

Evaluating Quantity, Quality and Comparability of Biopolymer Materials

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Rather than biodegradability the focus of current material development in the field of biopolymers is increasingly on a biobased raw material input to produce durable products, i.e. the use of resistant biopolymers in technical applications. And the properties required of the materials are increasing in parallel with the number of these different applications.

As a result of this current development more and more manufacturers are publishing material specifications. At first glance this can be seen as a positive move from the point of view of technical marketing support, however, the quantity, quality and comparability of available material data are still very unsatisfactory. When establishing such product data it is often the case, for example, that different standards are used for the tests, as well as different testing conditions, such as the prevailing environment when the sample was taken, the temperature conditions or humidity before and during the test, or the period of time over which the test was conducted. A further problem area lies in the fact that too little experience has been gained with new types of biopolymer to be able to lay down the optimum test conditions. Furthermore many of the published test results do not specify any standard test methods or conditions, or do not adequately define the selected conditions. Unfortunately consequence it is often in the case that the material performance specifications published until now have limited informative value.

The intention of this article is, with the help of various concrete examples, to point out some of the common mistakes made when attempting to ascertain the performance characteristics of biopolymers and to increase the understanding of testing of biopolymers.

Melt Index

An important value for plastics processors is, for example, the melt flow index (Melt mass flow rate = MFR [g/10 min]) as specified in DIN EN ISO 1133. Without quoting a temperature and the pressure applied as the significant parameters for the test, the readings cannot be evaluated. These data, which complement the values quoted, are therefore essential but are left out by many manufacturers and are missing from numerous published documents. In addition, with biopolymers there is often the problem that, unlike conventional plastics, the MFR of these new polymers no recommendations are given with regard to the test parameters when measuring. This leads to different companies choosing different test parameters, hence making it even more difficult to compare readings.

Temperature Resistance

Another very sensitive figure that should be known for practical application of a biopolymer is its resistance to temperature. In many documents published about biopolymers, or in press releases, we more and more often read, for

instance, about PLA/PLA blends with a temperature resistance of around 100°C. Since the low temperature resistance of PLA often seriously limits its use, this increase from the figure of about 60°C (which is normally quoted for this material) to values around 100°C is extremely significant. Unfortunately it has emerged that this impressive figure is not supported by the facts but can largely be traced back to widely varying test methods that are not really comparable. Here too it is absolutely essential that one is given details of the test method and conditions with regard to heat resistance values.

To measure heat resistance the following two different standard test methods are generally used:

Measuring HDT (Heat Deflection Temperature or Heat Distortion Temperature) in accordance with DIN EN ISO 75 and measuring the VST (Vicat Softening Temperature) in accordance with DIN EN ISO 306. For the HDT test a standard sample is placed in an oil bath and subjected to a defined and constant bending force under a constantly increasing temperature (120°C/h). The HDT is reached when the outer fibre distortion of the material reaches 0.2 %. In the Vicat test the sample is also placed in an oil bath with a defined temperature gradient. However the Vicat test is not based on bending but on point load deflection. The Vicat softening temperature is reached when a flat-ended needle of a defined geometry, penetrates 1 mm into the sample under a defined pressure [1].

Both methods permit variations of the load and temperature gradient within the norm. With the HDT method the central bending load can be chosen from the following values: 1.85 MPa (HDT A), 0.45 MPa (HDT B) and 8.0 MPa (HDT C). This means that even within one method there can be significant variations in the value depending on the chosen loading, which is often not specified in the quoted results, as can be seen in Fig. 1. If, for example, the temperature resistance of polyhydroxyalkanoates (PHA) is published it may seem high, returning a value of 140°C, or, with a greater loading, be as much as 60°C lower at about 80°C.

The situation is similar with the VST temperature resistance test. Here too the piercing needle force can be selected from either 10 N (VST A) or 50 N (VST B). In the VST method A represents a lower loading and hence higher resistance values, whilst method B, uses higher loading and hence a lower resistance value in contrast to method A. When comparing the temperature resistance of biopolymers the two methods can return figures that vary by as much as 100°C.

Furthermore when testing temperature resistance either of two temperature gradients may be selected; either 50°C/h or 120°C/h. At the faster rate the thermodynamic loading time of the biopolymer before reaching a certain temperature is less than at a lower temperature gradient. Hence the resulting values at the higher temperature gradient are likewise correspondingly higher.

It is therefore essential that the exact and full methodology used when measuring temperature resistance is specified. Where adequate data on the test methods is not supplied the temperature resistance cannot be properly evaluated.

