

TESTING PARAMETERS INFLUENCING THE STRAIN HARDENING MODULUS

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SHORT SUMMARY

The effect of eleven different test parameters on the strain hardening modulus was investigated using the Design of Experiments statistical method. The changes in strain hardening modulus due to temperature, tensile drawing speed and the cooling rate after annealing were assessed. The importance of taking account of proper preparation of the test setup was also demonstrated.

KEYWORDS

Strain Hardening Test, Design of Experiments, test variation, scatter

ABSTRACT

The Strain Hardening Test (SHT) is a simple tensile test carried out at 80°C (176°F) in accordance with ISO 18488. The effect of eleven different test parameters on the strain hardening modulus was investigated using Design of Experiments (DoE). This is a statistical method used to quickly determine and quantify the effect of multiple test parameters, including their interactions. It requires only a limited number of tests.

The statistical analysis demonstrated that the locations of the markers, the clamping area and the alignment of the test specimen have a statistically significant effect on the strain hardening modulus. This shows the importance of properly preparing the test setup. The test temperature and the cooling rate after annealing are also important. A change in test temperature of 10°C can result in a change of up to 19 MPa in the strain hardening modulus. This means that the 2°C temperature variation allowed by the ISO 18488 standard may lead to a variation of about 3.8 MPa in the strain hardening modulus.

The DoE statistical analysis also assessed any interactions between the test parameters. For example, it was found that the effect of temperature on the strain hardening modulus for first-generation PE differs to that for PE 100RC.

Finally, although the tensile speed on its own is not statistically significant, the tensile speed combined with the test temperature does have a statistically significant effect on the strain hardening modulus.

INTRODUCTION

The Strain Hardening Test (SHT) is a simple tensile test carried out at 80°C (176°F) in accordance with ISO 18488 [1]. It probes the disentanglement capability of the tie molecules in polyethylene, making it a quick method of obtaining a measure for the resistance to Slow Crack Growth (SCG) of polyethylene (PE) [2-6]. The resulting “Strain Hardening Modulus” or $\langle G_p \rangle$ is determined from the slope of the stress-strain curve in the region after the natural draw ratio.

The test standard [1] gives all the requirements that must be met to perform this test consistently and accurately. However, the variation in the outcome resulting from the

permissible tolerances in the test parameters was previously unknown. For example, the temperature must be $80^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ($176.0^{\circ}\text{F} \pm 1.8^{\circ}\text{F}$). This means that in extreme cases, the temperature may be somewhere between 79.0°C and 81.0°C . The potential magnitude of the change in $\langle G_p \rangle$ if the temperature between two tests differs by 2°C was unknown.

Moreover, some test parameters are not precisely described. For example, after annealing the oven must be “*slowly cooled down to room temperature by switching off the closed temperature chamber with an average cooling rate of less than $2^{\circ}\text{C}/\text{min}$.*” [1]. Different ovens will have different cooling paths, which may cause the crystallization structure of the PE sheet to differ between labs. Additionally, “room temperature” differs across the world. Cooling from 120°C (248°F) to 23°C (73.4°F) allows much faster cooling at the beginning of the cooling path than cooling from 120°C to 40°C (104°F), because the last part of the cooling path will be very slow.

Finally, variation between different equipment and laboratories in the exact execution will always occur due to normal laboratory practices. The deviations will be either systematic or random. The results in a Round Robin will therefore never be exactly the same (see Figure 1). This figure also shows that the PE materials with a higher $\langle G_p \rangle$ also have a greater standard deviation [7,8]. Again, little is known about the exact origin of the variations.

To find answers to these questions, the effect of eleven different test parameters on the strain hardening modulus was investigated using Design of Experiments (DoE) [9]. This is a statistical method used to quickly determine and quantify the effect of multiple test parameters, including their interactions. It requires only a limited number of tests.

