Handbook of Reinforcements for Plastics

Edited by

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Foreword

Plastics are playing an increasingly important role in our daily lives—in our homes, businesses, and environment. Until recently, their plentiful supply and low cost had been taken for granted. However, the oil shortage and subsequent materials shortages, plus escalating prices for monomers and polymers, have resulted in a rude awakening to the fact that new initiatives must be exerted in our field.

A more important role must now be accorded to the increased and more efficient use of fillers and reinforcements as a means for stretching the resin supply and lowering the cost of molding compounds.

In my past years of plastics engineering, I have strived to bring to the industry a greater awareness of the proper materials, design, fabrication methods, and economics. I consider this *Handbook* a giant step forward in that direction, and believe that it will accelerate the proper use of fillers and reinforcements and therefore be beneficial to the plastics industry.

J. HARRY DUBOIS

Morris Plains, New Jersey

Note: This was the Foreword of the first edition (1978), and we consider these comments by an outstanding person in the plastics field still pertinent to this second edition.

— The Editors

Preface

Prior to the publication of the first edition of *The Handbook of Fillers and Reinforcements for Plastics*, the plastics industry lived in a fool's paradise, where resins were inexpensive and plentiful; a condition that was expected to persist. Then came the rude awakening during the oil embargo of 1973; which caused a shortage of raw materials and resins, and initiated a series of escalations in the prices of polymers. This led to an increased interest in the use of fillers and reinforcements as a means of reducing the price of molding compounds and expanding the supply of resins. The editors were among those who considered it desirable, to make more extensive use of fillers and reinforcements, they realized that this goal would be aided by a unified compilation of information and data that would enable the rapid choice of the correct filler or reinforcement. As a consequence, they initiated *The Handbook of Fillers and Reinforcements for Plastics*. Prior to publication of the handbook, the choice of a filler and reinforcement usually involved many contacts with materials suppliers, compounders, design engineers, and molders in order to select candidate materials and formulations.

The great increase in technical articles related to new reinforcements, and other factors indicated a growing need for a continued updating of the information on reinforcements in this type of handbook. We believe that it is timely and useful to update the handbook that has served as a standard reference of information for everyone involved in the plastics industry. As the editors gathered information for the new edition, it soon became apparent that both the fillers and reinforcements industry have grown considerably and that it would be cumbersome to compile all of the information into one handbook. Therefore, it was decided that the revision would be two handbooks, one on fillers and the other on reinforcements. *The Handbook of Reinforcements for Plastics*, is the first handbook on reinforcements specifically devoted to the plastics industry. There has been a considerable expansion of the information found in the first edition and many new topics are included that have not been treated before in any major text.

This handbook is directed toward all individuals involved in the production, design, or specification of a molded end product. This includes design engineers, materials scientists, polymer chemists, compounders, and molders. The editors will welcome comments from every profession so that future editions of the handbook will provide the information required for more efficient utilization of reinforcements.

Since the publication of the first edition, much progress and growth have been made in the understanding and use of reinforcements. We have received many favorable comments on the original edition and believe that our effort and the efforts of all the chapter contributors have played an important role in accelerating the growth of the polymer composites industry. A more intensive insight into the science and technology of reinforcements is being used in their selection and application. Greater sophistication in the selection process has created a need for more complete information. In this edition, we have added new information on each reinforcement, and we have also added chapters on recently developed materials.

Compounders and end users are now more demanding in their request for specific properties of new materials. Complex design requirements often demand a combination of properties, rather than a few requirements such as cost, strength, and modulus. Thermal expansion, thermal conductivity, impact resistance, and many other properties may be essential for a specific application. Electromagnetic shielding and electronic applications require stringent control of electrical conducting or insulating properties, and these can be tailored to the desired end use by the judicious choice of reinforcements.

Multi-fiber and filler-fiber combinations are receiving more attention. During recent years, fiber suppliers have accepted the importance of packing concepts, and are marketing short fibers and fillers in multi-sized mixtures and combinations designed for good packing, efficient molding and reduced resin demand. The surface treatment of these materials is now receiving more attention and sales of surface treated products are growing rapidly.

