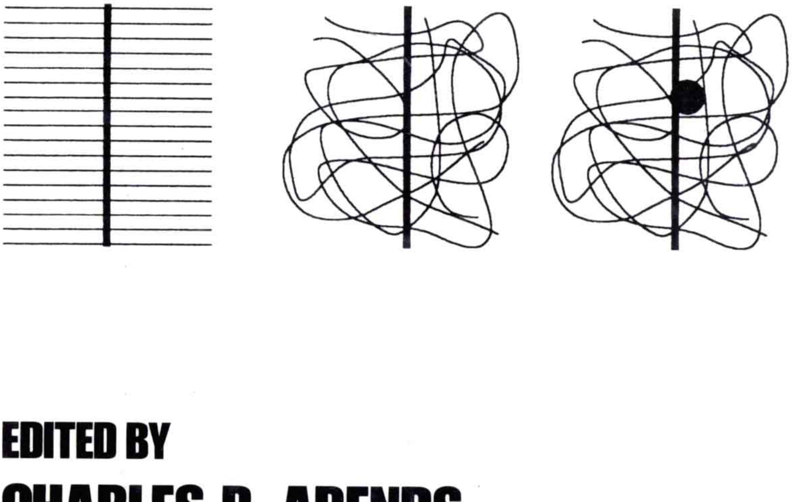
POLYMER TOUGHENING



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Preface

The Dow Chemical Company has been involved in the toughening of polymers for at least 50 years. In the early 1940s Larry Amos and co-workers first introduced rubber into polystyrene. Since then, the number of polymers that have been treated to a "toughening" procedure has grown to include almost every basic polymer product. It seems as though every manufactured polymer fails under some circumstance where just a little more resistance to failure is needed to make it work. The process of producing this increased resistance to failure under mechanical stress is called "toughening." When successful, it results in better materials for converters and users. It also results in knowledge and understanding for scientists who strive to make better things and, along the way, provides the rewards of a job well done to those who are involved in the process.

Progress in toughening is slow and painful. People working with a given family of materials tend to generalize about their mechanical performance, while interpreting toughness in relationship to end-use applications. Naturally, each family of materials has unique features that distinguish it from other materials. For example, its members may be intrinsically tough but suffer from being difficult to process, or they may have that worst of all flaws: they may be expensive. On the other hand, they may be processed easily but be intrinsically brittle.

Each material can be improved for its own particular uses. But rather than treat each material as a world unto itself—independent of all other materials—it is helpful to realize that interactions between families are not rare; as we shall see in the following chapters, there is a great deal of similarity between the methods of measurement and methods of toughness enhancement. The first five chapters explore some of these similarities as background for the remaining chapters, which concentrate on toughening within specific polymer families.

In assembling this book, we had several ends in mind. We wanted to provide a forum in which similarities among otherwise disparate polymers could be addressed. This is done by examining a large portion of the polymer lines sold by one company, The Dow Chemical Company. We wanted to demonstrate the interplay between molecular structure and second-phase toughening to show how methods of manufacture are used to incorporate some of the design concepts developed in laboratory environments. By following the development of some successful products, we also gain insight into industrial research. We hope that the readers of this volume who are already working at polymer toughening will find new ways of looking at their problems through other areas of polymer research. For those who are relatively new to polymer toughening, this book should provide a basic understanding of the processes involved as well as an understanding of the dynamics of doing polymer research. Finally, data on current research are presented for those who are concerned with recent developments. The chapters are written by experts in their respective fields.

This book provides a unique perspective on polymer research in the field of toughening. It demonstrates the thought processes and basic applied research used in the development of successful polymeric products. It also helps to introduce people who are involved in the process but who may not be familiar with the methods used in related fields because they work in an atmosphere that sometimes requires a modest level of secrecy. The book is ultimately intended to provide a comprehensive overview of polymer toughening as practiced in an industrial environment. We trust that it will encourage further progress in developing new and better polymeric materials that should, in turn, bring about a richer understanding of polymers and their properties.

This volume includes contributions from many of our colleagues, whose work has been reviewed and corroborated by co-workers and represents solid achievements in polymer science and technology. The information presented here is given in good faith. Although we believe that it is valid, no warranty is implied nor should one be assumed.

Charles B. Arends

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Contents

Preface *iii*
Contributors *ix*

1. Molecular Origins of Toughness in Polymers 1
Jozef Bicerano and Jerry T. Seitz

2. Multiphase Toughening of Plastics 61
Charles B. Arends

3. Grafted Rubber Concentrates 85
Dale M. Pickelman

4. Crazing in Intrinsically Tough-High-Performance Thermoset Resins 113
Philip C. Yang, Hung-Jue Sue, and Matthew T. Bishop

5. Fracture Behavior of Rubber-Modified High-Performance Epoxies 131
Hung-Jue Sue, E. I. Garcia-Meitin, and Dale M. Pickelman

