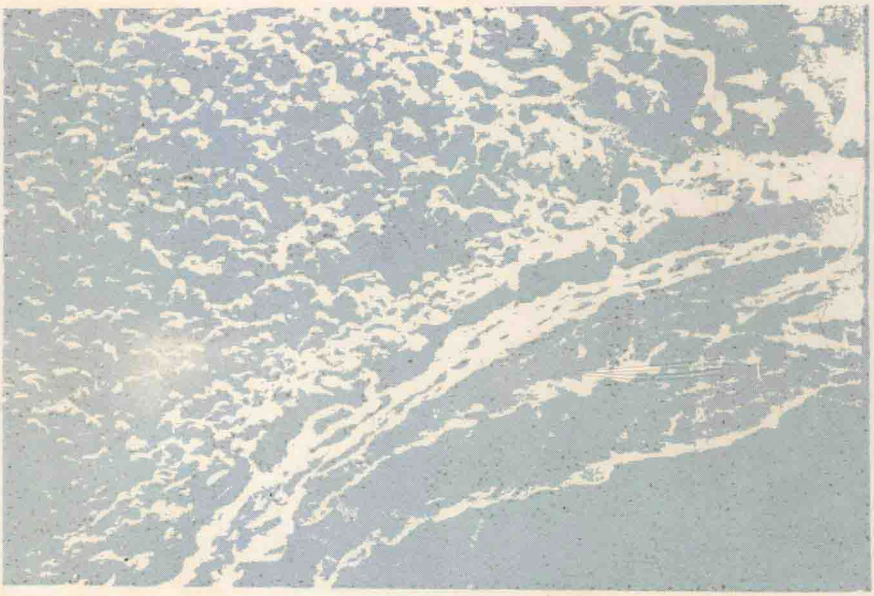
POLYMER - PLASTICS TEST METHODS

NICHOLAS P. CHEREMISINOFF



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Nicholas P. Cheremisinoff is employed by Exxon Chemical Company in the elastomers technology division where he supervises and conducts R & D programs in product development. He is the author/co-author of over fifty technical books and has contributed extensively to the industrial press. Dr. Cheremisinoff received his B.S., M.S. and Ph.D. degrees from Clarkson College of Technology.

Preface

This volume is intended as a handy desk reference on laboratory test procedures and instrumentation used for plastics and elastomer performance testing and materials characterization. The book provides descriptive information on a variety testing methods used for product quality control, as well as in the development and optimization of new polymers. Principal areas covered are molecular characterization, compositional character, physical properties testing, cure performance, rheological characterization and polymer processing properties. An overview of international standards is provided. The book is intended for use by engineers, product development personnel, and laboratory technicians.

Nicholas P. Cheremisinoff

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CHAPTER 1
PRINCIPLES OF PRODUCT TESTING

INTRODUCTION AND OVERVIEW

Ideas for new products generally develop in two ways. Researchers in product development can make technological forecasts of new developments in basic and applied research which could give birth to new products and processes. At the same time or separately, marketing and sales employ the tools of market research to identify unfulfilled needs in the marketplace or opportunities to compete with other products or applications. These two avenues often converge to embody the spirit of new product effort.

What ultimately ensures the financial success of any new product is the demand for it in the marketplace and its cost effectiveness in manufacturing. Another way of saying this is that when a product is properly designed, it has several key features.

- Unique performance properties that demand a premium in the marketplace, or at the very least, provide competitive alternatives to existing materials or products.

- The product can be manufactured to a specified consistency and in a cost effective manner.

- The product does not require alterations during or after production, which can increase the chances of inconsistency.

- The product performs to the expectations and claims of the manufacturer under the environmental conditions for which it is intended to be used.

It is a fair statement then the product design has a direct bearing on product quality. The poor design of any product, whether it is the raw plastic or elastomer material itself or the part into which it is ultimately fabricated, such as an insulating jacket for an electrical cable, is what limits 100% quality of conformance and is what will ultimately contribute to failure in the marketplace.

There are many factors which contribute to the success and failures of product development programs, which run the gambit from R & D philosophy, to management support, to the technical aspects of synthesis and product testing. It is beyond the scope of this volume to address the philosophy and management approach to proper product development, and indeed beyond the author's level of expertise. Instead, this volume is devoted to the technical aspects of plastics and elastomeric material testing which

plays a crucial role in polymer product development. The book addresses important test methods used in the plastics manufacturing and processing industries. This first chapter provides terminology and fundamental concepts of polymer science and philosophy of product development, orienting the reader for latter discussions.