Anyone attending a recent Exhibit and Conference of the Society of the Plastics Industry's Composite Division will realize the amazing recent advances in the art and science of the reinforcements field. We and the other authors of this handbook are proud that we have made a contribution that has played a role in stimulating the growth of this industry. We hope that these revised editions will continue to guide and encourage the increased and more effective use of reinforcements.

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Introduction

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Expanding horizons in industrial activities create a continual demand for improved materials that will satisfy increasingly more stringent requirements, such as higher strength, modulus, thermal and/or electrical conductivity, heat distortion temperature, and lower thermal expansion coefficient and cost. These requirements, which often involve a combination of many difficult to attain properties, may require the use of a composite material, whose constituents act synergistically to solve the needs of the application. As we crossed the threshold into the "composite materials age," it became increasingly important to understand the properties, performance, cost, and potential of the available composite materials.

Reinforcements have always played an important role in the plastics industry. The early growth of the phenolic plastics industry would not have been possible without the enhancement of properties by the use of fillers and reinforcements such as cotton fibers. The commodity resins, such as polyvinyl chloride, polystyrene, polyethylene, and polypropylene, have properties that meet the requirements of high volume end uses; thus, they have been sold and used as essentially pure resins. There was no incentive to use reinforcements in the resins. This situation has changed. Price escalations combined with the sporadic and possible future shortages of resins and petroleum feed stocks have established the urgent need for widespread utilization of fillers and reinforcements. This will apply especially to engineering resins, but also to the commodity resins. Composite systems afford a means of extending the available volume of resins while improving many of their properties. These improvements are often associated with economic advantages such as lower raw material cost, faster molding cycles as a result of increased thermal conductivity, and fewer rejects due to warpage.

At present, most molded products do not contain any fillers or reinforcements in spite of the fact that the judicious choice of a filler and reinforcement can result in a lower cost product with equivalent or improved properties. Recent technological advances, such as improved dispersion and new packing concepts, have not been widely applied and, as a consequence, much current information on filled and reinforced plastics indicate poorer qualities than the true potential of these composites. Also, there have been recent advances in equipment and procedures for compounding and molding highly filled polymers. Currently, there are few valid technical justifications for the use of an unfilled resin in most molded products, from considerations of physical properties, moldability, and cost. Moreover, as this technology advances, there will be increased benefits from the use of fillers and reinforcements.

The purpose of *The Handbook of Reinforcements for Plastics* is to present in one volume, all the basic and much in-depth information on reinforcements being used in industry today. It is the most complete and up-to-date volume published in this area of technology, and is a very convenient desktop reference book. The first edition of the *Handbook of Fillers and Reinforcements for Plastics*, has been called the "Bible" of the industry. This same high standard has been maintained in this second edition.

The very significant growth in the areas of both filler and reinforcements was the reason for this two-volume format. These new volumes are more than fifty percent larger than the first edition, with major revisions in every chapter.

There are new chapters on new materials. Six chapters have been added on materials that have not been well presented in previous books. These chapters cover short metal fibers and flakes, phosphate fibers, chopped and milled fibers, technology of cutting fibers, short organic fibers, and new polyethylene filaments.

The handbook is composed of five major sections comprising 21 chapters. In the Section I, Chapter 1 is an Introduction. Chapter 2 is Concise Fundamentals of Fiber Reinforced Composites; this chapter contains a brief, but significant coverage of the basic theory of fiber reinforcement with many references to more detailed theoretical considerations. Chapter 3 covers the classic theories of fiber-filler packing concepts. This volume and the first edition are the only two sources of this extremely vital information for making more efficient and economical, short-fiber-reinforced composites.

Section II is devoted to flake and ribbon reinforcements and presents an in-depth discussion of these materials.

Section III is about short fibers—the fastest growing area of new reinforcements. There are 8 chapters in this section, four are new chapters on materials which have not been discussed in detail in any previous book. These chapters cover short metal fibers and metal flakes; phosphate fibers; chopped and milled fibers; short organic fibers and the technology of cutting fibers. The other chapters are on Wollastonite, asbestos, inorganic micro-fibers and whiskers. All of these chapters have been substantially revised for this new edition.

Section IV is on fiber glass and basalt glass fiber; both have been brought up to date with the latest in-depth information.

