

POLYMER BLENDS
HANDBOOK

POLYMER BLENDS HANDBOOK

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Edited by

L. A. Utracki



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PREFACE

Science as a methodical investigation of Nature's capacities evolved from the humble craft tradition. Its goal is to provide the most general and the simplest possible description of the observable character of Nature. In the past the singular concept of "science" comprised all aspects of intellectual endeavor: the arts, the sciences and the crafts. It was Diderot's *Encyclopédie ou Dictionnaire Raisonné des Sciences, des Arts et des Métiers* of 1751-66 that first divided the old "science" into these three parts. The next split — that between the basic and applied sciences — is barely a century old. Basic science has been described as motivated by the desire to discover connections between natural phenomena, while applied science is the application of the discovered laws of nature for the material benefits of mankind. The boundary between the two is not rigid since experimental observation frequently provides a spur to fundamental discoveries.

In the golden times of the scientific institutions in Europe and North America, the most prominent scientists, often the Nobel Prize winners directed the work. In the USA, during the years 1945-75, basic scientific research was considered "essential for the national security, economic growth and survival of the basic democratic values" [J. Krige & D. Pestre, *Science in the 20th Century*, 1997]. In the 1960s several major corporations supported research institutes with total freedom of the research topics.

During last two decades of the twentieth century there has been an apparent reversal in the appreciation of science. Except for a few domains (*e.g.*, astrophysics or atomic physics, project *genome*), intellectual efforts are being directed toward short-term developmental work of a commercially pertinent nature. This tendency is global, evident in the industrial, academic as well as state-supported laboratories. The CEOs hired for a contract to manage an institution are focused on the present. Managing has become a profession divorced from technical knowledge — a research institute, finance company, or pig farm may "benefit" from guidance by the same person. These tendencies are reflected in the evolution of polymer science and technology.

The history of synthetic polymers is incredibly short. The term, *polymer*, was introduced in 1832. The first synthetic polymer (phenol-formaldehyde) was commercialized as *Bakelite*TM in 1909, while the first thermoplastic (polystyrene, *Trolitul*TM) six years later. The early polymer industry was developed by entrepreneurs that had little if any technical background. The commercial successes (and less known, but more numerous failures) predated even the fundamental idea of what constitutes the polymeric species. As late as 1926, Hermann Staudinger unsuccessfully advocated the concept of a linear, covalently bonded macromolecule. This idea was finally accepted during the *Faraday Society* meeting in 1935, only after Carothers reported on his polymerization studies, and demonstrated the validity of the polycondensation theory, developed by his younger colleague from du Pont de Nemours, Paul Flory. The theory provided the relationships between the molecular weights and the reaction kinetics, thus making it possible to ascertain validity of the newly formulated polycondensation principles that postulated sequential addition of bi-functional units to form linear macromolecules.

In 1900 the world production of plastics was 25 kton, doubling during the following 30 years, then re-doubling in five. The most spectacular growth was recorded in the early 1940s when the demand created by the convulsions of World War II engendered a spectacular growth of 25% per annum. During the first 30 post-war years the global plastics' industry sustained an average growth rate of 15%/year. By 1992 the world production of plastics had reached 102 million m³/year, while that of steel was 50 million m³/year. Furthermore, from 1980 to 1990 plastics production increased by 62% while that of steel decreased by 21%. Only during the past 20 years or so has plastics consumption shown smaller and more erratic advances. It is expected that by the year 2000 the world production of plastics will be 151 million tons/year. Considering the uneven polymer consumption around the world, polymer production has the potential to increase tenfold by the mid-21st century. Polymers are the fastest growing structural materials.

Rubber blending predates that of thermoplastics by nearly a century. In 1846 Parkes introduced the first blends of trans- and cis-1,4-polyisoprene, i.e., natural rubber (NR) with gutta-percha (GP). By varying the composition and/or adding fillers the blends were formed into a variety of flexible or rigid articles.

Polymer blends were developed alongside the emerging polymers. Once nitrocellulose (NC) was invented, it was mixed with NR. Blends of NC with NR were patented in 1865 — three years before the commercialization of NC. The first compatibilization of polyvinylchloride (PVC) by blending with polyvinylacetate (PVAc) and their copolymers date from 1928. PVC was commercialized in 1931 while its blends with nitrile rubber (NBR) were patented in 1936 — two years after the NBR patent was issued. The modern era of polymer blending began in 1960, after Alan Hay discovered the oxidative polymerization of 2,4-xylenols that led to polyphenyleneether (PPE). Its blends with styrenics, *Noryl*TM, were commercialized in 1965.

At present, polymer alloys, blends, and composites consume over 80 wt% of all plastics.

In addition, the polymer blends segment of the plastics' industry increases at about three times faster than the whole plastics' industry. Blending has been recognized as the most versatile, economic method to produce materials able to satisfy complex demands for performance. By the year 2000 the world market for polymer blends is expected to reach 51 million tons per annum, worth well over US\$ 200 billion. The tendency is to offer blends that can be treated as any other resin on the market; hence their processability must closely match that of single-phase polymer, but offer a much greater range of performance possibilities.

In the economically advanced countries, plastics have displaced conventional materials for most applications. Today the market pressure forces the resin manufacturers to provide better, more economic materials with superior combinations of properties, not as a replacement for wood or steel, but rather to replace the more traditional polymers. This has resulted in:

- Increased scale of production.
- Use of multicomponent and multiphase materials.
- New processing methods.

For example, twin-screw extruders with 80 tons/hr throughput and injection (100,000 kN) molding presses with shot size of 100 liters of polymer are available. Composites where the matrix is a polymer blend that comprises six different polymers have been introduced. Gas and multiple injection processes, melt-core technology, solid-state forming, microcellular foams all lead to new products with advanced performance. The polymer industry is becoming increasingly sophisticated.

