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ELASTOMERS AND PLASTOMERS

THEIR CHEMISTRY, PHYSICS AND TECHNOLOGY

Edited by R. Houwink

External Lecturer in the Technical University at Delft (Netherlands)

Vol. I. General Theory
Vol. II. Manufacturing, Properties and Applications
Vol. III. Testing and Analysis; Tabulation of Properties

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VOLUME III

TESTING AND ANALYSIS; TABULATION OF PROPERTIES

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CHAPTER 1.

INTRODUCTION

by

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In this volume the testing of physical, mechanical, electrical and chemical properties is discussed by DR. J. H. TEEPLE from a practical point of view. An endeavour has been made to survey the principal methods in the most important countries. The theoretical background for most of these tests is described in Volume I of this book in the chapters by DR. G. J. VAN AMERONGEN on the mechanical and physical properties, also in the chapter by DR. L. HARTSHORN on the electrical properties.

A detailed description of most properties, in connection with the applications of the materials involved, is found in Volume II.

The chemical analysis is treated by EPPRECHT in a systematic and complete way.

The tabulation of the different properties has been carried out by DR. B. B. S. T. BOONSTRA and J. W. F. VAN 'T WOUT in collaboration with the editor.

The properties of Elastomers have been tabulated separately from those of Plastomers since these two groups are characterized by completely different testing methods.

In cases of pure physical constants like the density or the refractive index, a sharp determination is possible and values can be given between narrow limits.

Most characteristics of polymers are not pure physical constants however; the tensile- and the impact strength are typical examples. The values are in such cases dependent on the velocity of the experiment, the type of equiment, the dimensions of the test pieces, etc. For such more or less arbitrary characteristics no sharp agreement between the values in the literature can be expected and the great variety makes a choice often very difficult.

In cases where reasonably narrow limits are available, these have been mentioned, for example: tensile strength of vulcanized rubber = 2,800—5,000 p.s.i. (= 200—350 kg/cm^2). In other cases no narrow limits are available however; an example of this is the tensile strength of wood flour containing phenolformaldehyde materials, for which the limits 4,000—11,000 p.s.i. (= 280—770 kg/cm^2) are mentioned [*] in the literature. Here obviously some extreme values have been found under abnormal conditions or for abnormal mixtures. These however give no idea of the real value of an average material in practice. In such cases a reasonable average, based on other sources or on the experience of the authors is tabulated.

Since most materials under consideration are applied in technical mixtures, containing a great percentage (say 50 %) of fillers, this offers a new source for variability in the technical literature. Of course it is always possible in such cases to make other mixtures with better properties in certain

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*) H. SIMONDS and C. ELLIS, Handbook of Plastics, New York 1943.

respects, but this will result in worse properties in other respects, each mixture being a compromise. No attempt has been made to include in the tables the data available for all these mixtures. An endeavour has only been made to express in numbers the most characteristic properties of those mixtures, which can be considered to be representative of the main groups of materials. An example of this is found in the phenol-formaldehyde laminates, where only the characteristics of the overall qualities are tabulated. For the special grades in such cases the reader is referred to Vol. II of this book.

The survey of the literature is restricted to citing the chief sources only.

In many cases the American, the British and the German specification methods have been applied in order to compare the results in various countries. In other cases one or two of these methods are mentioned only. The choice is then dependent on what is considered to be most characteristic.

For several properties the Units were expressed in the c.g.s. system and the Anglo-American system as well. These data differ only by a multiplication factor, unless otherwise indicated. In cases in which rounded-off numbers are mentioned, say 40 kg/cm^2, the corresponding value in p.s.i., which exactly speaking should be 569, is again rounded- off to say 550. A detailed number, like 569 would give a wrong impression about the precision.

For the Elastomers a great part of the tabulated values were measured by the Rubber Foundation at Delft; they have been completed by compilation from the literature.

CHAPTER 2.

METHODS OF TESTING *

BY

DR. J. H. TEEPLE

Celanese Corp. of America, Newark, N.J. (U.S.A.)

§ 1. Introduction.

The testing of plastics and elastomers is a relatively new technology. As a consequence, it has not reached a final form, but is constantly changing. This natural instability has been augmented by the rapid development of new types of plastics, by the application of existing types in new fields; and by the acceleration given by the war to the natural tendency to extend the range of atmospheric conditions under which testing is carried out.

