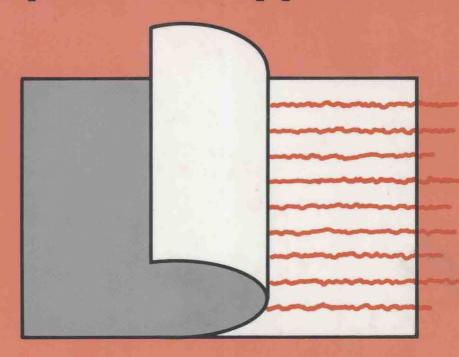
REINFORCED PLASTICS

Properties & Applications



Raymond B. Seymour



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REINFORCED PLASTICS

Properties & Applications

This book is dedicated to the many polymer scientists with whom I met and exchanged ideas at the Gibson Island Conferences in the late 1930s, the later Gordon Conferences, the annual meetings of the Society of Plastics Engineers, and the polymer-oriented divisions of the American Chemical Society.

I especially wish to acknowledge the contributions of Drs. William Bailey, Daniel Fox, Paul Flory, Carl Marvel, and Frank Mayo, who made numerous contributions to polymer composite science during their productive lives.

Preface

Most animals and plants are naturally occurring composites, and the relationships among the various components of these composites have been investigated for centuries. In contrast, most synthetic polymers, such as fibers, uncompounded elastomers, and unfilled plastics, are not composites. Their utility depends, to a large extent, on entanglement of the polymer chains and intermolecular attractions among these chains.

It is interesting to note that celluloid, the first man-made plastic, was a composite consisting of intractable cellulose nitrate and camphor, which served as a flexiblizer or plasticizer. Likewise, Bakelite, the first truly synthetic plastic, was a composite consisting of a phenolic polymer reinforced by a wood flour filler.

Since early developments in plastic technology were empirical and general-purpose thermoplastics such as polystyrene, polymethyl methacrylate, polyethylene, and polypropylene (commercialized in the 1930s and 1950s) were less dependent than celluloid and Bakelite on additives, composite science was neglected until a few decades ago.

Polyvinyl chloride, also a pioneer general-purpose plastic, had limited use until it was flexibilized by the addition of phthalic acid ester plasticizers. The plasticized PVC (Koroseal) served well as a flexible plastic, but the utility of PVC was increased dramatically when heat stabilizers were added in the 1940s. Likewise, because it was brittle, the use of polystyrene was somewhat restricted until it was toughened by the addition of an elastomer, such as styrene-butadiene rubber.

Despite their wide use, most general-purpose plastics could not function as components of aircrafts, boats, automobiles, or recreational equipment. Fortunately, advances in composite science have resulted in the production of plastic composites, which extend the usefulness of plastic far beyond that of the general-purpose thermoplastics. Fortunately, we are now living in the Age of Composites, in which the performance of both thermosets and thermoplastics is enhanced by compounding with properly selected additives.

The present state of the art of compounding of plastics is described throughout this book. Since it was written primarily for designers and engineers, the emphasis is on useful combinations of plastics and appropriate additives. Some essential theories are discussed and references to more complex theories are provided.

A large number of engineers are now employed in the composites field; this number should double in the next few decades as the annual use of composites increases from a few million tons to more than 20 million tons. It is hoped that this book will help continue the growth of plastic composites. The Composites Age will be a golden age for knowledgeable engineers.

Raymond B. Seymour Hattiesburg, MS

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CHAPTER 1

The Genesis of Plastic Composites

INTRODUCTION

Engineers, scientists, and technologists educated prior to World War II learned about early developments in their field by enrolling in a course on the history of science or technology. Unfortunately, most of these courses have been abandoned and replaced by more modern courses such as computer science. Nevertheless, as Goethe stated, "The history of science is science itself." It should not be ignored or overlooked.

The evolution of a new science is not a "Big Bang" event. Instead, developments generally occur at irregular intervals over a period of years, and continue into the future. A brief history of plastic composites will be outlined here to show the steps and missteps in their development. The compounding of materials has gradually evolved from a "black art" to at least a pseudoscience.

HISTORY OF POLYMERS PLUS FUNCTIONAL ADDITIVES

Some functional additives, such as curing agents and stabilizers, occur naturally in hevea rubber and thus may be the pioneer additives for polymers. Proteins found in rubber latex contain sulfur, which acts as a crosslinking or curing agent when heated, and quebrachetol, which serves as a stabilizer. The concentrations of these functional additives plus that of the phenolic stabilizers formed in the smoke of burning wood, used for coagulation, were acceptable for making tlachtli balls (the predecessors of modern basketballs). However, these concentrations are insufficient for other applications, such as waterproofing of textiles and modern radial tires.

White lead (2PbCO₃ · Pb(OH)₂, the first man-made pigment, served as a curing agent (drier) when it was used as a pigment in linseed oil coatings many centuries ago. The dream of the alchemist who developed the Dutch process, which was based on the corrosion of lead by vinegar and carbon dioxide, would be a nightmare for a modern chemical engineer. The utility of this metal salt as a drier or siccative was improved by the Egyptians, who made lime soap over 34 centuries ago. Heavy metal salts of organic acids continue to be used as driers, but their most important use as additives is as heat stabilizers in polyvinyl chloride.

Another ancient additive was tannin, used to tan hides. Nowadays, tannic acid has been displaced, to a large extent, by other crosslinking agents, such as chromium sulfate, and selected polymers are used in place of leather in shoes and many other applications.

Hayward's solarization process developed in 1838 for curing rubber with sulfur was improved by Goodyear, who substituted thermal energy for solar energy in 1939. This slow vulcanization (crosslinking) process was accelerated in the early 1900s when Oenslager added solid aniline derivatives, such as thiocarbanilide, to the mixture of sulfur and rubber. The principal accelerators used today are derivatives of 2-mercaptobenzothiazole (Captax). Ostromislensky cured natural rubber by the addition of benzoyl peroxide.

Prior to 2000 B.C., the Egyptians knew that crushed fruit, when stored in a warm place, produced an intoxicating drink, and the making of beer and wine was practiced before 1500 B.C. The carbon dioxide by-product of yeast fermentation (leaven) was used in the making of leavened bread. Leavening was also accomplished several centuries ago by the use of soda ash (Na₂CO₃), which was extracted from plant ashes.

The Solvay process, developed in 1865, produced sodium bicarbonate (NaHCO₃), which could be mixed with solid acid salts to produce baking powder. Carbon dioxide from both fermentation and baking powder has been used to produce cellular polymeric products. Schridowitz patented this foam-making process in 1914. Other physical blowing agents (PBA), such as Freon, and chemical blowing agents (CBA), such as azobiscarbonamide, are also used as propellants for polymeric foam production. However, the use of Freon and other chlorine-containing propellants is being discontinued because of their adverse effect on the ozone layer in the outer atmosphere. Fortunately, the cellular plastics industry in devel-