6. Rubber-Toughened Thermosets 175
Frederick J. McGarry

7. Polyethylene 189
George W. Knight

8. The Manufacture and Physical Properties of Rubber-Toughened Styrenics 237
David E. Henton and Robert A. Bubeck

9. Polyurethane Polymer Toughness 293
Ralph D. Priester, Jr., D. Roger Moore, and Robert B. Turner

10. Design of Tough Epoxy Thermosets 339
Bruce L. Burton and James L. Bertram

11. Toughness in Thermoset Coatings 381
Robert A. DuBois, David S. Wang, and David Sheih

Index *411*

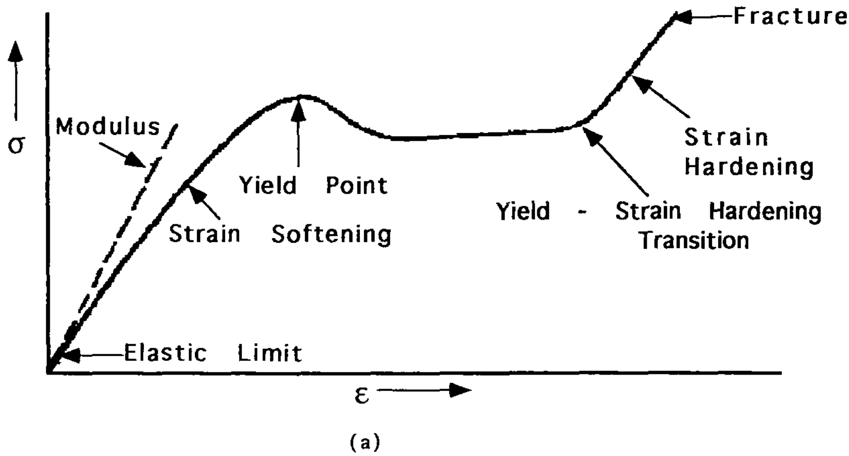
1
Molecular Origins of Toughness in Polymers

JOZEF BICERANO and JERRY T. SEITZ
The Dow Chemical Company, Midland, Michigan

I. STRESS–STRAIN CURVES AND "TOUGHNESS"

The mechanical properties of materials are of great importance in engineering applications [1]. When a mechanical force is applied to a specimen, the deformation of the specimen is described in terms of its *stress–strain behavior*. The stress–strain behavior quantifies the *stress* (mechanical load) σ required to achieve a certain amount of *strain* (deformation or displacement) ϵ, as a function of ϵ and variables such as the temperature T and the strain rate $\dot{\epsilon}$.

An example of a stress–strain curve for a uniaxial tension experiment is shown in Fig. 1a. The deformation is reversed upon removal of the applied stress up to the yield point, beyond which permanent (plastic) deformation occurs. Strain hardening occurs as the ultimate elongation is ap-



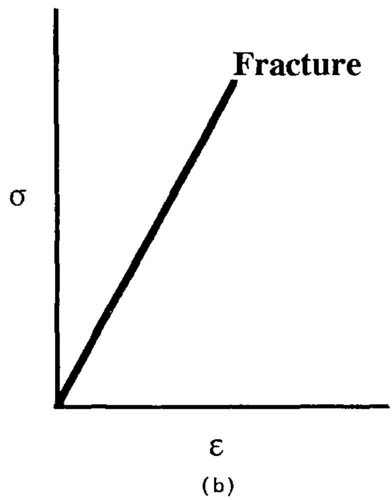


Figure 1 (a) General shape of the stress–strain curve. (b) Shape of the stress–strain curve of a very brittle material. "Toughness" is described by the total area under the stress–strain curve.

proached. Fracture occurs when the ultimate elongation is reached.

The stress has dimensions of force per unit area, that is, negative pressure. In this chapter all quantities with dimensions of stress are expressed in megapascals (MPa). The strain is always a dimensionless quantity. For a tensile deformation it is defined simply as the fractional change of the length of the specimen as a result of the deformation.

Stress–strain curves often do not show some of the features depicted in Fig. 1a. For example, for a very brittle material (Fig. 1b), they typically end abruptly in fracture after a small amount of linear elastic deformation.

Many different testing modes can be used to measure the mechanical properties of polymers. Uniaxial tension, uniaxial compression, plane strain compression, and simple shear, are among the most important testing modes. Each testing mode creates a different stress state along the three principal axes of a specimen during deformation. Several general types of stress–strain behavior are exhibited by specimens, depending on intrinsic material properties, the preparation and processing conditions of specimens, and the test conditions. See Fig. 1 for two examples. See standard references [2–6] for more detailed discussions of stress–strain curves.

There are significant differences between the *small-strain* (i.e., small deformation) and the *large-strain* behavior of polymers. Small-strain behavior will be discussed in Section II. It is mainly described by the moduli (or compliances) and Poisson's ratio. Large-strain behavior will be discussed in Section III. It refers to failure mechanisms observed in specimens, such as brittle fracture, shear yielding, and crazing, resulting in either their complete breakage or a catastrophic deterioration of their mechanical properties. In Section IV methods and computer programs that attempt to treat the mechanical properties of polymers in great atomistic detail will be discussed.

Within the context of fracture mechanics [2,6], the *toughness* of a specimen refers to the total amount of energy required to cause failure, that is, the total area under the stress–strain curve. For example, the specimen whose stress–strain behavior is shown in Fig. 1a is "tougher" than the specimen whose behavior is shown in Fig. 1b. Toughness is, in general, highly desirable. It can only be defined precisely for the behavior of a given specimen under a given set of test conditions. When a reference is made to the toughness of a polymer or other type of material rather than the toughness of a specimen, this describes the *statistical average* of the stress–strain behavior of a set of specimens of the material under a precisely defined set of test conditions.

Toughness is the net result of the superposition of the effects of many factors:

1. Molecular factors related to the nature of the materials. Attempts have been made to correlate these factors by means of a set of new quantitative structure–property relationships, which will be summarized later. These empirical and semiempirical relationships relate the observed behavior to the structure of the repeat unit of a polymer.
2. Chemical crosslinks, which are a special type of molecular feature that can also affect the toughness in a significant manner, as will be discussed later.
3. Effects of thermal history.
4. Effects of supramolecular organization (discussed later), as manifested by semicrystallinity, and/or other types of phase separation (as in block copolymers, immiscible polymers, and polymers reinforced with particulates or fibers).
5. Effects of anisotropy (orientation).
6. Effects of the temperature and the deformation rate during testing.
7. Effects of the mode of deformation. For example, at a given temperature and deformation rate, the proclivity to fail in