A true picture of the testing of these materials must therefore contain not only a description of existing methods, but also some indication of the directions in which changes are expected or needed. Such a picture, with its emphasis on limitations and obstacles may present a pessimistic view, and indeed many phases of plastics testing are still unsatisfactory. Frequently test results from one laboratory will not agree with those from another as closely as would be desired; the technique of predicting the behavior of a finished article from tests on the material from which it was made is insufficiently developed; and much of the data which would be useful for theoretical interpretations of the behavior of plastics and elastomers is lacking.

On the other hand the progress that has already been made is considerable. Specimens, equipment and procedures have been standardized for many tests to the extent that they are used satisfactorily for specification purposes. The standard test methods are subject to revision and they are being studied and refined. They are used widely with the result that published data are becoming more reliable and more readily comparable.

Much experience has been gained from attempts to correlate test results with the behavior of finished articles. This experience grows with each new use for which a material is tried. It may be expected eventually to serve as a background for the development of an accurate technique for the design of finished parts and the prediction of service behavior on the basis of laboratory test data.

§ 2. Standardization in various countries. **

It will appear that in various countries a reasonable status has been reached in standardizing test methods. It is however very regrettable that up to now hardly any cooperation between various parts of the world exists, resulting in the fact, that now "various technical languages are talked" and nobody can understand anybody else. The chief reason is that most testing methods are arbitrary, measuring no pure physical constants,

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* The theoretical considerations underlying the testing methods described in this chapter, are discussed in full in Vol. I of this book.

** This section was contributed by Dr. R. HOUWINK. See for details the special sections on normalisation in Chapter 4 and 5.

the values obtained being dependent on the dimensions of the test pieces, the speed of testing, the size of the apparatus, etc, etc.

The astonishing lack of cooperation already appears in such a simple thing as the form and the dimensions of test pieces. To mention one example only we refer to the impact specimen for molded plastics, for which the size of the notch has a radius at the base of 0.010 inch (0.25 mm) in the United States [49]. In Great Britain [49] the standard is 0.040 inch (1 mm) and in Germany no final dimensions have been settled up to now. Experiments have shown however [50, 51] that for rigid materials the results are strongly influenced by the form and size of the notch, showing the more clearly how necessary standardizing is in this field.

Broadly speaking one can distinguish between 4 major groups of standards:

a. *U.S.A.*

Here the A.S.T.M. specifications are most generally adopted but in addition to these one can find others [100]. They are on a high level and growing very rapidly since the outbreak of the war. A close cooperation between the government agencies (Nat. Bur. of Standards) and industry exists.

b. *Great Britain.*

The British Standards Specifications are also on a high level especially regarding rubbers and the thermosetting types of plastics [105]. In many respects they deviate considerably from the A.S.T.M. specifications.

c. *Germany.*

Germany had, before the war, developed a system of classification and of standardizing, far in advance of all other countries of the world. The V.D.E. specifications [101] in 1939 were already the 22nd edition of a steadily growing series of standards. One of the striking features in Germany was the very intensive collaboration along the whole line, starting from the manufacturer of raw materials, via the maker of mixtures, the molder and the fabricator to the final consumer. For all these groups the system was really alive and it was not considered as an unavoidable burden. The trade ordered its primary and final materials according to the specifications and a systematic control, carried out by the "Materialprüfungsamt" (Bureau for testing materials) in the producing plants, furnished the guarantee that all materials were constantly maintained up to standard. Practically all molders pressed "their number" in all their moldings, giving the guarantee to the consumer that they were under control of the central organization.

In this chapter the German specifications will only be stressed in certain cases, since it is to be expected that in the years to come Germany will play a less important part in the world economies.

d. *Other countries.*

About Russia no data are available. From the smaller European countries *Switzerland* has a system of its own [102], although a close analogy to the German testing methods can be traced. In our opinion it is much to be regretted that such small countries go their own way, making the international mutual understanding still more difficult. In this respect the situation in France [103] and in Holland [104] is much more to be welcomed, since practically the system of one of the larger units (Germany) has been adopted.

It is clear from the above survey that there is a very intensive need in the world for better international cooperation.

References p. 66.

§ 3. Range of physical properties covered by elastomers and plastics.

A further problem that must be faced in any attempt at standardization of testing methods for plastics is due to the wide variety of materials included under that name. Some of these materials are rigid and brittle, some are soft and rubberlike; some absorb water rapidly and approach equilibrium in a few hours or days depending on their dimensions; while others require years under similar conditions to approach saturation; and still others are scarcely affected by water at all.