EXPERIMENTAL

Design of Experiments

Much research is based on “one-factor-at-a-time” experiments. This means that all test parameters are kept as constant as possible, except for one parameter (factor), which is varied. Needless to say, the principle advantage of this method is that one can clearly see the effect of this varying factor. For example, if the material quality is to be investigated, all other test parameters are kept constant, and the only variable is the type of material.

If another factor must be investigated, such as the effect of temperature, all the experiments must be repeated, but this time for one material and a varying temperature. This method works very well and is therefore in common use worldwide, but has two significant downsides.

The first is that possible interactions may be missed. Using one-factor-at-a-time, one would for instance investigate three materials (three quality levels: poor, intermediate and good). To investigate the effect of temperature, one would select one material (e.g. with an intermediate quality, or very often the poor-quality material to limit the testing time) to be tested at three temperatures. However, to test whether the effect of temperature on poor materials differs from

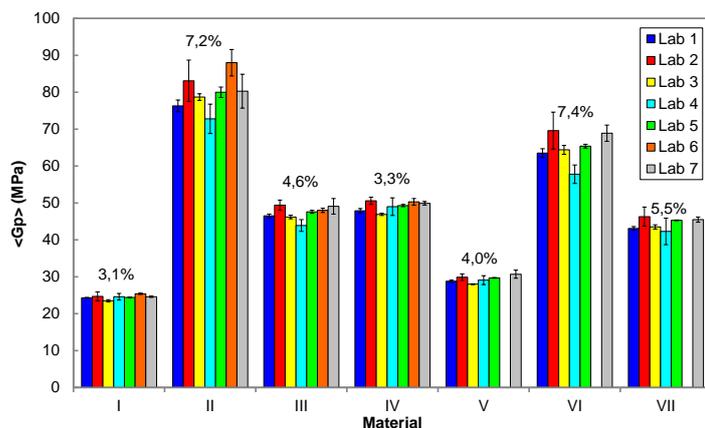


Figure 1. Results of a Round Robin test performed by seven laboratories on seven PE materials, in which each laboratory prepared its own 1 mm thick samples. The coefficient of variation (the relative standard deviation) based upon all individual samples is given (from [8]).

the effect on good materials, one would need to test every material at three temperatures. This would require $3^2=9$ experiments.

This highlights the second downside, which is the limited number of factors that can be investigated. Using one-factor-at-a-time without taking interactions into account, one would perform 33 experiments for 11 factors (each with three levels). But if interactions are taken into account, this number becomes gigantic, as shown below:

For example, if only two factors (e.g. material and temperature) are chosen for two levels (e.g. poor/good or low/high), 4 ($=2^2$) experiments are needed:

1. Poor material and low temperature
2. Good material and low temperature
3. Poor material and high temperature
4. Good material and high temperature

For 11 factors with only 2 levels, one would need to perform $2^{11}=2048$ experiments! For additional levels (e.g. an intermediate material or temperature) the number of experiments increases to a stunning 177,147!

Design of Experiments (DoE) [9] is a statistical method used to overcome these two limitations. By carefully planning the experiment, only 32 experiments are needed to investigate 11 factors with 2 levels, while maintaining sufficient certainty. It involves absolute randomization and carefully-chosen factors, to prevent overlap between possible interactions (to ensure they are not “confounded”).

Of course, a greater number of experiments will result in better statistical support, which means a higher degree of certainty can be obtained and/or more interactions can be found, including three-way or higher interactions. A three-way interaction is an interaction between three factors, rather than only two as explained above.