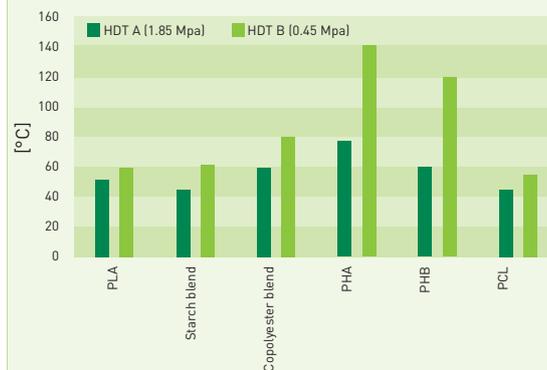


Fig.1: The influence of different bending loads on the measured temperature resistance using the HDT test.

Temperature gradient in each case = 120°C/h
(incomplete, just as an example)

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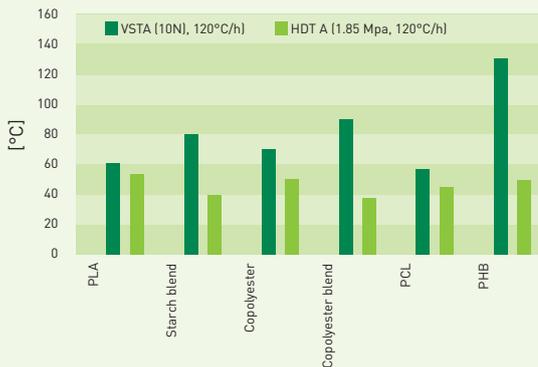


Fig.2: Influence of the test method used to determine temperature resistance (incomplete, just as an example)

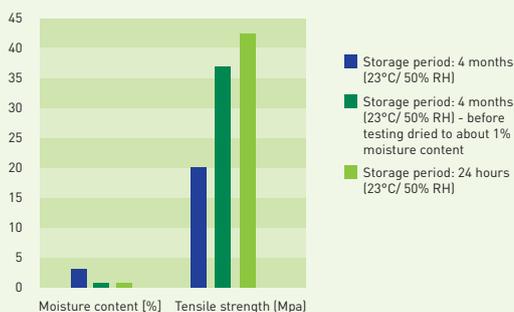


Fig.3: The effect of conditioning and storage on the tensile strength of a PLVA based polymer

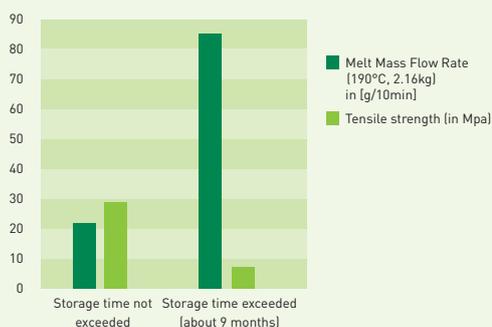


Fig. 4: Effect of extended storage period on the material (23°C, 50% RH)

For the values obtained using the VST test it is thus necessary to clearly distinguish between results obtained using, for example, VST A 50 (load applied to the needle = 10 N and temperature gradient = 50°C/h), VST A 120 (10 N @ 120°C/h), VST B 50 (50 N @ 50°C/h) and VST B 120 (50 N @ 120°C/h) [1].

Without these data mistakes are often made in the practical application of biopolymers, such as PLA, due to a lack of understanding of this problem and directly comparing temperature resistance values that have been obtained using different test methods and/or under different test parameters. As shown in the table of temperature resistance figures obtained using Vicat A and HDT A for various biopolymers (Fig. 2), these results are not at all comparable.

Alongside the often inadequate data concerning the test parameters there are other factors (such as storage time and/or conditioning/drying) that are not given with regard to the biopolymers being tested.

The chart in Fig 3 uses as an example the tensile strength of a polyvinyl alcohol (PVAL) based biopolymer to demonstrate the significant effect that humidity and/or length of storage may have on the mechanical properties of the material. It is important, when testing in line with an international standard, to supply information on the storage and conditioning of the sample as well as how much time elapsed between preparation of the sample and the actual test.

Fig. 4 also shows that with biopolymers it is not only conditioning and the age of the finished components that have a significant impact, but that also the effect of exceeding recommended storage times of the resins before processing is a factor not to be underestimated. The following chart shows the impact on a starch based biopolymer of exceeding the storage times.

