Kenton R. Osborn
Wilmer A. Jenkins

PLASTIC FILMS

Technology and Packaging Applications

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Kenton R. Osborn

*Formerly Technology Manager
Packaging Products Division
Polymer Products Department
E. I. du Pont de Nemours & Company, Inc.*

Wilmer A. Jenkins

*Formerly Director
Packaging Products Division
Polymer Products Department
E. I. du Pont de Nemours & Company, Inc.*

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PLASTIC FILMS

The commercialization of cellophane in the 1920s revolutionized the flexible packaging of consumer goods. For the first time, the buyer could see the contents of the package through a film that protected the packaged items from dirt, moisture, and atmospheric gases. Countless items previously packaged in heavy metal or fragile glass containers began to appear in this safe, convenient, light weight film. As a result, the flexible packaging industry grew from a small paper-based operation into the $5 billion giant it is today.

Cellophane rapidly grew to a multi-hundred million dollar business in the U.S. until the commercialization of high polymers in the early 1950s provided packagers with equally transparent films having better properties at lower cost. By the 1980s, plastic films had replaced 90% of the cellophane in flexible packages while plastics' versatility led to further growth in the use of lightweight, convenient, safe flexible packages as alternatives to traditional materials and packaging methods.

This book presents a comprehensive description of plastic films and their use in packaging. The reader will find a heavy emphasis not only on "what" and "how" but also on "why". The first three chapters are devoted to the technology of plastics and plastic films. Chapter 1 introduces the reader to polymer technology: what polymers are, how they are made, and how their properties are related to the structures and interactions of these long chain molecules. The second chapter describes the processes used to convert high polymers to thin, clear, strong plastic films. The third chapter completes the presentation of technology by describing how films are further processed to provide the properties needed for packaging applications.

The discussion then turns to those applications, beginning in Chapter 4 with a comprehensive description of the requirements of a package and the properties that any film must possess in order to meet these requirements. Chapter 5 deals with the complex world of packaging machinery: the equipment that has been developed to combine a plastic film with the prod-

uct being packaged in it and the properties a film must have to be success-
fully used on that equipment. With this background information in place,
Chapter 6 then describes the plastic films that are used to package the mil-
lions of items that are now packaged in this way, relating the requirements
of the contents to the properties of the films that are used.

Finally, in Chapter 7 the authors look into the future and describe what
they believe to be the likely evolution of plastic film packaging, with a dis-
cussion of the major factors, both positive and negative, that will shape
that future.

The Appendix contains a Glossary of Terms, Abbreviations and Test
Methods; a Table of Film Properties; information on the current prices of
plastic resins and films; and a description of how this complex industry is
organized.

A thorough understanding of the material in this volume, particularly
the technology presented in the first three chapters, requires that the reader
be generally familiar with the elements of chemistry and physics presented
in introductory college courses in those subjects. Additional technical
terms have been defined as they appear.

The information in this book should be of value to many audiences:

- employees of companies that package their products for
  distribution and sale
- specialists and managers in companies who manufacture plastic
  films and resins for packaging converters and end users
- flexible packaging converters who want to learn more about the
  plastic films they use
- college students pursuing a career in packaging
- those working in the field who feel they need a broader
  comprehension of its many aspects as well as a reference source
  to help them keep up-to-date with this rapidly evolving technology

Although this book is designed to be a comprehensive treatment of the
subject, three criteria have led to the deliberate exclusion of material that
could have been included.

First, the focus is primarily on technology and applications current in
North America. Modern film technology is much the same throughout the
industrialized world, but cultural tastes and product consumption habits,
particularly in food, vary from region to region, leading to significant re-
gional differences in packaging methods.

Second, the material on applications attempts to concentrate on package
types that are durable rather than transitory. As any supermarket shopper
knows, packages come and go, changing as manufacturers attempt to gain
market share by differentiating their offerings from those of their competi-
tors. Any attempt to exhaustively describe *all* current packages would be
tedious and soon outdated.