For this study, 32 “factorial experiments” were used to vary 11 factors (variables) at two levels (low and high) simultaneously. The following variables were investigated, each at a low and a high value, in partnership with a statistical consultancy company [10]:

1. PE type
 - a. Low: re-granulated excavated first-generation PE pipe (PE50)
 - b. High: virgin commercially-available PE 100-RC resin
2. Orientation during compression molding of the granulate
 - a. Low: the PE pellets were placed in a grid, so that they were evenly distributed across the compression molding surface
 - b. High: all PE pellets were piled up at one side of the compression molding surface
3. Cooling rate after compression molding
 - a. Low: the compression molding plates were opened slightly to let the plate cool down by exposure to the air
 - b. High: the plate was cooled down as fast as possible using water
4. Cooling rate after annealing
 - a. Low: the oven was turned off and allowed to cool down overnight ($< 2^\circ\text{C}/\text{min}$)
 - b. High: the plate was removed from the oven and waved in the air
5. Punching equipment
 - a. Low: old, rough and blunt
 - b. High: new and sharp
6. Test temperature
 - a. Low: 75°C (167°F)
 - b. High: 85°C (185°F)
7. Tensile drawing speed
 - a. Low: 15 mm/min
 - b. High: 25 mm/min

8. Adhesion of the markers on the test bar (see Figure 2 left)
 - a. Low: normal, the 3 mm markers adhere fully to the test bar
 - b. High: only the outer half of the markers can adhere to the test bar, because the adhesive on the inner half of the marker is obstructed
9. Clamping area (see Figure 2 middle)
 - a. Low: normal, 20 mm of each side of the test bar was clamped
 - b. High: partial, only 8 mm of each side of the test bar was clamped
10. Test bar alignment in the clamp (see Figure 2 right)
 - a. Low: out of alignment (oblique), within "reasonable limits"
 - b. High: normal (straight)
11. Test conditioning
 - a. Low: no conditioning was carried out and the tensile test was started directly after closure of the lower clamp at 75°C or 85°C
 - b. High: normal, 30 min conditioning at 75°C or 85°C with a 1 min wait after closure of the lower clamp at 75°C or 85°C

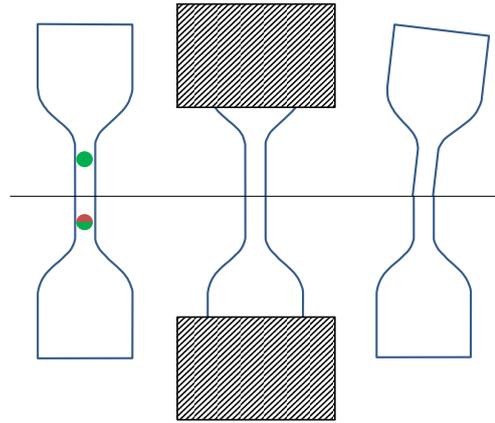


Figure 2. The top half represents the "low" level and the bottom half represents the "high" level. Left: the marker adheres to the entire area or only to the outer half of the marker (green), because the adhesive is obstructed on the other half (red). Middle: the test bar is clamped over 20 mm or only over 8 mm. Right: the test bar is installed obliquely or straight.

It is important to note that the difference between the "low" and "high" levels is often greater than the tolerances stated in ISO 18488 [1]. This is necessary to obtain sufficient variation in the strain hardening modulus, otherwise the difference may be as low as the natural scatter resulting from the test method.

The variables were often chosen in such a way that the values stated in the standard were in the middle of the range (e.g. the tensile speed and the temperature). Other variables were chosen from a practical point of view.

It must be noted that while the type of clamp in the tensile tester was originally also a factor, this factor had to be removed for practical reasons. Also, the thickness of the test specimens and many variables related to the molecular structure of the PE material were not taken into account. Results from other studies are briefly discussed and referred to later in this paper.

Each of the 32 experiments resulted in one test bar, which was completely randomized in preparation and execution. This means that the samples were not grouped for easier preparation. A statistical evaluation was subsequently performed by the external statistical company to determine the effect and interaction of various variables.

After these experiments, 12 additional experiments were performed *in duplo* to confirm the earlier results. In this case, only PE100-RC, with high orientation during compression molding, cooled down slowly after annealing, and punched with a new punching tool, was tested at 20°mm/min using normal marker locations and the normal 30 min sample conditioning as prescribed by ISO 18488. These experiments also used an intermediate temperature (80°C). Again, each experiment used one test bar, which was prepared and tested completely individually and randomly.

