Dietrich Braun

Simple Methods for

Identification of Plastics

Third Edition

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With the Plastics Identification Table
by Hansjürgen Saechtling

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Preface to the Third Edition

The First Edition of this small analysis book was well received by users and reviewers; it has also been translated into several languages. This shows that inspite of all the modern, and unfortunately often quite expensive, analytical methods and advances in the field of instrumental analysis, there still exists a need for simple methods for the identification of plastics.

The Second Edition, therefore, did not require very substantial changes. A table on polymer blends was added because these materials have become important industrially. Some additional tests were added to Chapter 6 which describes specific identification tests for different types of plastics. Chapter 5, on systematic analytical procedures, was enlarged and now incorporates the Plastics Identification Table of Dr. Hansjürgen Saechtling (currently in its 8th Edition). The Third Edition has been updated with respect to trade names, raw material suppliers and polymer blends.

With this edition, as with the earlier one, I owe thanks to Hanser Publishers (Carl Hanser Verlag) and especially to Dr. W. Glenz for their excellent cooperation during the production of this book. I also repeat my invitation to the users of the book to write me about their experiences with these analytical procedures and to send me suggestions for additions or improvements.

Darmstadt, Autumn 1995 Dietrich Braun

Preface to the First Edition

Processors and users of plastics often need to determine the chemical nature of a plastics sample. In contrast to the producers of plastics, however, they usually lack specially equipped laboratories and a staff with analytical experience.

The complete identification of a high molecular weight organic compound is often a rather complicated problem which can sometimes be solved only with the expenditure of a considerable amount of effort. For many practical situations it is often quite sufficient to determine the class of plastics to which an unknown sample belongs, for example, whether it is a polyolefin or a polyamide. To answer such questions one need have only relatively simple means at hand and some rudimentary knowledge of chemistry.

Several more or less comprehensive sets of instructions for carrying out simple analyses of plastics may be found in the literature. These include the Plastics Identification Table by Hansjürgen Saechtling (8th edition by Carl Hanser Publishers, 1979), which since many years has been a valuable instruction for the identification of plastics starting from their appearance. With the kind permission of the author the table has been included in this book. However, some of these are rather brief and others are experimentally too demanding. Many simpler testing methods are also scattered throughout the technical literature and are not always easily accessible.

I have therefore tried to collect in this book a selection of procedures from the literature and from my own years of experience. These are intended to enable the technician, the engineer, or the technical salesperson to identify unknown plastic materials. Of course, one cannot expect such simple methods to yield a high degree of information. Therefore one has to limit oneself to the identification of the plastic material; the analysis of fillers, plasticizers, stabilizers, or other additives, which are often present only in very small amounts, requires more extensive physical or chemical methods. It should also be pointed out that many industrial combinations of materials or copolymers cannot always be identified with simple methods. In such cases it is necessary to use more advanced methods of analysis.

This book does not require in-depth chemical knowledge, only a certain ability to carry out simple laboratory operations. I particularly remind the reader to use care in the handling of chemicals, solvents, and open flames. Special safety measures that have to be taken into account are pointed out at pertinent places in the book. The necessary equipment is listed in Chapter 8. It is useful in most of these tests to carry out comparative experiments with samples of known plastics. A collection of plastics samples is available from the Society of Plastics Engineers, Brookfield Center, CT 06805.

I have carried out all the tests mentioned in this book and have used them in teaching a number of courses.

That experience has been called upon in writing these chapters. Comments or recommendations for additions from readers of this book are most welcome.

We hope that this manual will close the gap between the rather large and complicated books on the analysis of plastics, which require an extensive background in chemistry and physics, and the various tabular compilations which usually limit themselves to certain preliminary testing. Of course, this requires a consideration of the compromise between the experimental effort and the efficient yield of simple qualitative analytical procedures.

The development and testing of simple methods for the analysis of plastic materials was the subject of a research project of the German Plastics Institute carried out with the financial support of the Arbeitsgemeinschaft Industrieller Forschungs-Vereinigungen e.V. In this program there were several collaborators whom I want to thank, especially Dr. J. Arndt, who helped me in putting the text together. I also thank Dr. W. Glenz for many valuable recommendations and Dr. E. Immergut for his careful translation of this book.