Third, rapid literary obsolescence has been avoided by dealing with process economics in a semi-quantitative, rather than a fully quantitative, manner. Thus, while absolute cost numbers are quoted in some cases, more often the cost of various processes are compared using phrases like "about twice" or "roughly three times" or "at least an order of magnitude greater than" rather than quoting actual numbers which unpredictable future events would soon leave outdated. The reader will find tables in the Appendix that show both plastic resin and plastic film prices. As time passes, these numbers will no longer be accurate in the absolute sense, but should have more enduring value as a portrayal of the relative price positions of these materials. The reader who needs precise cost information must always turn to suppliers for it rather than trust this or any other book, no matter how recent.

Many sources in addition to the authors' personal knowledge and experience have been used to compile the information presented here: packaging experts in many companies, trade literature, standard reference works, and other books that contain relevant, up-to-date material. The sources used will be found as footnotes on the pages where referenced and in the Bibliography section at the end of each chapter.

The authors are deeply grateful to the many individuals who made their time and knowledge available to help put this story together. The truth that appears here is often due to them, but never should they be held responsible for the inevitable errors and omissions — for these the authors are solely responsible.

BIOGRAPHIES

Wilmer A. Jenkins, Ph.D., received his Bachelor's Degree from Swarthmore College in 1949 and his Ph.D. in Chemistry from the California Institute of Technology in 1952. He then joined the DuPont Company as a research chemist, and went on to hold a variety of technical, manufacturing and sales positions in the fields of pigments, explosives, polymer intermediates and plastics. For the ten years prior to his retirement in 1989 he was Director of the Packaging Products Division of the Polymer Products Department. This division manufactured films (cellophane, Mylar®, Clysar® shrink films) and resins (EVA, ionomers, acid copolymers, HDPE, LDPE) for the flexible packaging industry. He was active in the Flexible Packaging Association during that period, serving on their Board of Directors and Executive Committee. Since retirement, he has been active as a consultant and co-author of books on plastics in food packaging and plastic films.

Kenton R. Osborn, Ph.D., received his Bachelor's Degree from Drew University and his Ph.D. in Physical Chemistry from the Illinois Institute of Technology. He joined the DuPont Company in 1955 as a research chemist in the Film Department and went on to hold a series of management positions in research and manufacturing. He was directly involved in all stages of the development and commercialization of new film products and processes, as well as the continual upgrading of technology. He has had first-hand experience with most of the commercially important products, including blown and oriented polyethylene films, oriented polypropylene film, oriented polyester film, polyvinyl fluoride film, polyimide film, cellophane, cellulose acetate film, shrink films, coated and coextruded films based on many of the above and numerous experimental films. For the fifteen years prior to his retirement in 1989, he was Technology Manager, directing all of the technical activities for DuPont's packaging products, including research and technical support for manufacturing and sales.

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CHAPTER 1
Polymers

INTRODUCTION

There is an almost bewildering array of plastic films for packaging that are commercially available today. Their evolution was driven by market need on the one hand and by advances in technology on the other. These technological advances included development of both the number of polymers that are the current components of plastic films and the variety of processes for converting these polymers into films and film structures. In this chapter, an understanding of these polymers and how they are made will be developed.

Polymers are very long molecules, and while a few of commercial interest are formed in nature, like cellulose, most are synthesized using a chemical process called polymerization. In this process small molecules, called monomers, are joined together, end to end, in a growing chain. Eventually, the length of the polymer chain reaches a point where commercially useful objects can be made from them. Films made from short chains are brittle, but above some critical length they become tough and ductile. This transition point is different for different classes of polymers, but for polyethylene commercially useful chains have a minimum of 1000 to 2000 monomer units. Thus, the most important characteristic of polymer molecules is their length since that determines whether they have any usefulness at all.

The next most important characteristic is the chemical nature of the units making up the polymer molecule. Degrees of toughness, stiffness, transparency, barrier to gases, etc. exhibited by films of chemically different polymers vary widely. Additional variation is also caused by the specific conditions under which the polymerization takes place. Also, combinations of monomer units can be caused to polymerize together forming a copolymer. Finally, different polymer molecules can be mixed together or blended leading to further proliferation of the levels and combinations of properties that are achievable in plastic films.

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In the next sections, an understanding of polymer molecules and their structure will be developed and used to explain their fundamental properties. The fundamental properties of polymers are those that are important regardless of how they are used; the properties of films will be described in Chapter 2 where film processes and products are discussed.

