be expected. We can assume that *commoditization* will contribute to this growth. Definitely, the price decrease of some structural polymers connected with their commoditization will play an important role. It should be stressed that price is an important material property together with strength, toughness and thermal resistance. In conclusion, research in polymer physics will not only affect property enhancement, but also the development of the global market in materials in the future.

Acknowledgement

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CORRESPONDENCE

Miroslav Raab
Institute of Macromolecular Chemistry
Academy of Sciences of the Czech Republic
Heyrovsky Sq. 2
CZ-162 06 Prague 6
Czech Republic
Tel.: + 420-296 809 281
raab@imc.cas.cz