Chapter 8
Mechanical Characterization of Biobased Products from Food Waste

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Biobased materials are increasingly being developed and used in a wide assortment of applications such as packaging, building products, medical devices, and electronics. For each function, the biopolymer must be investigated for processability and tested to guarantee suitability and conformity to regulations and legislation.

Product developers must characterize their biobased materials, which can be used as bulk polymers, films, fibers, or nanomaterials. The mechanical characterization is of utmost importance.

Test descriptions detailed in this chapter aim at providing a descriptive summary to enhance test understanding.

8.1 Tensile Testing

The ability of bioplastics to withstand tensile forces is important, as they are increasingly used in many different sectors. The tensile testing of plastics is standardized in ASTM D 638 (ASTM International 2014a), "Standard Test Method for Tensile Properties of Plastics". ASTM D 638 applies to rigid plastic samples with thickness ranging between 1.00 mm and 14 mm.

Mechanical loading of any material results in deformation, according to its specific mechanical behavior, which, in turn, depends on physical and chemical properties.

Tensile tests are performed by applying a tensile force to a sample specimen and measuring various properties of the specimen under stress. These tests (tensile strength, elongation at break, and modulus of elasticity) are conducted on a tensile testing machine on dumbbell-shaped (or "dog bone" shaped) test specimens. Specimens are placed in the (manual or pneumatic) grips of the testing machine; the crosshead speed is set at a specific value. The test object is drawn from two opposite directions: this way, the length increases, and the diameter shrinks. The amount of load as a function of the length increase is recorded during the test. Conditioning

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of the test specimens at 23 ± 2 °C with a relative humidity of 50 ± 5% for at least 40 h before testing is required. Testing is performed in the same conditions. At least five specimens for individual determinations of tensile properties must be made on each sample to be tested.

Through tensile tests, many different tensile properties can be calculated.

Stress and strain are the parameters that describe material behavior under mechanical loading.

If a tensile force is used to stretch the material, the Tensile Stress (nominal) is the force (F) per unit area acting on a plane in the material.

$$Tensile\,Stress\left(MPa\right) = \frac{Force\left(N\right)}{Thickness\left(mm\right) \cdot Width\left(mm\right)}$$

The tensile strength (nominal) represents the ability of a material to withstand a lengthwise stress; it is calculated by dividing the maximum load sustained by the specimen during the test by the average original cross-sectional area in the gage length segment of the specimens; the tensile strength can be calculated at yield or at break; more accurately, for plastics that exhibit yield points, it is defined as the stress at the first local maximum in the stress–strain curve:

$$Tensile\,strength\left(MPa\right) = \frac{Force_{local\max}\left(N\right)}{Thickness\left(mm\right) \cdot Width\left(mm\right)}$$

The deformation due to the effect of stresses is called elongation or strain, according to the apparatus used to measure it. The deformation will occur in the gage section whose crosssectional area is less than that of the shoulders and grip section.

Percent Elongation is the change in gage length relative to the original specimen gage length, expressed as a percent using an extension indicator (extensometer) that is able to measure the distance between two designated points within the gage length of the test specimen as the specimen is stretched.

Percent Elongation at Yield is calculated by reading the extension (change in gage length) at the yield point expressed as a percent.

Percent Elongation at Break is computed by reading the extension at the point of specimen rupture expressed as a percent.

Nominal Strain is the percent change in grip separation relative to the original grip separation. It is calculated using a crosshead extension indicator able to assess the change in the separation of the grips, that is, the crosshead movement.

Nominal Strain at break is of particular interest; it is the strain at the moment of rupture relative to the original grip separation.

Elongation values are needed for engineering design, but they are meaningful only if deformation within the specimen gage length is uniform. In the case of necking (the localized reduction in cross-section, which may occur in a material under

tensile stress) or non-uniform deformation within the specimen gage length, nominal strain values are reported even if they are of qualitative utility only.

The modulus of elasticity (also known as elastic modulus or Young's modulus) is the ratio of tensile stress (nominal) to corresponding strain below the proportional limit of a material. Since strain is dimensionless, the modulus of elasticity is expressed in force per unit area. It is obtained by dividing the difference in stress, corresponding to any segment of the section on the straight line (obtained by the least square fit) in the stress-strain plot, by the corresponding difference in strain. Elastic modulus values shall be calculated whenever possible but, for materials where no proportionality is evident, the secant value shall be calculated by dividing the corresponding stress (nominal) by the designated strain. The tensile modulus of elasticity is proportional to the stiffness of the material.