Darmstadt, Spring 1982 Dietrich Braun

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Plastics Identification Table
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1 Plastics and Their Appearance

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) or 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 Fig. 1). This degree

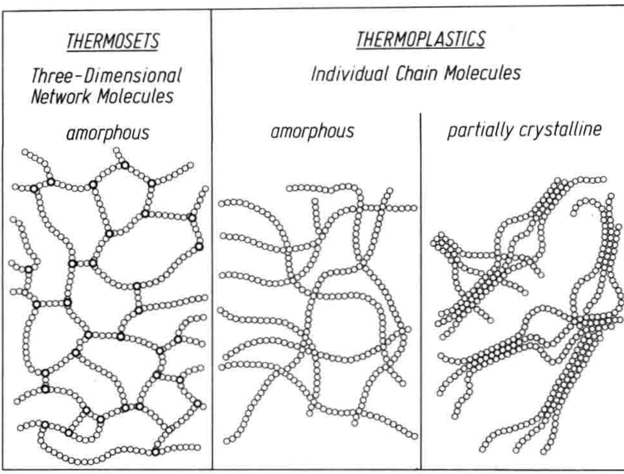

Figure 1. Schematic representation of the structure of plastics, showing the three major types of macromolecular arrangements. Approximately 1,000,000 times actual size and greatly simplified. (Crystallites can also occur as the result of chain folding.)

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 interaction between the chains, in which case, on heating, the plastic undergoes chemical changes before it reaches its softening or melting point. 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 affects 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 threedimensional 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, from their physical appearance, we may distinguish the elastomers, rubberlike elastic materials consisting of usually 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.

Table 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, for example, carbon black or glass fibers, lead to considerable deviations from these properties. Therefore it is not always possible to identify polymeric materials on the basis of these criteria. The densities listed in Table 1 are only rough approximations for some solid materials. For example, foams have densities of approximately 0.1 g/cm^3 or less. Structural foams with integral skin and cellular core have densities between 0.2 and 0.9 g/cm^3 and often cannot be recognized as foams from their outer appearance.

It is not possible to discuss here the special properties of all the different types of plastic materials that can occur within the main groups. The plastics industry today, by employing copolymerization or chemical modification, is capable of producing an extraordinary number of combinations of properties, making the identification of corresponding plastics more complicated. Its physical appearance and its classification as a thermoplastic, thermoset, or elastomer therefore permit us to draw conclusions about the chemical nature of the plastic only in simple cases. But they often provide a useful additional way of characterizing the material.

In the last few years a number of products consisting of a mixture of different plastics have made their appearance; they are usually called polymer blends and polymer alloys. Their identification using simple methods presents considerable difficulties because flame tests and pyrolysis tests are usually not unambiguous. Also a separation into different groups according to the pH-value of the pyrolysates does not permit a definite conclusion. In some cases it is possible to separate polymer mixtures into their components if these have different solubility characteristics and then to identify the components. However it is not possible to recommend a generally applicable separation procedure.

The examination of mixtures of polyamides and polyolefins is relatively easy because the polyamide component can be degraded by acid hydrolysis and the resulting low molecular weight fragments can be identified according to the procedure described in Section 6.2.10. Table 5 lists some of the most importat polymer blends together with their trade names and suppliers.

Although synthetic fibers and synthetic elastomers have the same chemical structure as plastics, they are not included among the latter group. Their identification will therefore be treated in this book only if they also occur as plastics. For example, polycaprolactam (nylon 6) is used both for fiber production and as a molding material.

Tables 2–5 contain a compilation of the plastics discussed in this volume, their chemical abbreviations, and some selected trade names. An extensive table of polymer acronyms on ASTM, DIN and ISO standards can be found on pages 100–105 (Chapter 10).

Table 1. Comparison of Different Classes of Plastics

	Structure	Physical Appearance*	Density (g/cm^3)	Behavior on Heating	Behavior on Treating with Solvents
Thermo-plastics	Linear or branched macromolecules	Partially crystalline: flexible to horn-like; hazy, milky to opaque; only thin films are transparent	0.9–1.4 (except PTFE: 2–2.3)	Material softens; fusible and becomes clear on melting; often fibers can be drawn from the melt; heat-sealable (exceptions exist)	May swell; usually difficult to dissolve in cold solvents, but usually readily dissolved on heating the solvent, e.g., polyethylene in xylene
		Amorphous: colorless; clear and transparent without additives; hard to rubbery (e.g., on adding plasticizers)	0.9–1.9		Soluble (with few exceptions) in certain organic solvents, usually after initial swelling