MOLECULAR STRUCTURE

The simplest member of the family is polyethylene. It is made up of repeating units with the chemical structure CH_2, as in Figure 1.1.

Much of the discussion that follows on polymer structure and its relation to properties will be based on polyethylene since it serves as a good model for polymers in general. Later in the chapter, the effects of the chemical structures of other more complex polymers will be covered. Polyethylene is made from ethylene gas. The process will be described in detail later but for the purposes of this discussion can be simplified as follows. When the ethylene molecule is attacked by a free radical (designated as $R \cdot$), the free radical bonds to the ethylene and transfers the free radical site to the ethylene end of the new molecule, as in Figure 1.2. The new molecule is still a free radical, so it can attach itself to another ethylene molecule, again transferring the free radical site to the growing end of the molecule. This process of repeated additions is the dominant one because of the high concentration of ethylene molecules and the small concentration of free radicals. However, two free radical ends occasionally meet and join together completely eliminating the free radical nature of the two molecules. When that happens, the polymer molecule ceases to grow.

Other chemical reactions also terminate the growth of the polymer molecule. These involve reactions of the free radical entities with chemically active sites on the polymer molecule or with other chemically active molecules that are present as impurities or are deliberately added to control the length of the polymer molecule. Thus, for one reason or another, the polymer chain does not grow indefinitely. Finished polymer chains vary in length since the events that compete with the polymerization process are controlled by probabilities that depend on relative rates of the various possible chemical reactions and on the relative concentrations of
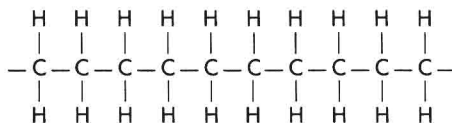

Figure 1.1 The Structure of Polyethylene.

$$R\cdot \; + \;\; \underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}} = \underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}} \;\; \longrightarrow \;\; R - \underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}} - \underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}} \cdot$$
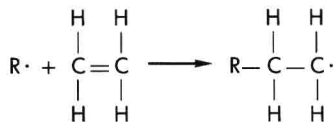
Figure 1.2 The Reaction of Ethylene with a Free Radical.

the reacting chemical species. As a result, there is always a distribution of polymer lengths.

Molecular Weight and Molecular Weight Distribution

The length of a linear polymer chain is usually described by its molecular weight, which is simply the molecular weight of the monomer multiplied by the number of monomers in the polymer chain. For polyethylene, the molecular weight of the monomer (CH_2–CH_2) is 28 and a common number of these units is about 5,000. Thus a typical molecular weight for polyethylene is 140,000. Commercial polyethylenes range in molecular weight from about 50,000 to over 1,000,000.

The distribution of molecular weights for polymers is described by curves similar to the idealized Gaussian curve shown in Figure 1.3. This curve is constructed by plotting the molecular weight along the x axis and the number of molecules having that molecular weight on the y axis. How the curve is determined experimentally will be described later. If the curve had always exactly the same symmetrical shape as defined in Figure 1.3, then a single number, defined by A, the intersection of the axis of symmetry with the curve (as shown below), would suffice to describe the distribu-
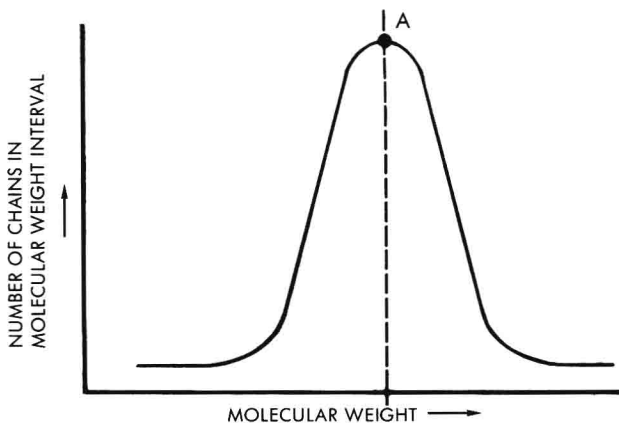

Figure 1.3 Idealized Curve of the Molecular Weight Distribution for Polymers.

tion. This single number could be called the average molecular weight. Everyone would know that equal quantities of polymers would be present with higher and lower molecular weights and, for that matter, could define from the curve exactly those quantities for any given range of molecular weights.