It has to be emphasized that only plastics 1.0 mm or greater in thickness are eligible for this test. Tensile properties determined according to Test Method D638 need dumbbell specimens of appropriate dimensions for sheet, plate, and molded plastics. Dimensions of specimens are also detailed for rigid tubes and rods. The physical dimensions of specimens must be measured according to the ASTM D5947 protocol (ASTM International 2018a) since the size of the samples will affect the results.

ASTM D 638 (ASTM International 2014a) does not cover the determination of tensile properties of rigid plastic samples less than 1.0 mm in thickness. Since tensile properties can vary with specimen thickness, tensile properties of thin plastic sheeting can be obtained using ASTM D882 (ASTM International 2018b). Materials that fail by tearing are not eligible for this test since they give anomalous and unreliable data.

8.2 Hardness Testing

The hardness testing of plastics is standardized in ASTM D2240 (ASTM International 2017a).

The term hardness can be defined as the resistance that a material offers against penetration of a harder body, which wears or scratches the softer material that is tested. It's a crucial parameter for engineers if one takes into account the adverse cosmetic effects of worn or scratched surfaces and moving parts.

There are five methods of hardness measurement: Rockwell, Brinell, Vickers, Knoop, and Shore. The hardness testing of plastics is usually measured by the Shore and Rockwell scales for softer and harder plastic materials, respectively. The hardness value is obtained from the penetration of the durometer indenter foot into the sample specimen, which increases with decreasing resistance of the plastic toward indentation.

The Rockwell scale is commonly used for hard thermosets, as indicated by ASTM D785 (ASTM International 2015a).

There are several Shore hardness scales for measuring the hardness of different materials. Shore A scale is the preferred method for soft vulcanized rubber, natural rubber, nitriles, thermoplastic elastomers, wax, felt, and leathers. Instead, Shore B, Shore C, and Shore O scales are not commonly used. Shore D scale is used for hard rubber and plastic.

Both Shore A and D scales are from 0 to 100, and when Shore D is 58, the corresponding Shore A is 100. A correspondence table between them is available.

8.3 Tear Strength

Testing is performed by pulling specimens apart using a tensile test machine. The maximum force required to tear the tested sample specimen is used to calculate the tear strength. Tear strength is defined as force per unit thickness necessary to start a tear through the specimen tested. This test provides a measure of resistance to tearing and reveals the possible anisotropy of a material.

ASTM D624 (ASTM International 2020a) is the testing standard for measuring the tear strength of thermoset rubbers, thermoplastic elastomers, and silicones.

ASTM D1938 (ASTM International 2019) is the standard test method for tear-propagation resistance (Trouser Tear) of plastic film and thin sheeting by a single-tear method. The method is not applicable for brittle film or sheeting material.

Conditioning of the test specimens at 23 ± 2 °C with a relative humidity of 50 ± 5% for at least 40 h before testing is required. Testing is performed in the same conditions. At least five specimens for individual determinations of tear strength must be made on each sample to be tested.

ASTM D1922 (ASTM International 2020b) is the standard test method for propagation tear resistance of plastic film and thin sheeting by pendulum method.

8.4 Flexural Testing

The flexural testing of plastics is standardized in ASTM D790 (ASTM International 2017b).

A bar of rectangular cross-section, held by two supports, is loaded by a loading nose midway between the supports. The specimen is deflected until rupture occurs or until a maximum strain of 5.0% is reached, whichever occurs first. Conditioning of the test specimens at 23 ± 2 °C with a relative humidity of 50 ± 5% for at least 40 h before testing is required. Testing is performed in the same conditions. At least five specimens for individual determinations of flexural properties must be made on each sample to be tested.

The flexural properties obtained are different. When a homogeneous elastic material is tested in flexure, the maximum stress in the outer surface of the sample specimen is at the midpoint. This is the Flexural Stress, and it may be calculated for

any point on the load-deflection curve. The Flexural Strength is the maximum flexural stress sustained by the test specimen during a bending test.

The Tangent Modulus of Elasticity, or "modulus of elasticity," is the stress to the flexural strain ratio within the elastic limit. It is calculated from the tangent to the initial straight-line portion of the load-deflection curve.