The starch based polymer was tested immediately on delivery and then after a clearly excessive storage period. The almost quadruple melt flow index points to a reduction in the length of the molecular chain as a result of the polymer degradation. The same applies to the tensile strength. Here again the material was tested immediately upon delivery and again after an extended storage period. The significant drop of the mechanical specification also points clearly to a molecular breakdown.

Barrier Properties of Films

Further examples of a lack of data when evaluating biopolymers is also seen in the area of biopolymer films. This can be testing oxygen permeability in line with DIN 53380 for example. In this process a permeation cell is separated by a sample of the film. The test gas, i.e. the oxygen, is introduced into one half of the cell. It will permeate to a greater or less degree through the film and into the other half of the cell where it is perceived by a carrier gas. A sensor and appropriate software are used to measure the amount of oxygen in the carrier gas and so determine the oxygen permeability of the film. In addition to temperature, the relative humidity of the oxygen and the carrier gas can also be regulated. When stating the barrier property of a film, i.e. the coefficient of permeation, the temperature and relative humidity parameters often fail to be supplied, but as can be seen in Fig. 5 the moisture content of the oxygen (or other gases being tested), and the carrier gas have a significant influence on the permeability especially of biopolymers.

Film Thickness

Another difficulty with biopolymer film lies in the presentation of performance data without mentioning the film thickness. With barrier performance in particular it is important to state the film thickness concerned or to adhere to a recognised standard with a unified film thickness. In some published data we still find barrier properties of film being quoted without any mention of the thickness.

Test Speed

A further shortcoming with regard to biopolymer film lies in the testing of its mechanical performance and in particular the tensile test. With regard to the speed applied during the tensile test there is no specific standard laid down by DIN EN ISO 527; several speeds (1, 2, 5, 10, 20, 50, 100, 200, 500 mm/min) may be applied by the tester. In practice a speed of 1, 2 or 5 mm/min is chosen to determine the secant modulus. For other mechanical values (e.g. tensile strength) higher speeds are usually selected. The chart in Fig. 6 shows the effect of test speed on the secant modulus of a regenerated cellulose film.

As is clear from the illustration, the secant modulus measured at 1 mm/min lies well below that of the modulus measured at the higher speed by almost 1000 MPa. At the lower speeds the molecular chains have more time to change shape and orient themselves. Hence the film is less resistant to elastic deformation.

The effect of testing speed on mechanical values is also seen with injection moulded parts, but the effect on films, due to their much reduced thickness, is more significant. Hence, when tensile testing films in particular, it is very important to have information on the test speed in order to be better able to assess and compare data on different materials.

For the future it can be assumed that the development of biopolymers will move ahead swiftly and more and more materials will be presented to the market. It is however important at this stage that the performance characteristics published for new types of biopolymers are comparable and meaningful.

Help on this whole topic is available from a freely accessible database at www.materialdatacenter.com, assembled by the authors of this article in collaboration with the company M-Base GmbH and with support of the German Federal Ministry of Food, Agriculture and Consumer Protection (the BMELV). All commercially available polymers are tested under standardised conditions in line with the published norms here, and are can find all of the necessary information regarding the relevant test parameters in parallel with the numerical specifications of biopolymers.

More information about biopolymer testing can be found in the book 'Technical Biopolymers' [1]. This book can be ordered via the bioplastics MAGAZINE website. It is available in German language, an English version is expected for spring 2010.

 www.fakultaet2.fh-hannover.de
www.materialdatacenter.com

[1] Endres, H.-J.; Siebert-Raths, A.: Technische Biopolymere, Carl Hanser Verlag, München 2009

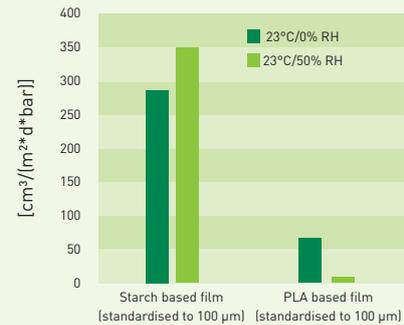


Fig.5: Oxygen permeability in relation to the relative humidity of the gas being tested (oxygen) and the carrier gas.

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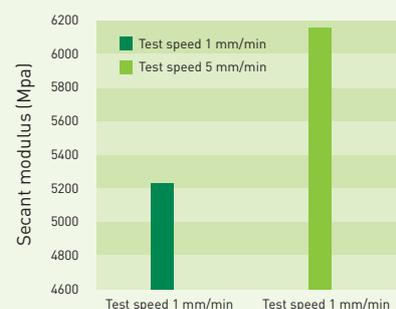


Fig.6: Effect of test speed on the secant modulus