PRINCIPLES OF POLYMER SCIENCE

In this section, we shall review the basic concepts and principles of polymer science. Its purpose is to orient the reader and to aquaint the less experienced user with concepts and terminology referred to in the latter discussions.

The word "Polymer" comes from the Greek words Poly (many) and mer (small units). In other words, many monomers are chained together to form a polymer. For instance, polyethylene is formed by polymerization of many ethylene monomers. Polymers are synthesized by the process of polymerization, of which there are several.

Addition polymerization is also known as radical chain polymerization. The addition reaction starts with a free radical which is an initiator for the polymerization reaction. The free radical is usually formed by the decomposition of a relatively unstable component in polymer structures. In the reaction, repeating units add one at a time to the chain so monomer concentration decreases steadily throughout the reaction.

$$Mx^{-} + M \longrightarrow Mx + 1$$

High polymers can be formed at once by this type of polymerization. Long reaction times give high yields but do not

affect molecular weight (refer to Fig. 1). Polymers made by chain reaction often contain only carbon atoms in the main backbone chain. These are called "homo chain polymers".

Condensation polymerization (also known as step reaction polymerization) is analogous to the condensation of low molecular weight compounds. In polymer formation, condensation takes place between two polyfunctional molecules to produce one larger polyfunctional molecule with the possible elimination of a small molecule such as water. The reaction continues until almost all of one of the reagents is used up. The structural units of condensation polymers are usually joined by inter unit functional groups. The types of products formed in a condensation reaction are determined by the functionality, i.e., by the average number of reactive functional groups per monomer molecule.

$$Mx + My \longrightarrow Mx + y$$

Generally, mono-functional monomers form low molecular weight products. Bi-functional monomers form linear polymers and poly-functional monomers give branched or cross-linked polymers. In this polymerization, molecular weight rises steadily throughout the reaction as shown in Figure 2. Therefore, a long reaction time is essential for high molecular weight polymers. Polymers made by the step reactions may have other atoms, originating in the monomer functional groups as part of the chain. This is called "hetero polymers."

The length of the polymer chain is specified by the number of repeating units in the chain. Polymers which have fully extended linear structure are unstable; however, the

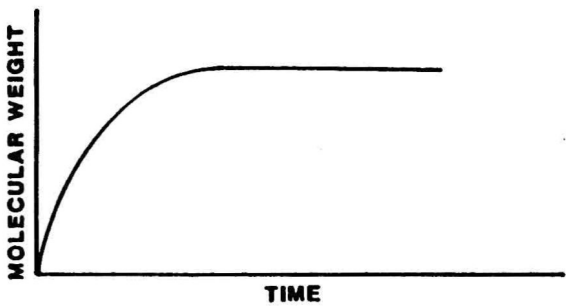

Figure 1 Shows molecular weight as a function of time in an addition reaction.

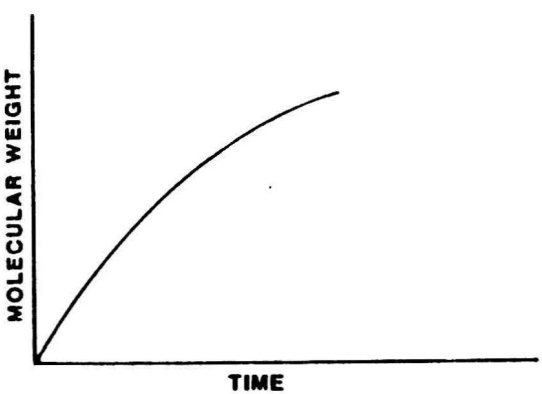

Figure 2 Shows molecular weight as a function of time in a condensation reaction

polymers that have random structure (random coil) are stable. These are illustrated in Figure 3. Bifunctional monomers in condensation polymerization normally form linear polymers. Linear polymers can be dissolved, melted, molded and have finite molecular weight. Poly-functional monomers in condensation reaction normally form branched polymers or cross-linked polymers. Cross-linked polymers (Network) are insoluble, infusible (i.e., have no melting point), non-moldable and have infinite molecular weight (refer to Figure 4).