Strain Hardening Test method

The SHT is a modified tensile test performed at 80°C on specially-prepared thin samples (Figure 2) of 0.3 mm (0.0118 inch). The test was performed in accordance with ISO 18488 [1] as summarized below, except for the changes in variables as explained above.

The 0.3 mm thick samples were punched from a compression molded sheet made from PE granules. The samples were clamped and pulled at 20 mm/min with an Instron Electro-Mechanical Single Range Testing Machine type 3365, using a 500 N force transducer. During extension of the samples, the elongation was carefully measured using an advanced video (non-contact) extensometer (AVE) with a 500 mm field of view. A subsequent data treatment using the Neo-Hookean Strain Measure (NHSM) model was used to determine the slope after the natural draw ratio. This slope was correlated to the strain hardening modulus [2,7].

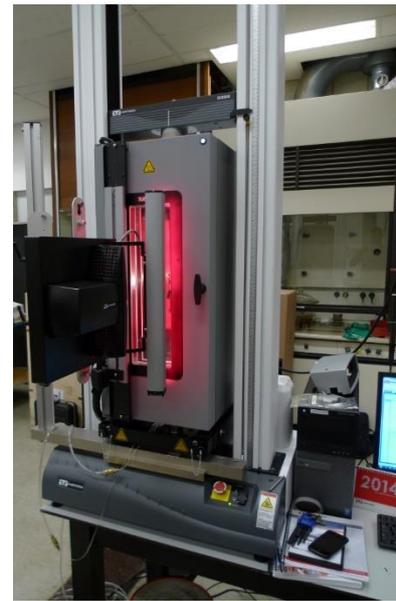


Figure 3. Test setup for the SHT at Kiwa Technology.

RESULTS

A factorial regression was used to prepare an optimal model. The model was found to be reliable, since:

- the statistically significant factors explained 99% of the variation in the <Gp>.
- the standard deviation was found to be 2.84 MPa, which is comparable to private historical data from Kiwa Technology using many different PE qualities.
- the “lack-of-fit” had a high p-value.
- the residuals plot did not show any strange patterns, as should be expected from a sound model.

The statistical analysis of the 11 factors demonstrated that there are 6 factors that have a statistically significant influence on the resulting <Gp>, while 5 factors do not. Moreover, 6 two-way interactions were found to be statistically significant. Because of “confoundment”, where interactions overlap one another, the most likely interaction is selected and presented here.

As expected, there was a clear difference in strain hardening modulus between the two PE types (PE50 and PE100-RC). Nevertheless, it was important to include this variable, because other variables may be dependent on the PE type. For example, it was also found that the effect of temperature on the strain hardening modulus for first-generation PE50 differed to that for PE100-RC. This shows that there is a two-way interaction between PE type and temperature.

It was found that a 10°C change in test temperature can result in a change of about 7 MPa in the strain hardening modulus. This means that the 2°C temperature variation allowed by the ISO 18488 standard can introduce a statistical deviation of about 1.4 MPa.

Because temperature and PE type interact with each other, this 7 MPa is only an average value. The change in strain hardening modulus due to the 10°C temperature difference was 2 MPa greater for PE100-RC (about 9 MPa) and 2 MPa lower for the first-generation PE (about 5 MPa).

The additional experiments, which used only PE100-RC and involved tests at 80°C, demonstrated a linear correlation between the temperature and the strain hardening modulus in this temperature range. These experiments also showed that a change of 10°C may have an even greater effect on the strain hardening modulus, possibly 13 - 19 MPa (see Figure 4). This means that a temperature variation of 2°C may introduce a statistical deviation of up to 3.8 MPa.