Section V is about high modulus filaments and contains a new chapter on polyethylene, plus major revisions on aramids, boron and silicon carbide filaments, carbon/graphite, ceramic filaments, and continuous metallic filaments.

One of the most significant subjects that is covered by this book is filler-fiber combinations. This information has revolutionized the short fiber industry by improving performance, efficiency, and economics.

The short metallic fiber information is especially important to the rapidly growing static charge elimination and electro-magnetic shielding applications, and for improved thermal conductivity applications.

The information on the new phosphate fiber will be of special interest to all those looking for asbestos replacements. Chapter 8, Wollastonite, and Chapter 10, Inorganic and Micro Fibers, provide information on other potential asbestos replacements. Those interested in the technology of chopping and cutting fibers will find the first really complete, well-illustrated work on this subject in Chapter 11.

Those interested in short organic fibers as a reinforcement will find the first detailed coverage of this subject in Chapter 12. The expanding growth in whiskers is well-documented in the wealth of new information and sources contained in Chapter 13.

A material for water cables, advanced composites, and armor is the new polyethylene filament. Many detailed examples of applications of this material are given.

This Handbook satisfies the need of the user. It is a handy complete reference on the subject of reinforcements presenting detailed data from hundreds of companies as well as thousands of products in an extremely well-organized manner. There is no other book that is specifically devoted to this subject.

The book will be of interest to the compounder guiding him in the selection of the most efficient and economical source of raw materials. Although primarily intended for those in the reinforced plastics market, this Handbook will be useful for everyone involved in the rapidly expanding fields of metal and ceramic matrix composites.

Recently, continuous filaments and fibers like boron, silicon carbide, and aluminum oxide and short micro fibers and whiskers are being used for new applications in both metallic and ceramic matrix composites.

As noted above, Sections II through V present all of the significant materials used as reinforcements. The editors presented the contributors with a suggested outline that might be used as a standard format for the chapters. However, it is apparent that they required some latitude for variation from the standard format. In spite of some of these differences, the reader will note that most chapters follow the same basic format in presenting their data, which will facilitate locating specific information on a particular material.

The field of reinforcements is growing rapidly and encompasses a wide variety of materials. This handbook has been designed to present a complete and orderly discussion of pertinent information in this field. However, there have been some arbitrary choices and, undoubtedly, some omissions. Nevertheless, the editors are confident that the reader will find this a useful and rewarding book. In addition, it is hoped that this presentation will act as a catalyst to inspire the increased use of reinforcements.

The editors anticipate that there will be periodic revisions of this handbook. Therefore, any comments and suggestions on a more useful format and additional data on current and new materials will be appreciated.

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Concise Fundamentals of Fiber-Reinforced Composites

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1. INTRODUCTION

Fibers have extremely high tensile strengths and moduli. A fiber can be defined as a particle longer than 100 μm with a length to diameter, or transverse dimension, ratio greater than 10. The tensile strength of a fiber is many magnitudes greater than the strength of the same material in bulk form. For example, bulk graphite is a brittle material with a tensile strength below 10,000 psi, whereas commercial graphite fibers have tensile strengths to 800,000 psi, and laboratory research on graphite whiskers yielded a 3,000,000 psi tensile strength. As another example, nylon plastic has a tensile strength of about 12,000 psi, whereas nylon fibers have tensile strengths in the order of 120,000 psi. Similarly, the tensile strengths of E-glass at 500,000 psi, boron fibers at 500,000 psi, and alumina fibers at about 150,000 psi are far above the strength levels of the bulk materials. Thus, it is apparent that when these high-strength fibers are used effectively in a matrix, composites with strength levels above those of bulk materials can be produced.

Since fibers are the highest-strength materials, they are the best reinforcements for many applications, ranging from improvement of the strength of low-cost materials or composites to acceptable levels, to the production of superior structural aerospace components. Therefore, everyone involved in the production, design, specification, or use of plastics should be familiar with the fundamental characteristics of fibers as reinforcements.

