Advanced Polymer Concretes and Compounds

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Foreword

At the beginning of the 21st century, nanoscale engineering became a driving force for discovery and innovation, not only in electronics and medicine, but also in materials and civil engineering. In the past 25 years, technology for corrosion protection has been advanced by the development of more corrosion-resistant structure materials and protective coatings. The authors of this book are well-known scientists in this area. Professor Oleg Figovsky is a leading inventor with more than 500 patents in the area of materials and civil engineering. The authors have published many articles on these topics in the last 10 years, but a complete book has not been published until now.

This book was written for engineers, students, and others who are interested in advanced materials. It reports the current status of advanced polymer and silicate polymer concretes and compounds. The scope of this book includes rubber concrete based on nanostructured polybutadiene binder, and silicate polymer concretes based on nanostructured organosilicate binder. It examines their physical, mechanical, and technological properties; their behavior upon exposure to harsh environmental factors; and the issues of durability and reliability. Additionally, the scope of this book includes novel polymer and silicate polymer coatings for corrosion and fire protection. One of the more important parts of this book is the chapter in which the authors present data regarding non-isocyanate polyurethane material for monolithic flooring and protective coating—the first nanostructured environment-friendly polyurethane coatings.

The emphasis in this book is on the service abilities of novel concretes and protective compounds for various environments, such as those involving water, pollutants, acid, and alkali substances. The book draws on much of the excellent research already performed on the durability and corrosion resistance of these materials.

Professor Vladimir Kestelman
kvnint@verizon.net

Preface

Developments in civil engineering and the growth of industry have created a continual demand for building materials with new and improved performance attributes. One of the current intensively progressing ways of improving efficiency of building structures is the use of a new class of building materials—polymer composites. It is now virtually impossible to find technical, transport, or building structures in which there are no composite materials. This progress is the result of the unique quality of these materials—a combination of high strength, at the level of structural steel—and the inherent features of nonmetallic materials.

New technological processes closely related with aggressive environments require increases in the manufacture of durable and effective composite materials that can withstand hostile media. Corrosion, the negative effects of radiation and temperatures, high UV radiation, and other adverse natural and anthropogenic effects on building structures are real problems that affect the human living environment.

A radical way to increase the durability of composite materials and products is the use of composites based on polymer binders. The first scientific results in this field were developed by Professor O. Figovsky and are protected by more than 25 patents in the United States, Germany, and Russia.

This book contains the descriptions and results of theoretical and experimental research in the field of efficient building material composites based on advanced polymer binders that were carried out by scientific teams from Polymate Ltd., International Nanotechnology Center (http://www.polymateltd.com, Israel) and Voronezh State University of Architecture and Civil Engineering (VGASU, Russia) with the direct participation or under the leadership of the authors. Physical and mechanical characteristics of these composites, including chemical resistance in various aggressive environments, are discussed in this book.

It is well known that polymer concrete (PC) is used in severe conditions in industrial and public buildings, as well as in transportation and hydraulic structures. The main advantages of polymer concrete over ordinary concrete are improved mechanical strength, low permeability, and improved chemical resistance. The main limitation is their relatively high material cost. For this reason, it is important to find the optimum technical–economic compromise.

This book examines the design issues related to the composition and properties of two new polymer concretes in relation to the polymer matrix and its material and building structure: rubber concrete based on polybutadiene binder and silicate polymer concrete with an organic–silicate matrix. Application of these polymer concretes in construction allows the builder to solve the problems of corrosion, the negative influence of temperature, degradation of a material at increased UV exposure, γ-radiation, and to increase the period between repairs, reliability, and durability of buildings and structures, especially those in aggressive environments. The complexities of physical–mechanical, heat–physical, and technological properties of these PCs, their behavior in environmentally aggressive conditions, and problems of durability and reliability are studied.

Special chapters are devoted to new environmentally friendly polymer compounds for monolithic industrial floor coverings and coatings. Well-known features of conventional polyurethane coverings are porosity, poor hydrolytic stability, and increased permeability. The involvement of toxic components, such as isocyanates, in the fabrication process make it extremely toxic and dangerous. New and promising methods for producing an epoxy–urethane hybrid compound allowed the material to be obtained with lower permeability, improved physical–mechanical characteristics, and safe manufacturing. The environmentally friendly two-component polyurethane binders for monolithic flooring and industrial coatings do not consist of isocyanate components at any stage of preparation, are insensitive to the moisture in the air or the coated surface, and have a number of advantages over conventional polyurethane materials.