In reality, however, there are two complications. The first is that the distributions are not symmetrical and the shapes of the distribution curves depend on the process used to make the polymer. A curve for a typical polymer is shown in Figure 1.4. Note here the existence of high molecular weight "tail": that is, a much higher fraction of high molecular weight polymer molecules than would be the case for a symmetrical distribution curve. This, and a low molecular weight tail, are both common occurrences in the polymerization process. The presence or absence of such tails can have a subtle but significant effect on the physical properties of polymers and hence, it is important to be able to characterize the distribution curve.

The second complication is that different methods of measuring an average molecular weight can lead to different numbers as shown in Figure 1.4. For example, one number is a number average molecular weight (M_n). This is derived from the total weight of polymer molecules divided by the total number. Another kind of number is a weight average molecular weight (M_w) which is determined by multiplying the weight of each chain of a given number of repeat units by the number of such chains and dividing by the total weight of chains. When both of these are known, they can be used to characterize the shape of the distribution curve. The ratio, (M_w/M_n) is used to judge whether the distribution is narrow or broad. For example, a ratio of 6 is considered a narrow distribution for polyethylene while a ratio of 12 is considered a broad distribution.
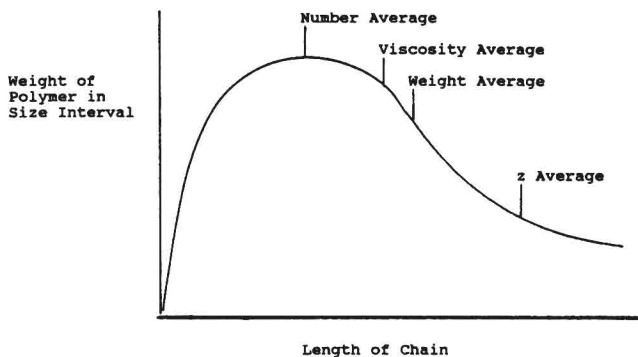

Figure 1.4 Molecular Weight Distribution and Molecular Weight Averages in a Typical Polymer.

Measurement of Molecular Weight and Molecular Weight Distribution

The behavior of a polymer molecule in the solid or melted state is influenced heavily by interactions with neighboring molecules. Therefore, measurements that reflect the characteristics of an isolated molecule (such as its molecular weight) are made in very dilute solutions. One of the traditional measurements of molecular weight is based on the osmotic pressure of dilute solutions. This pressure is the differential pressure sustained across a membrane that separates the pure solvent from a dilute solution of a polymer and that permits the passage of solvent only. The osmotic pressure is a function only of the number of molecules in solution. Therefore, knowing the total weight of polymer, a number average molecular weight can be calculated.

Another determination derives from light scattering measurements using a wave length of light that approximates the dimensions of the polymer molecule. This leads to a weight average molecular weight and represents the statistically expected size of the average molecule. As such it is very sensitive to the presence of larger molecules. Measurement of the rate of sedimentation in a dilute solution subjected to high centrifugal forces will also yield an average molecular weight. This is the "z average" molecular weight shown in Figure 1.4.

All of the above techniques are difficult and tedious and not suitable for the routine measurements needed to control a commercial process. Therefore, simpler measurements that correlate empirically with molecular weight are employed. One of these is the measurement of viscosity in dilute solution. A correlation can be established between viscosity and molecular weight from the viscosities of samples of known molecular weight and with a narrow molecular weight distribution. This "viscosity average molecular weight" falls in between the number and weight average molecular weights as shown in Figure 1.4.

As mentioned earlier, some indication of the breadth of the molecular weight distribution curve can be made if both the number average and weight average molecular weights are known. A more complete description can be established by fractionation of the sample using a technique that depends on the size or weight of a molecule. A quick and convenient technique for this determination is gel permeation chromatography or GPC. Here a solution of a polymer is passed through a column consisting of beads of porous glass, or cross-linked polymer containing pores of a controlled size. Smaller molecules from the solution penetrate and are retained for a time in the pores while larger molecules pass directly through the column. Thus at the exit of the column the highest molecular weight fraction appears first followed by fractions of decreasing molecular