There are many good reasons for adding a high volume fraction of low-cost fillers to plastics, especially from the standpoint of stretching the resin supply. However, high particulate filler loadings will usually result in a substantial reduction of physical properties. For the many end uses where the reduced physical properties would be unacceptable, the addition of fibers to the compound formulation can be a means for increasing the properties to a satisfactorily high level. Many subtle considerations are involved in the science and art of formulating and fabricating a fiber-reinforced composite. There have been many programs in this field during the past two decades, and continued advances may be anticipated. An important aspect that will form the basis for future progress in improved molding compounds is the study of the packing of fibers with spheres and particulate fillers, as presented in Chapter 3.

The use of fibers as a reinforcement can lead to superior materials, in some cases, at a premium cost; or they can be a means for achieving improved properties while maintaining low costs and stretching the resin supply. The choice of the fiber reinforcement will depend on the requirements of the different end products. At the present time, the highest volume fiber reinforcement is glass fiber, but the near future will undoubtedly lead to the increased use of competitive materials, such as carbon-graphite filaments, whiskers, and microfibers. As industrial competition becomes more sophisticated, and end uses more demanding in performance and cost, it will be essential to continue the rapidly expanding use of fiber-reinforced composites.

This chapter is intended to give the reader insight into the principal characteristics of fiber-reinforced composites. A number of excellent books give comprehensive treatments of important topics, including theoretical analyses of the strength and modulus of various composite structures, crack propagation theories, and the stress analysis of advanced composite materials. These books are listed in the references at the end of this chapter.

2. COMPOSITE ELEMENTS

There are three basic elements in a fiber-reinforced composite: fiber, matrix, and the fiber–matrix interface. Each of these elements must have appropriate characteristics and function both individually and collectively in order for the composite to attain the desired superior properties.

The fiber contributes the high strength and modulus to the composite. It is the element that provides resistance to breaking and bending under the applied load.

The main roles of the matrix are to transmit and distribute stresses among the individual fibers, and to maintain the fibers separated and in the desired orientation. The matrix also provides protection against both fiber abrasion and fiber exposure to moisture or other environmental conditions, and causes the fibers to act as a team in resisting failure or deformation under load. The maximum service temperature of the composite is limited by the matrix. Other desirable features of the matrix are resistance to liquid penetration and freedom from voids.

The fiber–matrix interface is the critical factor that determines to what extent the potential properties of the composite will be achieved and maintained during use. Localized stresses are usually highest at or near the interface, which may be the point of premature failure of the composite. The interface must have appropriate chemical and physical features to provide the necessary load transfer from the matrix to the reinforcement. The use of a coupling agent can provide improved interfacial conditions. The interfacial bond must resist stresses due to differential thermal expansion of fiber and matrix, and shrinkage of the resin during cure. The interface also assists the matrix in protecting the fibers.

As indicated above, the presence of a coupling agent at the fiber–matrix interface can be the means for obtaining the optimum physical properties of the composite, and retaining these properties after environmental exposure or aging. This fact became apparent in early studies of fiberglass-reinforced polyester laminates, when the simple test of putting a panel into boiling water for 2 hours showed an amazing difference in strength retention between the composite utilizing a fiberglass treated with a silane coupling agent and a control containing untreated fiberglass.

Silanes have been the most frequently used type of coupling agent. The silanes provide dual functionality in one molecule, such that one part of the molecule forms a bond to the glass filament surface while another part forms a covalent bridge with the matrix molecule. There are many different silanes, and the choice must be based upon the matrix to be used. Silanes and other coupling agents such as the titanates are discussed in detail in the *Handbook of Fillers for Plastics*.

3. COMPOSITE PROPERTIES

As composite technology has advanced, it has become imperative that the properties of a composite be predictable from a knowledge of the constituent matrix, fiber, fiber volume, and fiber orientation. This is especially true in the case of advanced composites, where fiber and fabrication costs may be high, and the end product must be extremely reliable in performance, so that a trial-and-error approach cannot be tolerated. There has been good progress in the theoretical analysis and design of composite materials, so that even critical aerospace structures can be designed with assurance that they will safely meet the material property requirements.

In the analysis of the theoretical properties of different types of composites, various analytical models and failure theories have been used. There are different considerations involved in the case of a randomly oriented discontinuous fiber composite than for a continuous-filament unidirectional or angle-ply laminate.