Novel hydroxyurethane modifiers (HUM) for cold-cured epoxy composite materials were synthesized. It is established that the compositions with HUM demonstrate a significant increase in the speed of the curing process, a nontrivial increase in abrasion resistance, and a marked improvement in strength properties. The HUM, which possesses a wide range of hydrogen bonds, is embedded in an epoxy polymer network without a direct chemical interaction.

Advanced crack-resistant coatings based on water dispersion of chlorine-sulphopolyethylene (CSPE, Hypalon®) vulcanized by a Mannich alkali (MA) water solution were obtained. Application of MA as a CSPE structure component makes it possible to produce a vulcanized net of saturated polymer, and thus to develop an ecologically safe, impenetrable crack-resistant coating for any substrata (concrete, metal, plastic, etc.). The coatings can be applied in the aircraft, automotive, shipbuilding, paint, and varnish industries, civil engineering, and so on as a corrosion-resistant material. The optimal coating composition and its mechanical properties have been studied.

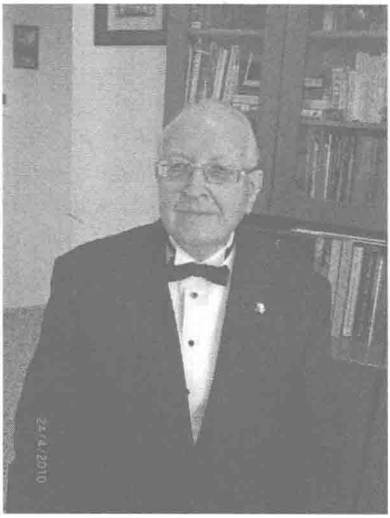
A new type of epoxy composition with nano-heterogenic structure based on epoxy resin, liquid rubber, amine hardener, and fluorinated surfactants of various chemical structures were developed. Formation of nano-heterogenic systems with fluorine-containing surface-active additives of optimal chemical composition is an effective method of obtaining advanced coatings. It has been shown that the mechanical properties and chemical resistance of nano-coatings are significantly higher with the use of surfactants, with the most effective surfactants being those with linear molecules containing carboxyl groups.

Acid-resistant building materials based on liquid glass find wide application in construction as silicate polymer concretes, filler pastes, putties, and so on. A significant increase in strength, heat, and fire resistance of the silicate matrix was achieved by introducing tetrafurfuryl esters of orthosilicic acid (tetrafurfuryloxisilane, or TFS) in the composition. Introduction of the TFS additive in the binding medium leads to the formation of the cross-linked polymer. The resulting nanostructured binder provided the basis for obtaining the acid-resistant silicate polymer concrete and void fillers.

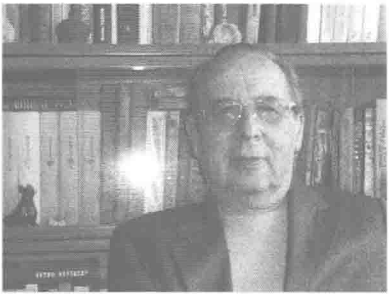
The last chapter is devoted to the development of an advanced waterborne environmentally friendly and weather-resistant fire-protective coating composition. The composition consists of a combination of intumenscent organic and inorganic particles, an inorganic water glass, a water dispersion of chlorine-sulphonated polyethylene, and pigments and/or silicon dioxide. These fire-protective coatings are intended for indoor and outdoor application to flammable substrates such as wood, plastic, and so on. Standard laboratory tests of this coating composition have confirmed its excellent fire-protective of properties, corresponding to Class A fireproofing. The series of fire and heat-retardant coatings can have applications in the construction of wooden items and structures, plastic pipes, facings, and so on.

The major results of the works presented in this monograph were primarily published in the journal *Scientific Israel Technological Advantages* (http://www.sita-journal.com) from 2000 to 2013.

About the Authors



Professor Oleg Figovsky is the founder of the Polymate Ltd.-International Nanotechnology Research Centre (www.polymateltd.com), and its director of R&D, where he is working on research in nanostructured corrosion-resistant composite materials and protective coatings based on a polymer and silicate matrix. Novel nanotechnologies invented by Prof. O. Figovsky were the basis for establishing industrial production in the US, Canada, China, Mexico, Russia, and Israel. He is a member of the European Academy of Sciences, two Russian academies of sciences (RAASN and REA) and head of the UNESCO Chair "Green Chemistry." For his inventions in nanotechnologies he was awarded gold and silver medals at IENA-98 and the Gold Angel Prize at the Genius 2006 exhibition. Prof. O. Figovsky has authored books, more than 300 scientific articles and 500 patents.



