Determining Thermal Stretching & Shrinkage Using the Hot-Set Method

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A description of the hot-set (hot-creep) method for measuring the degree of crosslinking for QC purposes and for development of improved (crosslinkable) polymer compounds and other plastic materials.

Degree of Crosslinking
The hot-set (hot-creep) measuring method is used essentially to determine longitudinal stretching under defined test conditions. Many industries where crosslinked polymers, copolymers, rubbers and elastomers are currently being used, apply this measuring system.

The hot-set test method is particularly effective in determining the degree of crosslinking. Alternatively, a chemical gel-sol measuring method can be used. The measuring results from both methods correlate with each other and can be ascertained by means of a material specific calibration curve. Depending on the material, only one calibration curve can do the job.

Crosslinking Processes
In the case of cross-linked products, a basic distinction has to be made between a physical process and a purely chemical one. Physical polymer crosslinking can be carried out with efficient electron accelerators. In-house crosslinking or crosslinking at irradiation service centers with electron energies of approximately 0.3 to 10 MeV, allow the crosslinking of cable insulation or (heat-shrinkable) tubing up to 10 mm wall thickness or even more.

A well-known alternative crosslinking process is the silane crosslinking method, which is often utilized in the manufacture of polyethylene water pipes, heat-shrinkable tubing and wire and cable.

Another process is crosslinking by using peroxide. This process has become established mainly in injection molding and extruded products with in-line CV, salt bath, IR or other crosslinking equipment.

Quality & Process Control
There is a permanent requirement for quality control in this wide spectrum of crosslinked products to check the custom designed material characteristics. The demand for rapid and accurate test methods is increasing in order to better monitor crosslink processes.

The drive towards worldwide harmonization of standards and for international quality assurance certification is continuously increasing.

Well-introduced test methods will prevent complaints and returns from customers. Quality helps to save money. Quality must be monitored rapidly, safely and by easily reproducible methods.

The hot-set test method is such a method because of its accuracy. Easy-readable and high-precision instruments are available. These measurement instruments are integrated in the oven that meets requirements like precision temperature control, measurement accuracy by using an integrated calliper (±0.01 mm) and specially developed opto-electronic laser line diode. A data cable can be connected to a computer system for Excel spreadsheets. The oven should have a controlled air exchange rate and low air speed, meeting the requirements for aging ovens in IEC 811 for aging tests for cable materials. Preferably, the measurements are made through the window with the laser line that is mounted on a moving measuring scale placed on the door of the oven.

Hot-Set Compared to Gel-Sol
Measuring results have to be available very quickly. The hot-set method is vastly superior to the gel-sol method. It requires only a 15-minute measuring period to determine the measured value of thermal expansion \( \varepsilon_{\text{wd}} \). Compared to the gel-sol method, which requires a minimum period of 24 hours, the hot-set method is an excellent method to monitor a crosslink process. The hot-set method is a physical measuring system that uses only electric energy. The chemical gel-sol measuring method requires 24 hours of heating and a relatively expensive process to prepare and recycle the solvent. Gel-sol and thermal expansion behavior measurement data can be compared with each other as shown in Figure 1.

Other Areas of Application
The long-term aging behavior of polymers is being measured in the continuous process to develop and improve compounds and plastic materials.

It is well known that polymers will degrade under thermal and mechanical stress. The addition of stabilizers usually prevents thermal degradation. This test method enables manufacturers and research and development specialists to find an optimum of the quantity and quality of the stabilization package.

Observation of the thermal stretching behaviour over a very long test period has shown that the thermal stretching value \( M_{\text{wd}} \), which in theory approximates asymptotically to a final value, actually creeps linearly away from it. The gradient of this curve corresponds to the thermal degradation of polymers and over time finally leads to disintegration. It is possible to accelerate this process by changing the test

![Fig. 1 — Comparison of gel-sol and thermal expansion behavior measurement data.](image)
temperature (temperature increase), thus creating a kind of artificial ageing.