3.1 Rule of Mixtures

A first approximation of the tensile modulus and strength of a fiber-reinforced composite can be obtained from the rule of mixtures. The modulus of a continuous filament composite with filaments oriented longitudinally can be estimated, with good precision, for the direction parallel to the fibers, by:

$$E_L = V_f E_f + V_m E_m \qquad (2\text{-}1)$$

where:

E_L is the longitudinal modulus of the composite.
V_f is the volume fraction of the filaments.
E_f is the tensile modulus of the filaments.
V_m is the volume fraction of the matrix.
E_m is the tensile modulus of the matrix.

Equation 2-1 assumes that all filaments are perfectly bonded to the matrix.

Equations analogous to Eq. 2-1 may be used to express either the longitudinal Poisson's ratio or the tensile strength of the composite. This prediction of tensile strength will not be as accurate as in the case of the modulus. Actual strengths are usually lower than the predicted strengths, and this ratio has been used as an indication of the fiber efficiency in the composite. In the case of some metal matrix composites, however, the indicated fiber efficiency has been greater than 100%, because of factors such as favorable residual stresses in the matrix.

In a discontinuous fiber composite, the stress along the fiber is not uniform. There are portions along the fiber's ends where the tensile stresses are less than that of a fiber that is continuous in length. This region is often called the fiber ineffective length. The tensile stress along the fiber length increases to a maximum along the middle portion of the fiber. If the fiber is sufficiently long so that the ratio of length to diameter, or aspect ratio, equals or exceeds the critical aspect ratio, the middle portion stress will be equal to that of a continuous filament. The shear stress at the fiber–matrix interface is a maximum at the ends of the fiber, as shown in Fig. 2-1.

The critical aspect ratio $(l/d)_c$ which would result in fiber fracture at its midpoint, can be expressed as:

$$\left(\frac{l}{d}\right)_c = \frac{S_f}{2Y} \qquad (2\text{-}2)$$

where:

l and d are the length and diameter of the fiber.
$(l/d)_c$ is the critical aspect ratio.
S_f is the tensile stress of the fiber.
Y is either the yield strength of the matrix in shear, or the fiber–matrix interfacial shear strength; whichever value is lower will determine the critical aspect ratio.

If the fiber is shorter than the critical length, the stressed fiber will de-bond from the matrix

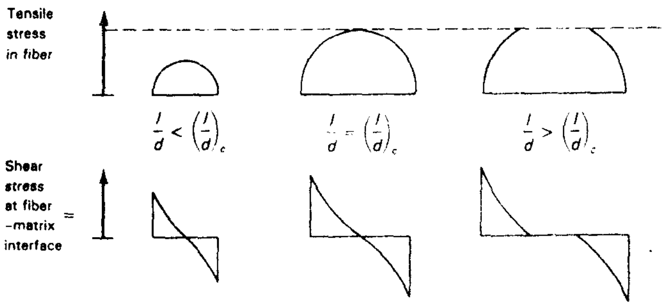

Fig. 2-1. Shear stresses at fiber-matrix interface.

and the composite will fail at a low strength. When the length is greater than the critical length, the stressed composite will lead to breaking of the fibers and a high composite strength.

The rule of mixtures for discontinuous composites may be expressed as:

$$S_c = V_f S_f\left(1 - \frac{l_c}{2l}\right) + V_m S_m \quad (2\text{-}3)$$

where:

S_c is the tensile strength of the composite.
V_f and V_m are the volume fractions of the fiber and matrix.
S_f and S_m are the tensile strengths of the fiber and matrix.
l_c is the critical length of the fiber.
l is the length of the fiber.

The rule of mixtures does not apply at low volume percentages of fibers. In order for the composite to have a higher strength than the matrix, a minimum V_f must be exceeded. This value may be 0.1 or greater for plastic matrix composites, but can be much lower for metal or ceramic matrix composites. Also, at high V_f, on the order of 0.7, the composite properties may decrease sharply, due to practical problems such as the difficulty in avoiding fiber-fiber contact, which results in stress concentrations that initiate failure. If the load is compressive, the theoretical problem is more difficult because of the possibility of fiber buckling. A number of theories have been proposed to predict the strength of discontinuous fiber composites. These theories indicate that, primarily because of high stress concentrations at discontinuities that occur at the fiber ends, the tensile strength of a discontinuous fiber composite will be from 55% to 86% of the tensile strength; and the modulus can approach 90% to 95% of the tensile modulus of the corresponding continuous filament composite.