Dr. Dmitry Beilin is head of the laboratory at the Polymate Ltd.-International Nanotechnology Research Center in Israel (http://www.polymateltd.com). His fields of interest include structural theory, thin-walled space structures, NDT diagnostics in industry and construction, and the strength of polymer composite materials. Dr. Beilin has authored more than 100 scientific articles and holds 5 patents.

Acknowledgments

The authors are happy to express profound gratitude to the research teams of Polymate Ltd.-INRC, including O. Aksenov, N. Blank, O. Birukova, V. Karchevsky, A. Leykin, R. Potashnikova, L. Shapovalov, and VGASU, led by Professor Yu. Borisov and Professor Yu. Potapov.

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Contents

1 State of the Art in Polymer Concrete

NATURE OF POLYMER CONCRETE

Developments in civil engineering and industrial growth have created a continual demand for building materials with new and improved performance attributes. Nowadays, requirements to be met by construction materials include not only strength features but also chemical resistance, resulting from the increasing contamination of the natural environment, leading to the need to protect and increase the durability of building structures. Polymer concrete is an innovative and modern material that satisfies all the strict requirements of durability and chemical resistance, while offering high mechanical strength [1].

Polymer concrete (PC) is a composite material in which the binder consists entirely of a synthetic organic polymer. It is also known as *synthetic resin concrete*, *plastic resin concrete*, or simply *resin concrete*. Because the use of a polymer instead of Portland cement represents a substantial increase in cost, polymers should be used only in applications in which the higher cost can be justified by superior properties, low labor cost, or low energy requirements during processing and handling. It is therefore important that architects and engineers have some knowledge of the capabilities and limitations of PC materials in order to select the most appropriate and economic product for a specific application [2].

There are many situations for which polymer concrete proves to be the most appropriate material for the intended application, since conditions often dictate specific material requirements that may be met by PC when several composite properties are considered simultaneously.

The fast curing, excellent strength and durability, excellent damping properties, and wide range of elastic moduli available have made PC a very versatile material with many applications. Its primary disadvantages are high cost (binder cost ranges from less than $1 per pound to many dollars per pound); sensitivity of properties to temperature; volatility and flammability of monomers and resins; and lack of experience with PC by many users [3,4].

Polymer concrete consists of a mineral filler, for example an aggregate, and a polymer binder, which may be a thermoplastic, but more frequently is a thermosetting polymer (Figure 1.1).

When sand is used as a filler, the composite is referred to as a *polymer mortar*. Other fillers include crushed stone, gravel, limestone, chalk, condensed silica fume (silica flour, silica dust), granite, quartz, clay, expanded glass, and metallic fillers. Generally, any dry, nonabsorbent, solid material can be used as filler [4].

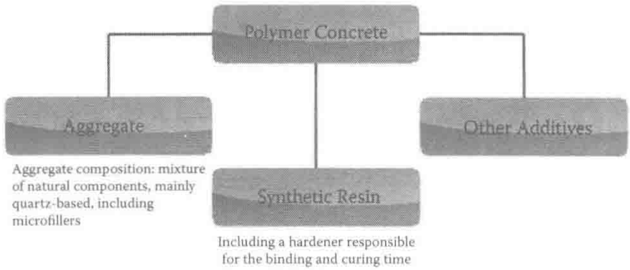

FIGURE 1.1 Composition of a polymer concrete. "Intended Use of Polymer Concrete," *Systemy i Technologie*, http://www.sytec.pl/en/polimerobeton-en.php#wlasciwosci-betonow-zywicznych.

Understanding of the nature of PC is necessary for the design of the most cost-effective PC composites and to produce materials with desired properties.

The polymer industry has made tremendous strides in the past 50 years, but it is quite likely that new and improved polymers will be developed [3], such as

- Polymers with more stable properties over a wide range of temperatures
- A much wider range of polymers that are compatible with fresh concrete
- Monomers, perhaps in the form of vapors, that can be used for producing PC much more rapidly and simply
- Resins that are designed to be recycled

COMPOSITION OF POLYMER CONCRETES

Polymer concrete (PC) is a composite material in which aggregates are bonded together with resins in a polymer matrix. Performance of PC is strongly dependent on various types and the mixed proportions of aggregates and resins [5].

