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5th Edition

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Preface

Processors and users of plastics often, for many different reasons, have to determine the chemical nature of a plastics sample. In contrast to plastics producers, however, they lack the specially equipped laboratories and the analytically trained staff for this purpose.

The complete identification of a high-molecular weight organic material is a rather complicated and often expensive problem. For many practical needs it is often sufficient to determine to which class of plastics an unknown sample belongs, for example, to find out whether the material is a polyolefin or a polyamide. To answer such a question, one usually only needs to use simple methods that do not require special chemical expertise.

In this book, now in its fifth edition, the author has compiled a selection of proven procedures which, based on his own experience, will enable the technician, the engineer, and also the technical customer service representative to identify an unknown plastic, e. g., for purposes of quality control or plastics recycling. All described procedures were carried out by the author as well as by students in courses at the German Plastics Institute. Additional experience with these procedures was thus obtained and included in the book. The author welcomes any other comments and suggestions for additions by readers and users of this book.

Clearly one should not expect to obtain sophisticated information from these simple methods. In most cases, one has to be satisfied with the identification of the plastic material, whereas the analysis of sometimes very small amounts of fillers, plasticizers, stabilizers, or other additives is only possible through the use of more advanced physical and chemical methods.

Similarly, it is not possible with simple methods to identify with certainty such combinations as copolymers and polymer blends. In such cases more sophisticated methods of analysis are required.

As this book has also been found useful by collectors of historical plastics articles, professional conservators, restorers, and students of conservation sciences, in this new edition a small chapter on identification of frequently used natural resins and some other early plastics has been included.

The good reception that previous English, German, Spanish, and French editions of this book have received from users and from reviewers in various plastics journals and magazines shows that in spite of all the modern analytical methods and advances in instrumental analysis, there is still a need for simple methods for the identification of plastics. The analytical procedures described in this book do not require special chemical knowledge but they do require skills in carrying out simple operations. It is most important to remember to be careful in handling chemicals, solvents, and open flames; other precautions will be pointed out in the pertinent sections. The necessary equipment is listed in the Appendix. With most experiments it is recommended that parallel experiments with known materials are also carried out (a Plastics ID Kit is available through the Society of Plastics Engineers).

It is hoped that this edition fills the gap between the extensive plastics analysis volumes covering various methods in great detail and the tabular compilations of selected samples. Naturally, this entails a compromise between investing in a greater experimental effort or being satisfied with the more limited information that can be obtained from simple qualitative analytical methods.

The development and testing of the methods described in this book were part of the research programs at the German Plastics Institute and the author is grateful for some financial support from German research organizations. The author also thanks the various people who collaborated on this project, especially Dr. R. Disselhoff, Dr. H. Pasch, and Dr. E. Richter and also Ms. Ch. Hock who obtained the IR-spectra. As in previous editions, the author thanks the Carl Hanser Verlag for good collaboration and for taking the author’s wishes into consideration.

Darmstadt, March 2013 *Dietrich Braun*

Contents

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Plastics and Their Characteristics

Plastics are high molecular weight (macromolecular or polymeric) organic substances that have usually been synthesized from low molecular weight compounds. They may also have been obtained by chemical modification of high molecular weight natural materials (especially cellulose). The raw materials are most often petroleum, natural gas, and coal. They can be reacted with air, water, or sodium chloride to prepare reactive monomers. The most important industrial synthetic processes for the preparation of plastics from monomers may be classified according to the mechanism of the formation reaction of the polymer, such as polymerization and condensation reactions. Since several chemically identical or similar plastics can be prepared in several different ways and from different raw materials, this classification has little meaning for the analysis of unknown plastics samples. On the other hand, in addition to chemical investigations, the appearance of a plastic as well as its behavior on heating yields useful information for its identification.

There are physical interactions between the individual macromolecules that constitute a plastic material, just as there are between the molecules of a low molecular weight compound. These physical interactions are responsible for cohesion and related properties such as strength, hardness, and softening behavior. Plastics that consist of linear threadlike molecules (several hundred nanometers (nm) long and a few tenths of a nanometer in diameter) ($1\ \text{nm} = 10^{-9}\ \text{m} = 10\ \text{Å} = 10^{-6}\ \text{mm}$), i. e., of macromolecules, that are not strongly crosslinked can usually be softened on heating. In many cases they melt. Thus, when a polymeric material is heated above a certain temperature, the macromolecules which are more or less oriented with respect to each other at low temperatures can glide past each other to form a melt of relatively high viscosity. Depending on the degree of order of the macromolecule in the solid state, it is possible to distinguish between partly crystalline and (mostly disordered) amorphous plastics (see Figure 1.1). This degree of order also has an effect on the behavior of the plastic on heating and on its solubility.