Clearly no single set of test methods would be completely suitable for all these materials. Workers have borrowed or adapted methods which were originally developed for other materials e.g. rubbers, metals and textiles, which showed promise of being useful in evaluating the particular types of synthetic materials they had under consideration. Standardization of tests for any given property has involved the selection from among these methods of one or more which are applicable to a wide range of plastic materials. Where practicable, these methods have been expanded by the addition of extra procedures to extend the range of their applicability e.g. The Tentative Method of Test for Deformation of Plastics Under Load of the American Society for Testing Materials[1] permits the use of three different loads and three different temperatures for testing various types of rigid plastics, and a different load, specimen and time of test for non-rigid plastics.

But in cases where the required procedures differ too widely, separate test methods have been established to measure a similar property for separate groups of materials, e.g., ASTM D 638—46 T[2] is used for tensile properties of rigid plastics while ASTM D 412—41[3] which is a test method for vulcanized rubber, is used for tensile properties of many non-rigid plastics.

As a rule, the use of different test methods for different materials does not cause any practical difficulty, because the end uses of these materials are generally so different that direct comparisons of their properties are rare. It is essential, however, to recognize, in any attempt at comparison, that two different methods may measure related properties, but not identical ones.

§ 4. Conditions which affect test results.

For any single type of these materials there are a number of factors which must be carefully controlled if consistent results are to be obtained. The relative importance of each depends on the material.

a. Moisture content.

Moisture exerts a decided effect on the mechanical properties of most plastic materials, and consequently on the serviceability of articles made from them.

Burns and Werring[4] have shown the effect of average monthly indoor relative humidity on the breakage of telephone equipment in New York City. They point out that telephone breakage is usually due to impact forces resulting from accidental dropping. Their curves Fig. 1 show clearly the influence of moisture on the resistance of the material, a phenolic plastic, to these forces.

These observers showed that the exposure of dry phenolic test specimens to an atmosphere of 90% relative humidity for 12 days caused an increase in their Izod impact strength of about 30% and, since these materials absorb water very slowly, a longer exposure would be expected to produce a considerably greater change. Some of the cellulosic plastics and vinyl butyral plastics are much more rapidly affected. Other materials e.g., the vinyl chloride plastics and polystyrene are substantially unaffected by moisture.

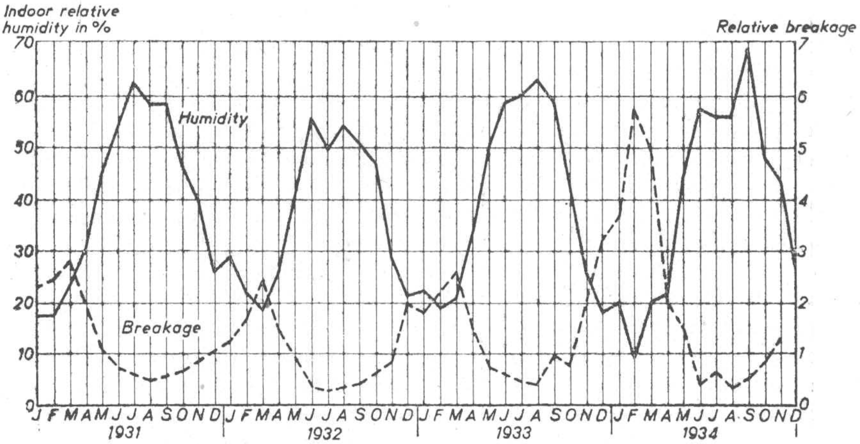

Fig. 1. Apparatus breakage and indoor relative humidity, New York City.

The speed with which some plastics absorb moisture makes it imperative to test them in the same atmosphere to which they were conditioned; since otherwise their properties would change during the test. Table 1[5] shows the effect of time of exposure to 50% relative humidity on the flexural strength of specimens of a cellulose acetate plastic which had previously been kept over water for one week. The first value under "Flexural Strength" is the average result for the control, which had not been exposed over water. The second is the result for a set of bars that were tested under water, and represents the correct value for throughly wet specimens. The remainder of the data are for bars on which tests were finished after the times shown in the third column.

TABLE 1.

THE EFFECT OF TIME OF EXPOSURE TO 50 % RELATIVE HUMIDITY ON FLEXURAL STRENGTH OF A CELLULOSE ACETATE PLASTIC.