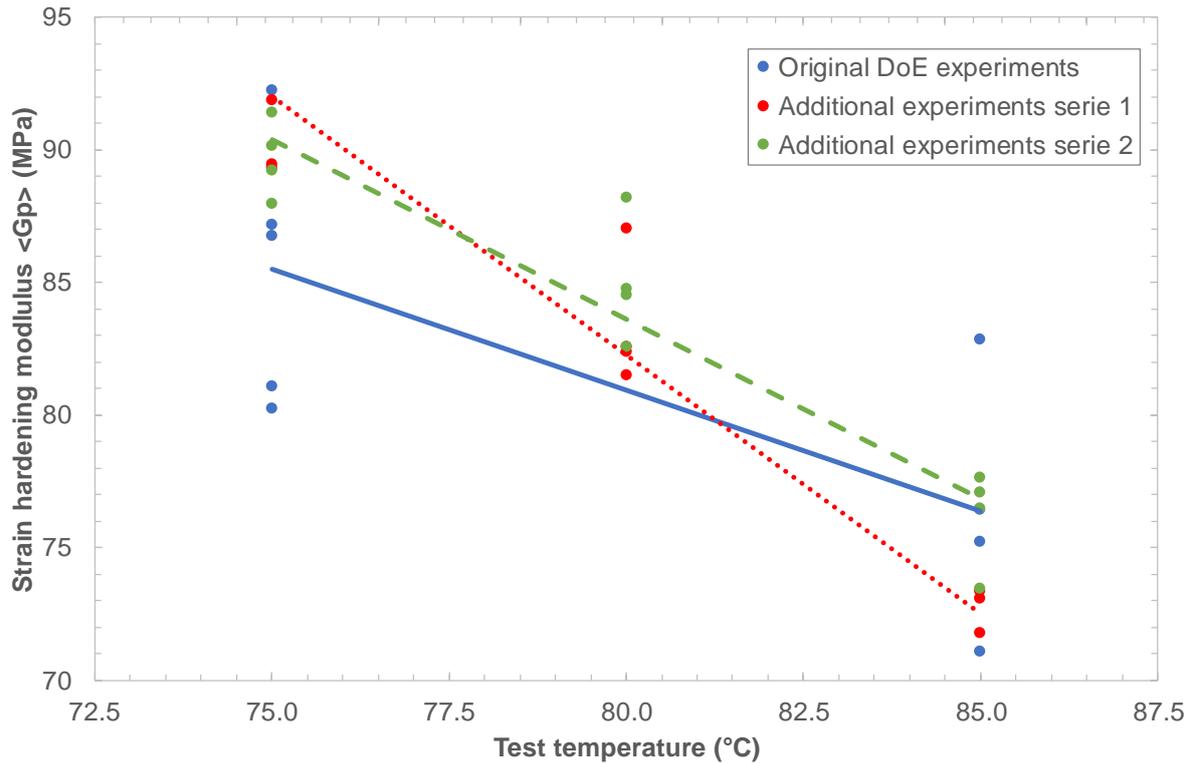


Figure 4. Scatter plot of the original and two additional experiments using DoE, where the strain hardening modulus ($\langle G_p \rangle$) is plotted against the test temperature (°C).