A Secant Modulus is calculated as the slope of the straight line that joins the origin and a selected point (chosen at prespecified stress or strain in accordance with the appropriate material specification or by customer contract) on the actual stress-flexural strain. Similarly, a chord modulus may be calculated from two discrete points (in accordance with the appropriate material specification or by customer contract) on the load-deflection curve.

8.5 Impact Resistance Testing

The impact resisting testing of plastic is standardized in ASTM D256 (ASTM International 2018c).

The Izod pendulum impact test indicates the energy to break standard specimens under specific parameters of specimen mounting, notching, size, and pendulum velocity-at-impact.

The presence of a notch generates a stress concentration that increases the probability of a brittle, rather than a ductile, fracture. Four similar methods are available. They all use the same testing machine and specimen dimensions, but correspondence tables, useful for correlating the results from the different test methods, are not available. The testing apparatus comprises a massive base with a vise for holding the specimen, and a pendulum-type hammer, connected through a rigid frame and bearings to the base. It also has a device to measure the energy loss and indicate the breaking energy of the specimen. Conditioning of the test specimens at 23 ± 2 °C with a relative humidity of 50 ± 5% for at least 40 h before testing is required. Testing is performed in the same conditions. At least five specimens for individual determinations of impact resistance must be made on each sample to be tested. The Notched Izod impact strength is a relative measure of the materials resistance to impact.

8.6 Density Testing

Density measurements are performed according to ASTM D792 (ASTM International 2020c) that applies to plastic sheets, rods, tubes, or molded items.

Solid plastics can be tested in water (method A) or, in specific cases, in other liquids (method B).

Specific gravity or Relative Density is "the ratio of the mass in air of a unit volume of the impermeable portion of the material at 23°C to the mass in air of equal

density of an equal volume of gas-free distilled water at the same temperature". Density is the mass in air in kilograms per cubic meter of an impermeable portion of the material at 23 °C, that is the mass per unit volume of a material.

Density testing is important because density can identify a material; density changes can be caused by crystallinity variations, absorption of solvent, thermal history, or a low degree of uniformity among different specimens.

Conditioning of the test specimens at 23 ± 2 °C with a relative humidity of 50 ± 5% for at least 40 h before testing is required. Testing is performed in the same conditions.

The method involves weighing a one-piece specimen of 1–50 g in air and in air-free distilled water, using a sinker if the density of the specimen is lower than that of water and taking into account the weigh the sample holder (and sinker, if used) immersed under the same conditions. Specimens can be wet by, but otherwise not affected by water.

8.7 Compression Testing

Compression measurements are performed according to ASTM D695 (ASTM International 2015b) that represents the standard test method for compressive properties of rigid plastics.

Loading a specimen at a relatively low and uniform rate enables the study of the behavior of materials under crushing pressure. The specimen is compressed by compressive plates, and deformation is recorded as a function of the applied load. Compressive stress and strain are measured. The resulting stress-strain diagram provides information on the elastic limit, proportional limit, yield point, yield strength, compressive strength. An extensometer is used to determine the modulus of elasticity, following the usual procedure for other stress-strain curves.

Specimens are typically blocks (12.7 × 2.7 × 25.4 mm) but cylinders are also used (12.7 mm in diameter and 25.4 mm long).

8.8 Creep

Creep, also called "cold flow", is a slow but permanent deformation phenomenon over time due to stress; ASTMD 2990 (ASTM International 2017c) provides standard test methods for tensile, compressive, and flexural creep and creep rupture of plastics under specified environmental conditions. For measurements of creep-rupture, tension is the selected stress mode.

These test methods measure the extension or compression as a function of time and time-to-rupture or failure of a specimen subject to constant tensile or compressive load under specified environmental conditions. The creep modulus and strength

of materials are calculated from creep and creep-rupture tests data. They are relevant to engineers because they allow them to predict the behaviour of materials under long-term loads and to predict dimensional changes that may occur as a result of such loads.

Selection of temperatures for creep and creep-rupture testing depends on the intended use of the test results.