Conditioning time at			Flexural strength		% of original strength
50%	100%	50%	kg/mm²	p.s.i	
7 days	0	0	6.16	8750	100
7 „	7 days	0	2.93	4160	47.5
7 „	7 „	1½ min	3,04	4310	49.3
7 „	7 „	1 h	3.46	4930	56.4
7 „	7 „	24 h	4.62	6560	75.0
7 „	7 „	64 h	5.25	7480	85.4
7 „	7 „	192 h	6.02	8550	97.8
7 „	7 „	312 h	6.17	8770	100

Materials whose properties change thus rapidly with changing ambient relative humidity are usually conditioned[6] at 50 ± 2% relative humidity, and are tested in the conditioning atmosphere. Those whose properties change more slowly require too long to approach equilibrium values under these conditions to warrant the practice except for special studies. It has been shown [4], however, that at elevated temperatures they can be dried out very quickly. It is customary therefore [6] to dry them in an oven at 50°C (122°F) for 48 hours followed by 16 hours in a desiccator over calcium chloride. Their low rates of water absorption generally make it possible to test them at the prevailing humidity without any appreciable change of properties during the test.

b. Temperature of the specimen.

The properties of all plastics are affected by temperature, but it is only with the thermoplastics that the effect is so large as to constitute a serious problem in testing. Values for strength properties of some of the commoner thermoplastics at two or more temperatures have been given by BURNS and WERRING [4], BARTOE [7], LAWTON, CARSWELL and NASON [8] and WALL [9].

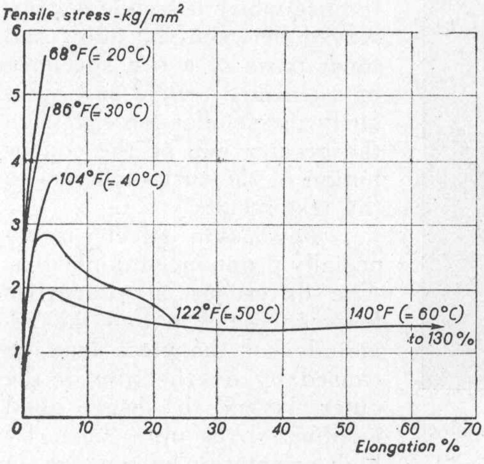

Fig. 2. Effect of temperature on the tensile stress strain properties of methyl methacrylate.

Fig. 2 shows stress-strain curves given by WALL for a cast methyl methacrylate resin, at 6 temperatures between + 20°C and + 60°C (+ 68°F + 140°F). In this temperature range the material has changed from a very hard brittle plastic at the lower temperature to a very soft one with properties approaching those of an elastomer at the higher.

Correspondingly great changes in strength with temperature change are shown by other thermoplastics.

It is customary, therefore, to test thermoplastics and, frequently, thermosetting materials, in a room maintained at a constant temperature. The standard laboratory atmosphere is defined [6] as having a relative humidity of 50 ± 2%, and a temperature of 25 ± 1°C [10] (77° ± 1.8°F).

For tests at temperatures for which a controlled room is not available, the testing machine, or the parts that come in contact with the specimen are inclosed in an insulating container and air at a suitable temperature is circulated through the enclosure. Units for supplying the conditioned air are supplied by several manufacturers. Fig. 3 shows the flexural tool of a testing machine enclosed for low temperature testing. The enclosures [11] and servicing units [12] have been specified by the A.S.T.M.; and methods for testing for tensile and compressive strength[13] and for impact strength [14] at high and low temperatures have been standardized.

When tested at high temperatures, specimens lose moisture during the test and during the time required to reach equilibrium at the test temperature. For this reason all specimens intended for testing at high and low temperatures are conditioned by drying [6] and are moved directly from desiccators to the atmosphere in which they are to be tested.

c. *Size effect and skin effect.*

It is customary to express test results in terms of specimens of unit dimensions, as, for example, pounds per square inch or kilograms per square centimeter for tensile strength, implying that specimens of any size would give test results reducible to the same figure. It is well established however, that the dimensions of the test piece frequently exert a large influence on the test results. One of the causes is the existence of microscopic defects in all test specimens. The defects cause concentrations of stress in the test piece as a whole. The larger the piece the greater will be the number of these defects, and the greater the probability of the existence of more severe defects [15].

A second cause is the difference which is frequently observed between the outer and inner parts of a test specimen or a finished article and obviously the smaller the specimen the greater will be the contribution of the surface layers to the test results.

This "skin effect" is especially pronounced in plastics. The difference in properties between the skin and the remainder of the piece may be caused by overheating of the outer layers to insure good molding of the inner ones, by high orientation of the skin in injection molding of materials with chain molecules; by plasticizer loss due to evaporation from the surface in plasticized materials; or by a flow of resin to the surface of an object during the molding operation. In the second part of this book (Chapter on Phenol-formaldehyde plastics) it will be shown, that P. F. molded objects can have a skin of pure resin of 0.04 mm thickness, due to this last mentioned effect.