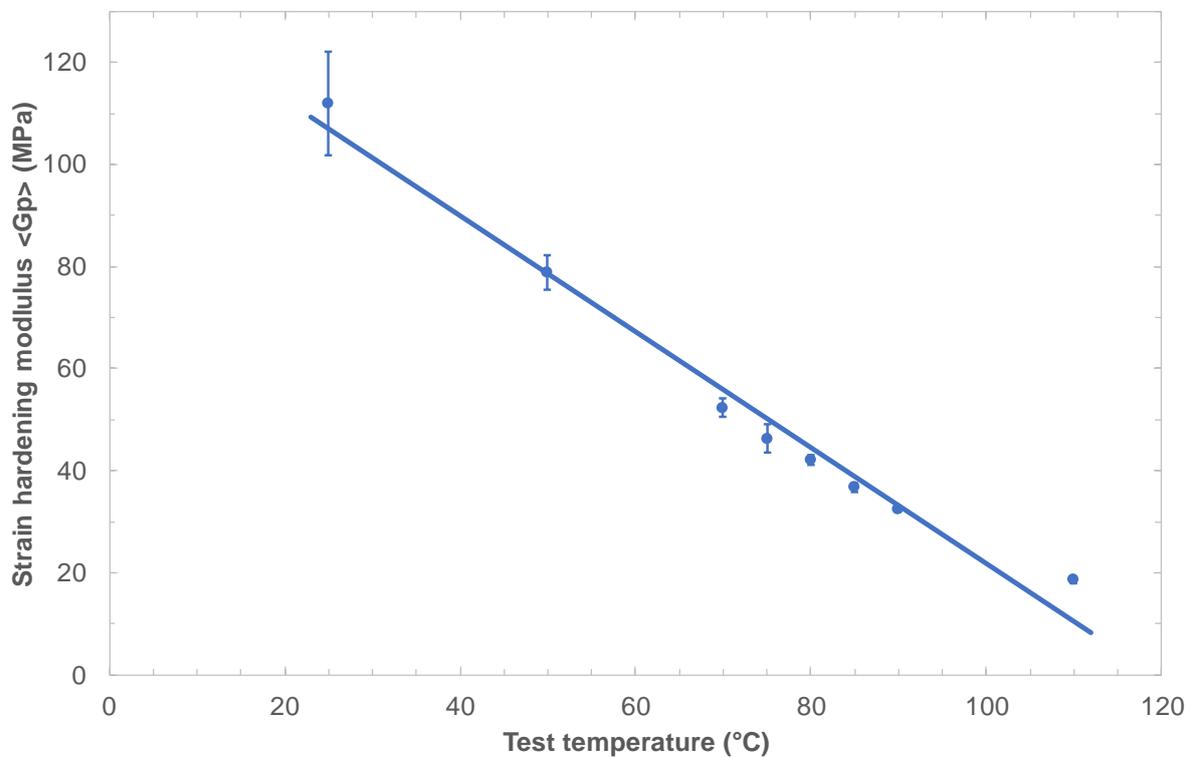


Figure 5. The strain hardening modulus as a function of test temperature using the one-factor-at-a-time method [11].

A similar effect was previously found by Kiwa Technology [11], where the test was performed in accordance with ISO/DIS 18488 [12] and only the factor “temperature” was changed over a wide range (see Figure 5). The difference in $\langle G_p \rangle$ between 75°C and 85°C was about 10 MPa for this PE100 material.

Gerets and Engelsing [13] also obtained results of this order of magnitude. However, they found that the effect of temperature is greater for materials with lower stress cracking resistance than for those with a higher stress cracking resistance, which is the opposite to what was found in this study. However, it should be noted that in Gerets and Engelsing’s study, the test was performed on very small test specimens of 1 mm (0.039 inch) thick using 15 mm/min as the crosshead speed and a different data evaluation method.

The first series of DoE experiments also demonstrated that the adhesion of the markers, the clamping area and the alignment have a statistically significant influence on the strain hardening modulus. The additional experiments could not confirm the statistical effect of clamping and alignment. Nevertheless, it is important to take account of proper preparation of the test setup.

The cooling rate after annealing is also important. This is currently not well described in the standard, which simply mentions “*slow cooling*” [1]. However, very fast cooling does have a statistically significant effect on the strain hardening modulus of about -2.7 MPa compared to slow cooling. However, it should be noted that such rapid cooling is an extreme example, which is not permitted by ISO 18488. It does show that the changes in the molecular structure due to differences in crystallization are of importance to the strain hardening modulus.

The orientation due to compression molding, the punching equipment, the cooling rate after compression molding, the tensile drawing speed and the test conditioning were found to have no statistical significance.