Plastics that soften on heating and start to flow are called thermoplastics. On cooling, such plastics become solid again. This process can be repeated many times. There are several exceptions, as when the chemical stability (expressed in terms of the temperature at which chemical decomposition starts) is lower than the cohesion between the macromolecules due to interactions between the chains, in which case, on heating, the plastic undergoes chemical changes before it reaches its softening or melting point.

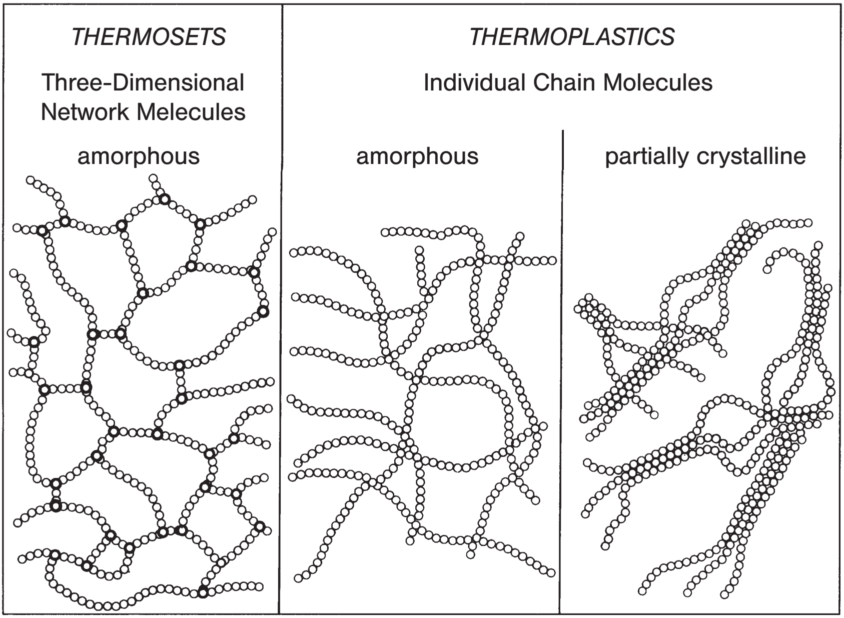

FIGURE 1.1 Schematic representation of the structure of plastics, showing the three major types of macromolecular arrangements. Approximately 1 000 000 times actual size and greatly simplified. (Crystallites can also occur as the result of chain folding.)

A further indication, with few exceptions, that macromolecules are linear or branched is their solubility in many liquids, such as organic solvents. This process also reduces the interaction between the macromolecules; solvent molecules insert themselves between the polymer chains.

In contrast to thermoplastic materials, there are the so-called thermosetting materials. These, after processing into their final state, are crosslinked macromolecules that can neither melt nor dissolve. For such products one generally starts with liquid or soluble raw materials of a rather low molecular weight. These may be crosslinked by heating with or without pressure or through chemical reactions with additives and concurrent molding conditions. The results are crosslinked (hardened) high molecular weight materials in three-dimensional networks. These giant molecules can be broken down into smaller and therefore meltable and soluble fragments only by chemical destruction of the crosslinks. This may occur at rather high temperatures or with certain chemical reagents. Thermosets often contain fillers that may strongly influence the appearance and properties of the products.

Finally, we may distinguish the elastomers by their physical appearance which is a rubberlike elastic material that usually consists of relatively weakly crosslinked macromolecules. Crosslinkages of natural or synthetic rubber are formed during the molding or vulcanization process. Because of their crosslinked nature, elastomers do not melt on heating until just below their decomposition temperature. In this sense they behave differently from many other elastic thermoplastic materials such as plasticized polyvinyl chloride (PVC). In contrast to the chemically crosslinked elastomers (rubber), e. g., by sulfur or peroxides, network formation in the so-called thermoplastic elastomers (TPE) occurs through physical interactions between the macromolecules. On heating, the physical interaction forces between the chain molecules decrease, so that these polymers can be thermoplastically shaped. On cooling, as the physical interaction between the molecules becomes stronger, the material again behaves like an elastomer.

Table 1.1 lists the most important characteristics of these three groups of polymeric materials. In addition to elasticity, behavior on heating, density, and solubility can be used to differentiate between these materials. However, it should be kept in mind that fillers, pigments, or reinforcing agents,