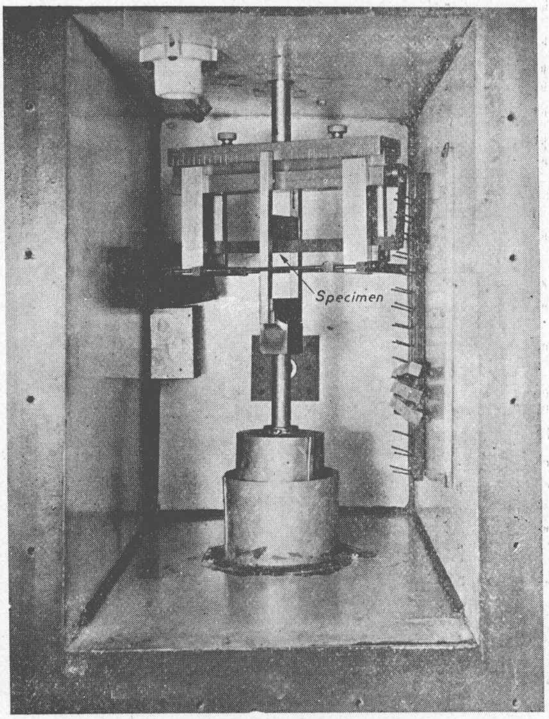

Fig. 3. Flexural tool inclosed in an insulating cabinet for low temperature tests.

Courtesy Tinius Olsen Co.

An illustration of the size effect is shown in Fig. 4. The data were obtained by LAWTON, CARSWELL and NASON [8] on sheets of various thicknesses all cut from a single block of cellulose acetate plastic. It is probable that an additional factor beside size effect is involved in the rapid decrease of tensile strength with increasing thickness, since these sheets were made by a process requiring the use of solvents which are subsequently removed by "seasoning" in hot air, and the difficulty of thorough removal of solvents increases disproportionately with increasing thickness. This added factor may very well be considered as one of the causes of the size effect in this type of plastic, though it is doubtless not the major cause in this case.

Means of eliminating or correcting for the size effect in plastics have not been standardized except insofar as the specifying of the dimensions of a test piece may be said to do so. Care in molding, seasoning or polymerization processes can reduce its magnitude, wherever these processes are contributing factors; but until the effect has been more thoroughly studied for these materials, it will be necessary to continue to supplement laboratory tests with tests on finished articles when the dimensions of articles and test pieces differ widely.

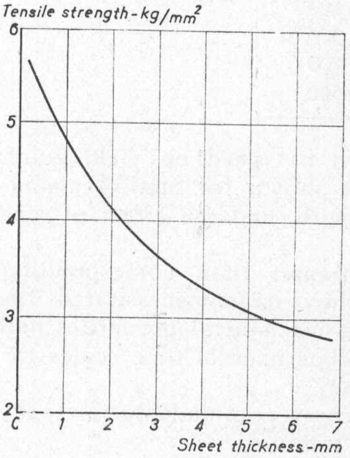

Fig. 4. Effect of test specimen size on the tensile strength of a cellulose acetate plastic.

d. Effect of testing speed.

Since high polymeric materials possess viscosity as well as elasticity it is to be expected that their mechanical properties would vary with testing speed. A striking example of this effect is shown by C. S. Myers [16]. His equipment consists of a massive wheel which rotates at a controlled speed. Projecting from the periphery of the wheel is a tool with an edge for impacting. When the wheel is operating at the desired speed the specimen, a thin strip of sheet material mounted in a vise as a cantilever beam, is thrust into path of the impacting edge and is struck on one face. If the speed of the wheel is sufficiently low the specimen bends easily out of the way and allows the tool to brush past it. When, however, the speed of the wheel is so high that the viscosity of the specimen prevents its bending away rapidly enough, it is shattered like a brittle material. The test consists of finding the speed at which shattering just occurs.

This type of test has found its greatest application with some of the vinyl copolymers which are sensitive to testing speed variations. A modification of it has been used for determining the "brittle point" of plastics and elastomeric materials [17].

Another illustration of the effect of viscosity at lower testing speeds is given by Findley [18, 19] for a cellulose acetate plastic. Some of the data taken from his curves are given in Table 2. They show the effect of testing speed on tensile strength and the time required to break identical specimens under constant tensile load.

Table 2.

TENSILE TEST 25°C (77°F) 50% RELATIVE HUMIDITY.

Testing speed. No Load crosshead separation		Tensile strength	
cm per min.	inches per min.	kg/mm²	p.s.i.
0.13	0.052	3.24	4500
1.6	0.63	3.55	5050
2.9	1.13	3.70	5250
4.8	1.88	4.10	5800

References p. 66.