The hot-set procedure results in high disintegration, so it is extremely simple to determine the quantity of stabilizers required for specific products and/or applications. In principle, the results are presented in the form of a family of curves (Figure 2).

A gentle gradient means high stabilization. A steep gradient means that a compound is only slightly stabilized or not stabilized at all.

The hot-set measuring method is widely used in the manufacture of heat-shrink products (both thick and thin wall, shrink sleeves and heat-shrinkable moulded shapes). In these cases, the process ability can be deduced directly from the test results. Their model character with regard to the large-scale expansion and processing of shrink products permits the results to be transferred 1:1.

Hot-set testing not only provides data about the degree of crosslinking, which directly affects shrinkage performance, it also provides information about the expansion rate of specific polymer compounds. Crosslinking homogeneity, in parts with extremely varied geometry, is also a very important factor as far as processing is concerned.

The hot-set method can also be used in a modified form to measure contraction and/or shrinkage during manufacture of sheets and foils in a wide variety of polymers and compound formulations.

**Defined Test Conditions**

Temperature and oxygen substantially affect the aging of plastics, which also includes the hot-set test method. In the case of heating ovens in particular, a distinction also has to be made between natural and forced ventilation. As the temperature rises, the forced air accelerates all chemical reactions in a plastic compound. The atmosphere has an oxidative effect, while the air speed encourages the transfer of heat onto the sample and the degradation of the diffusion layers on its surface. However, oxidation does not play an important role because the hot-set test lasts for only a relatively short time (approximately 15 minutes).

The decisive factor in hot-set testing is the temperature. Homogeneous spatial distribution as well as short recovery times after the sample has been inserted into the preheated oven are important for accurate and reproducible measuring results. Specially built hot-set heating ovens (like the PTL-brand hot-set oven seen in Figure 3) meet these stipulated requirements and are suitable for determining the hot-set properties.

Temperature deviation at test temperatures of 200°C or 250°C in the region of the sample, amounts to ±3 K at the most (Figure 4).

Heat recovery time at 98% of the initial value is approximately five minutes following a door opening time of 30 seconds (Figure 5).

Oxidation is also taken into account by defining pre-set air change rates at eight to twenty times per hour. The air change rate determines the inflow of fresh air into the interior and it is this inflow which governs the oxygen content of the test area atmosphere, in the final analysis.

An (optional) airflow regulator and meter will result in a precise control and monitoring of the airflow.
Which Oven is Right for the Job?

The ventilation system is an important feature of the oven. The tempered air by design has to create a kind of “air jacket” so that the sample is always in a homogeneous temperature field without being exposed to a direct airflow. This means that the test conditions are similar to those in naturally ventilated heating ovens, although electric fans have to be used for forced air circulation in order to shorten recovery time, to start the hot-set test.

The major considerations when buying a hot-set oven include the following points:

• A large glass observation panel should be present to detect the final length of the specimen, because the thermal stretching of plastics can exceed 200%. This especially SnO2-coated glass observation panel in the door should have no significant negative effect on the heat distribution in the oven.
• Homogeneous heat distribution in the interior and short heat recovery time after insertion of the test specimen.
• Once the test temperature has been reached, a provision should be present to switch off the air circulation if required, ensuring that the test result will not be affected by forced air convection.
• A side-mounted access port, preferably a minimum of 50 mm in diameter, should enable you to introduce additional measuring instruments and tools into the interior without opening the door.

• Availability of an airflow meter and regulator in case specific tests require precise regulation of the airflow.
• Availability of data cable to be connected to a computer system.
• Presence of an opto-electronic laser pointer on a moving measurement scale.
• Compliance with international standard IEC 811-2-1.

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Company Profile:
Inhol/PTL is a worldwide operating source for PTL-brand hot-set ovens and special compounds for wire and cable and heat shrink products. The heat-shrink activities include technology and equipment. The PTL-branded compounds are based on polyolefins, elastomers and fluoropolymers. All PTL compounds and materials are RoHS and REACH compliant.

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