3.2 Micro/Macromechanics

Analytical methods for composite materials can be divided into two main types, micro- and macromechanics.

Micromechanics analysis is applied to the basic filament-matrix microstructure in order to determine the strength and elastic properties from the properties and arrangement of the constituent filament and matrix materials. Micromechanics attempts to predict fracture behavior of the composite from the state of stress and strain at the micro level. Much progress has been made during the past 10 to 15 years in developing mathematical procedures and corresponding computer programs for estimating the elastic moduli and strength of composites.

Macromechanics encompasses the analytical methods that are used to predict the strength and elastic properties of an advanced composite laminate from the known properties of the individual unidirectional monolayers or plies. Macromechanic studies have been essential for design guidance in the rapid progress of advanced composite development in the aerospace industry.

The elastic properties of a plate consisting of

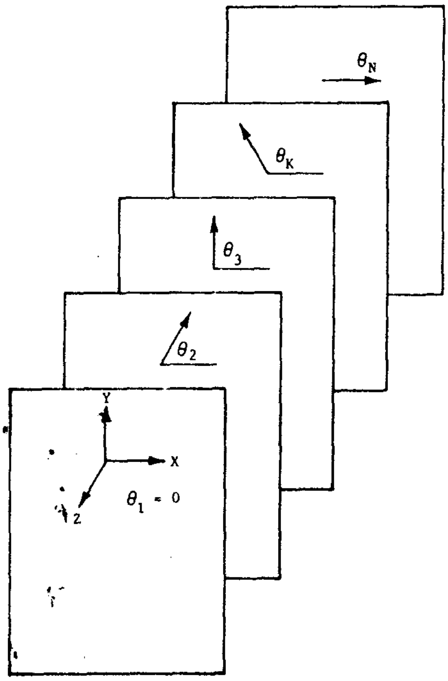

Fig. 2-2. Laminated plate, *N* plies.

N plies, in which the filament orientation may vary from ply to ply as shown in Fig. 2-2, may be obtained by summing the contribution of each ply. As the elastic properties of each ply vary with direction, angle θ in Fig. 2-2, these properties must first be transformed to the same coordinate system. Details of this procedure are contained in the references at the end of this chapter.

There is a large body of literature on composite failure criteria. The most used criterion at present is based on strain energy. Its advantage, compared to the maximum stress and maximum strain criteria, is that it considers the entire stress state at a point in a composite.

Only a few years ago, the complex calculations required to estimate a composite's elastic and strength properties required a large-scale computer. The recent development of programmable calculators and microcomputers has resulted in the availability of a number of inexpensive programs for laminate analysis. Some of these programs and their sources are:

1. "Advanced Composite Materials Laminate Plate Programs," for Hewlett-Packard 41 series programmable calculators, from:
   Intellicomp, Inc.
   292 Lambourna Ave.
   Worthington, OH 43085
   (614) 846-0216
2. "LAMINATE," for IBM PC/XT, AT, or their clones, from:
   Engineering Software Company
   Three Northpark East, Suite 901
   8800 North Central Expressway
   Dallas, TX 75231
   (214) 361-2431

In addition, members of the "Think Composites Software Users Club" (Box 581, Dayton, OH 45419) receive a set of Apple MacIntosh or IBM PC software. Finally, Texas Instrument Model 59 programmable calculator programs are available from the authors of *Introduction to Composite Materials* (see bibliography at the end of this chapter).

One advantage of these programs to the designer and materials engineer is that they enable a material selection based on the properties of realistic ply orientation patterns rather than the unidirectional properties that are provided by materials suppliers. In addition, they reduce some of the time-consuming material testing that otherwise would be required.

3.3 Design

The design of a part that will be fabricated from an isotropic material, such as a structural metal, has become relatively simple and straight-forward, as the result of a long history of use and complete design data that have been generated. In contrast, composite materials and their fabrication processes are generally unfamiliar tc the designer, and the available information may not be complete. In spite of these drawbacks, which are rapidly being overcome, the use of composites has been expanding in all markets, and excellent progress has been made in the design of more intricate and larger parts. Notable accomplishments have been attained in the au-