Most linear polymers can be made to soften and take on new shapes by the application of heat and pressure. These changes are physical rather than chemical. This type of material is referred to as a thermoplastic resin and it is reprocessible.

Thermosets are materials that have undergone a chemical reaction (curing) by application of heat, catalyst, etc. The cross-linked network extending throughout the final article is stable to heat and cannot be made to flow or melt. Curing of thermosets are described by A, B, and C stages upon degree of curing reaction. "A" stage is the earlier stage, "B" stage is an intermediate stage, and "C" stage is the final stage of the curing reaction. This type of material is not reprocessible. Rubbers or elastomers are materials that deform upon application of stress and revert back to their original shape upon elimination of applied stress. It is capable of rapid elastic recovery. Materials are usually vulcanized by sulfur, however, peroxide cures are also common. Natural rubber is an elastic substance that is obtained by coagulating the milky juice of any various tropical plants. In contrast, a synthetic rubber is one in which two or more monomers are artifically combined together

1. RANDOM COPOLYMER : A BBB AA B AAA BB AA BBB

2. UNIFORM COPOLYMER : AB AB AB AB AB

3. BLOCK COPOLYMER : AAA BBB AAA BBB AAA BBB

4. HOMOPOLYMER : AAAAAAAAA OR BBBBBBBBB

Figure 3 Illustrates linear and random structure polymers

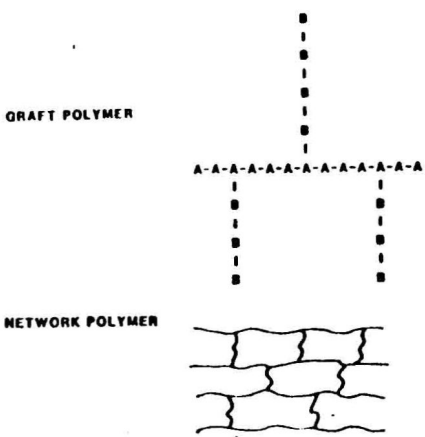

Figure 4 Shows graft and network polymers

through chemical reaction. Therefore, many rubbers are copolymers.

A crystal is an orderly arrangement of atoms in space. The polymer crystallizes under a suitable condition and it is called a crystalline polymer. Phase transition of the polymer occurs from solid to liquid. The transition temperature of this polymer is called the melting temperature and is often designated at T_m. All crystalline polymers contain non-crystalline portions as well as crystalline portions. There are many polymers which fall into the semi-crystalline region.

An amorphous polymer does not crystallize under any condition. Phase transition of this polymer occurs from glassy state to rubbery state. The transition temperature of the polymer is called the glass transition temperature and is often designated as T_g. Most polymers have both T_g and T_m. The melting temperature and glass transition temperature can be found by measuring the specific volume or enthalpy of the polymer as a function of temperature.

Glass transition temperature is the temperature of onset of extensive molecular motion. The slope of the temperature-specific volume curve above the glass transition temperature is characteristic of a rubber, and below the transition temperature is characteristic of glass. T_g decreases with decreasing amorphous content. Therefore, T_g is sometimes difficult to detect in highly crystalline polymers.

Molecular weight (Mw) is defined as the sum of the atomic masses of the elements forming the molecule. The structural formula of Polyethylene is often expressed as

shown in Figure 5. Therefore, the molecular weight of polyethylene can be calculated as n multiplied by the Mw of repeating units. As an example, suppose we mix lg of polymer of 1,000,000 Mol. wt. with lg of polymer of 1,000 Mol. wt. What is weight average molecular weight (Mw)? The Mol. wt. of 2 g of the polymer mix is 1,001,000.

Therefore, Mw = 500,500.

The number average molecular weight (Mn) is calculated from, Avogardro's number. If two molecules which have a ratio of 1:1000 molecules of polymer 1,000,000 to polymer 1,000 mixed together, what is Mn? The solution is:

1 molecule	1,000,000
1,000 molecule	1,000,000
1001 molecule	2,000,000

Therefore, Mn = 1,998

Normally, Mw > Mn

The ratio of Mw and Mn is sometimes used as a measure of the breadth of the Molecular Weight Distribution (MWD). The Molecular Weight Distribution range of typical polymers are from 1.5 - 2.0 to 20 - 50. The MWD for the above example is:

MWD = Mw/Mn = 25.6.

The subject of molecular weight and molecular weight