Polymer concrete, as highly filled polymer compositions, can be prepared on any synthetic binding. However, due to the requirements for density, strength, deformability, chemical resistance, and other characteristics, about 10 different types of monomers or oligomers are used in practice. In combination with modifying additives, they provide more than 30 varieties of polymer concrete.

The polymer concretes are distinguished by the nature of the binder; e.g., furan, polyester, epoxy, phenol formaldehyde, carbamide, and so on. The classification of the main types of polymer concrete according to the kind of synthetic resins involved is shown in Figure 1.2 [7].

A variety of aggregate types have been used in PC silicates such as gravel, limestone, calcareous rock, granite, clay, quartz, crushed stone, silica sand or calcium carbonate ($CaCO_3$), as well as fine fly ash, phosphor-gypsum, cinder, and silica fume. Several silica sands have been used in the foundry industry [8]. Aggregates used must be usually dry and free of dirt to get the best bond between aggregates and resin. Figure 1.3 shows some aggregate systems used in PC mixtures [9].

The mix design of PC typically uses an aggregate size gradation to provide the lowest possible void volume and require the least polymeric binder necessary to coat

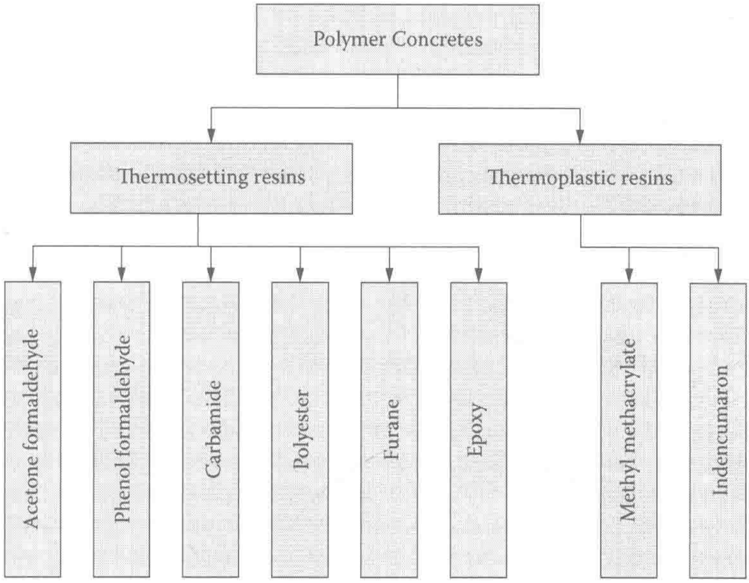

FIGURE 1.2 Classification of polymer concretes. (From V. Chmyhov, "Resistance of Rubber Concrete to Action of Aggressive Environments," doctoral thesis, Voronezh, 2002 [in Russian].)

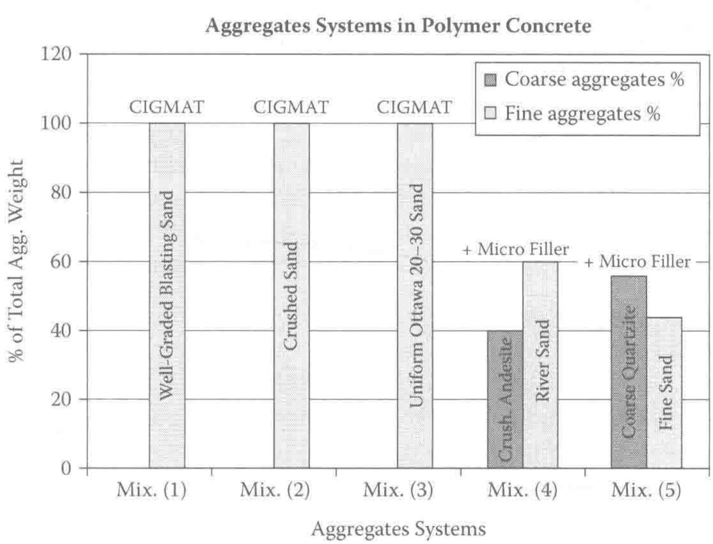

FIGURE 1.3 Most common aggregate systems used in PC. (From V. Y. Garas and C. Vipulanandan, "Review of Polyester Polymer Concrete Properties," http://www2.egr.uh.edu/~civebl/CIGMAT/03_poster/11.pdf.)