8.9 Fatigue

Fatigue is related to the weakening of materials from repeated use, leading to eventual failure. ASTM D7791 applies to rigid and semi-rigid plastic materials. It is used to determine the fatigue limits under repeated uniaxial stress for a large number of cycles (ASTM International 2017d). It is no surprise that plastics will fail at stress levels well below their tensile or compressive strengths when subjected to cyclic loading. Accelerated tests aim at getting end results sooner, but the heat has to be promptly removed to avoid results that might not be equitable to normal service conditions since temperature has a strong influence on the mechanical properties.

Once the specimens are prepared in accordance with the standard, they are loaded into the test machine. The test is performed with a cycling of a proper frequency because properties can vary with specimen depth and test frequency. Test frequency can be up to 25 Hz, but a frequency of 5 Hz or less is recommended.

The tests should be conducted at the same temperature and humidity each time, as prescribed by the test standard; hence a temperature chamber and a humidity chamber for non-ambient temperature and humidity levels are recommended.

If the specimen does not exhibit an elastic behaviour, plastic deformation will occur during fatigue testing and caution shall be taken when interpreting the results.

This test method can be used with a procedure for fatigue testing in tension and another procedure for fatigue testing in compression (only for rigid plastics). Uniaxial loading systems with tension and compression capabilities are used to determine these properties.

8.10 Friction

The “Standard Test Method for Static and Kinetic Coefficients of Friction of Plastic Film and Sheeting” is ASTM D1894 (ASTM International 2014b).

The static and kinetic coefficients respectively indicate the static (starting) and kinetic (moving) resistance of one surface being dragged across another. They can be obtained from the force necessary to get the sled started, and to maintain motion, respectively. In order to calculate these coefficients, a 64 mm square specimen is attached to a sled of specified weight that is pulled across a second surface (254 mm × 127 mm) at a specific speed.

The static coefficient of friction is the initial force to the sled weight ratio. The kinetic coefficient of friction corresponds to the average force needed to achieve a uniform sliding of the surfaces the sled weight ratio.

Atomic Force Microscopy in friction mode proved to be a powerful tool for studying nano-friction. Surface properties depend on the nature of the polymer (Maurice et al. 2014).

8.11 Wear

The laboratory testing of the wear of materials during sliding is described in the standard ASTM G99 "Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus" (ASTM International 2017c). Materials are tested in pairs: one, a pin, is positioned perpendicular to the other, usually a flat circular disk, and the test machine causes a circular sliding path on the disk surface when the pin specimen is pressed against the disk at a specified load. The amount of wear is reported as volume loss in cubic millimeters for the pin and the disk separately.

Wear results are determined by measuring linear dimensions and converting linear measures of wear to wear volume. If loss of mass is measured, the density of the material is used to convert the mass loss value to volume loss.

8.12 Mechanical Performance of Bioplastics

Among bioplastics, only a few are commercialized, and they only have a $< 1\%$ plastic market share because they are seldomly able to address industrial applications. Apart from drop-in bioplastics (biobased plastics chemically identical to the fossil-based analog), PHAs and PLA are the most used bioplastics because they are reasonably able to match the functionalities of common fossilbased plastics, namely LDPE, HDPE, PP, PS, PVC, PU, and PET. The mechanical properties of bioplastics are probably the most important of all the physical properties of bioplastic for most real-field applications.

The mechanical performance of PBS makes it a good competitor of PP and PE; it is highly crystalline and has good processability and thermal stability even if ductility decreases in time due to the cold crystallization phenomenon. PLA has high strength and high modulus, similar to PS. However, its brittleness and low heat deformation temperature limit its applicability. The thermal degradation under melt processing and the slow biodegradation rate are additional issues. Hydrolytic sensitivity prevents PLA packaging of moisture-sensitive long shelf-life products frozen baked; PLA films laminated with barrier materials (PP, PE) or coated with inorganic silicon and aluminum oxides can be used in this respect.

PHAs have good heat resistance and gas-barrier properties similar to polyvinyl chloride (PVC) and PET thermoplastics. PHAs are quite rigid, and the use of PHB

is limited by its brittleness and poor processability. PHAs are less thermally stable than conventional plastics. Copolymerization is useful in this respect. Application in the packaging sector requires laminating with paper and other polymers and plasticization, copolymerization, blending, and reinforcement with inorganic or organic fillers (Zhao et al. 2020).

Disclaimer Readers are referred to the most recent and up-to-date ASTM standards available on https://www.astm.org, the only authentic reference. The information provided in this chapter does not constitute legal advice. The Author does not accept any liability as regards the contents of this Chapter.

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