It was also found that, although the tensile drawing speed on its own is not statistically significant, the interaction between “tensile drawing speed” and “test temperature” is. This means that the tensile drawing speed combined with the test temperature influences the strain hardening modulus.

Earlier research [11] on a PE100 material has shown that the tensile speed does change if more extreme values are chosen (see Figure 6). The other test parameters were chosen in accordance with ISO/DIS 18488 [12].

Domínguez et al. did find distinct lower $\langle G_p \rangle$ values using a lower tensile speed (tested with 3, 10 and 20 mm/min using ISO/DIS 18488, but with slight modifications to the geometry of the specimen and the test conditions) [14].

Gerets and Engelsing [13] found a linear correlation between the strain hardening modulus and the logarithm of the crosshead speed up to 7 mm/min at 23°C. It is not known if such a correlation is valid at the normal test temperature of 80°C.

They found that, in this range, an increase in the testing temperature of $\Delta T=10^\circ\text{C}$ corresponds to a decrease in crosshead speed of about one decade (using test parameters other than those prescribed by ISO 18488). Above this crosshead speed, the intrinsic heating of the specimens influences the transition from cold drawing to the strain hardening region.

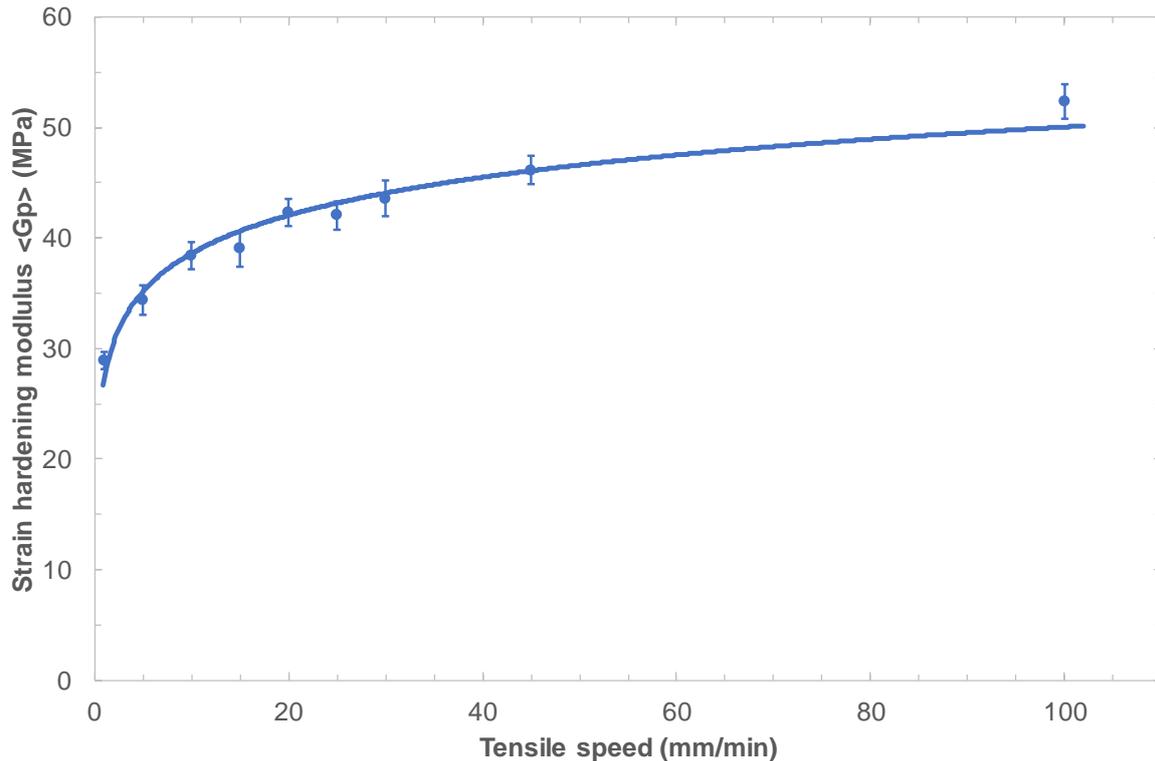


Figure 6. The strain hardening modulus as a function of tensile speed using the one-factor-at-a-time method [11].