To support these new tendencies the research community has been asked to provide better predictive methods for the multicomponent blends as well as improved sensors for the closed-loop process control. In particular, the evolution of morphology during the compounding and processing steps is of paramount importance. Microrheology and coalescence are the keys to describing the structure evolution of polymer blends.

In the early 1990s, the first mathematical models capable of predicting the evolution of morphology during compounding of polymer blends were developed. The fully predictive model provided good agreement with the experimentally determined variation of morphology inside a twin-screw extruder. However, it must be recognized that the morphology developed inside the compounding or the processing unit is dynamic. Upon removal of stress and in the absence of effective compatibilization the morphology changes with time.

Today, very few unmodified resins are being used. Some polymers require less modification than others. For example, the semi-crystalline polymers that already have a two-phase structure may need modification less urgently. By contrast, the amorphous resins, such as PVC, PS, PPE, or polycarbonate of bis-phenol-A (PC), are brittle and require blending more frequently. The advantages of blending fall into two categories.

A. Blending may improve resin or product performance by:

1. Producing materials having a full set of the desired properties at lowest cost.
2. Extending the engineering resins' performance by incorporation of less expensive polymers.
3. Improvement of specific properties.
 - Toughening brittle polymers, thus eliminating the need to use low molecular weight additives (*e.g.*, plasticizer in the flexible PVC formulations).
 - Blending with more rigid and more heat resistant resin may lead to improved modulus and dimensional stability.
 - Incorporation of semicrystalline polymer into an amorphous resin to improve solvent and chemical resistance (*e.g.*, in blends of PC with PEST).
 - Incorporation of non-flammable resin into a flammable one improves flame resistance (*e.g.*, styrenics or acrylics with PVC).
 - Blends with polymers having either –OH or –SH functionality leads to permanently anti-static blends (*e.g.*, ethylene oxide-co-epichlorohydrin with ABS/PC blend).
 - Biodegradable materials produced by incorporation of a biodegradable resin.

• Blending makes it possible to produce integrated multi-layer structures.

4. Providing means for recycling of industrial and/or municipal plastics waste.

5. The blending technology makes it possible to rebuild high molecular weights of partially degraded polymers, thus to produce high performance articles from the plastics waste.

B. Blending may lead to improved processability:

1. Incorporation of a miscible resin with a lower glass transition temperature (T_g) makes it possible to process the high T_g resin at temperatures well below the thermal degradation limit (*e.g.*, PS/PPE blends).

2. Incorporation of an immiscible, low viscosity resin makes it possible to reduce pressure drop across dies or runners, thereby increasing productivity (*e.g.*, LCP/PEEK blends).

3. Blending with resin that either by itself shows high strain hardening (SH) (*e.g.*, LDPE in blends with another PO), or when reactively blended forms long chain branches (*e.g.*, PS in blends with PO) results in blends having a controllable degree of SH. These materials show better processability in technologies where the extensional flow field is important, viz., film blowing, blow molding, wire coating, foaming, etc.

4. Incorporation of elastomeric particles improves nucleation of gas bubbles, hence it stabilizes the foaming process, reduces bubble size and the final foam density.

5. Incorporation of a degradable resin into an engineering or specialty one provides the means for generation of a controllable amount of the foaming gas during the ensuing stages of processing, viz., injection molding.

6. Blending different grades of the same resin broadens the molecular weight distribution, which in turn results in easier, more stable processing (as well as better mechanical performance).

7. Blending improves product uniformity (scrap reduction) and plant economy.

8. Blending ascertains quick formulation changes, thus plant flexibility and productivity.

9. Blending reduces the number of grades that need to be manufactured and stored.
10. Blending technology offers methods for producing higher esthetic value materials, e.g., films or coatings without gel particles (or “fish eyes”), moldings with streak-free surface finish, etc.

The aim of the *Polymer Blends Handbook (PBH)* is to provide the most comprehensive information on all aspects of polymer blend science and technology. The book will be useful for students entering the field as well as to seasoned professionals. The contributors to *PBH* are renowned experts from eight countries and four continents, who work in academe, government laboratories and industry.

In consequence, the book may be considered comprising two parts: 1. Fundamental principles (nine chapters), and 2. Technology (eight chapters and four Appendices). Each chapter provides an introduction to the pertinent topic, discusses the principal aspects, the typical approaches used by the experts in the area, provides numerical values of pertinent parameters, and gives extensive references that facilitate further topical studies.

PBH comprises seventeen chapters that contain 1. *Introduction to polymer blends*, 2. *Thermodynamics*, 3. *Crystallization*, 4. *Interphase and compatibilization by addition of a compatibilizer*, 5. *Reactive compatibilization*, 6. *Interpenetrating Polymer Networks*, 7. *Rheology*, 8. *Morphology*, 9. *Compounding*, 10. *Processing*, 11. *Use of radiation*, 12. *Properties and performance*, 13. *Applications*, 14. *Degradation and aging*, 15. *Commercial blends*, 16. *Role of polymer blends' technology in polymer recycling*, and 17. *Perspectives*. Furthermore, the Appendices provide information on 1. *International abbreviations for polymers and polymer processing*, 2. *Miscible polymer blends*, 3. *Examples of commercial polymer blends*, and 4. *Dictionary of terms used in polymer science & technology*.

Finally, the Editor wishes to express thanks and personal appreciation to the contributors. They invested much time outside their regular duties, collecting the material and setting it into uniform text. They showed a high spirit of cooperation and great patience. The *Polymer Blends Handbook* is a testimonial of their efforts.

L. A. Utracki, Editor

Montreal, 25.12.1999

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