Finally, in this Design of Experiments statistical model, higher $\langle G_p \rangle$ values resulted in more scatter (also relatively), although the difference is limited. This is similar to the results found in earlier Round Robin data (see Figure 1).

It is not known why this happens, but it is probably influenced by the fact that materials with a higher slow crack growth resistance have a lower draw ratio at break than materials with a lower resistance to SCG (see Figure 7).

ISO 18488 states that the data must be evaluated from $\lambda = 8.0$ to $\lambda = 12.0$ or breakage. If the material breaks relatively quickly (e.g. at $\lambda = 9$), the fit is performed on a relatively small data set in a narrow draw ratio range.

In contrast, a material that breaks after $\lambda = 12$ allows the entire draw ratio range to be used to fit the slope. A wider range gives a better fit and thus less scatter. This is especially true if the correlation between the $\langle G_p \rangle$ and the Neo-Hookean constitutive model is not completely linear.

It should be noted that many variables related to the material have not been taken into account, although these can have a major influence on the $\langle G_p \rangle$. For example, Domínguez et al. demonstrated that the $\langle G_p \rangle$ depends on the co-monomer type and the catalyst [16].

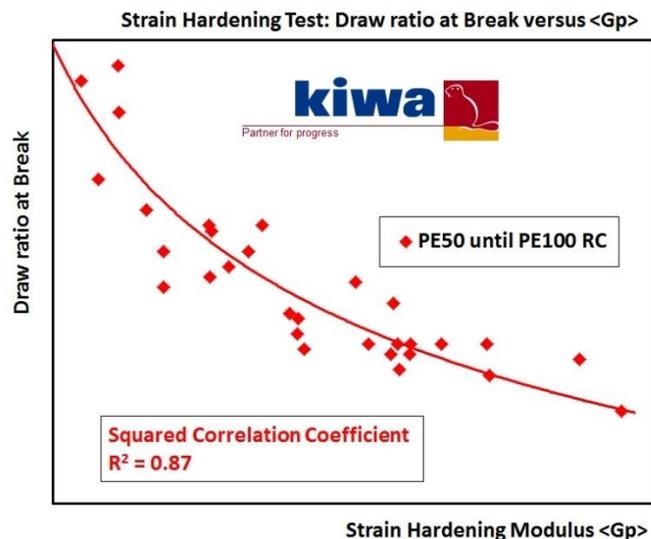


Figure 7. The draw-ratio-at-break as function of the strain hardening modulus at 80°C. From Scholten [15].

Deveci and Fang evaluated the correlations between morphology, molecular weight, molecular weight distribution and the rheological properties of different PE materials, with their slow crack growth resistances obtained using the strain hardening test [17]. They also found that the SHT is affected by the co-monomer type.

During this conference, Deveci et al. will publish more information on the sensitivity of the strain hardening modulus to molecular properties [18].

The effect of thickness was also not taken into account in the DoE investigation. Kiwa Technology (see Figure 8) and other research institutes [19] have previously demonstrated that the thickness is of no importance for samples up to at least 1 mm, and possibly even thicker. However, Dominguez et al. did find slightly lower values for 2 mm thick samples than for 0.3 mm thick samples [14].

The reason thicker samples may give deviating values is due to intrinsic (adiabatic) heating of the sample during plastic deformation. Black samples would be particularly affected by this. Gerets and Engelsing [13] showed this effect very clearly when performing a tensile test at 7, 30 and 70 mm/min at 23°C. They concluded that “*small deviations between the intrinsic heating detected for differently coloured material but are negligible compared to the influence of the crosshead speed*”.

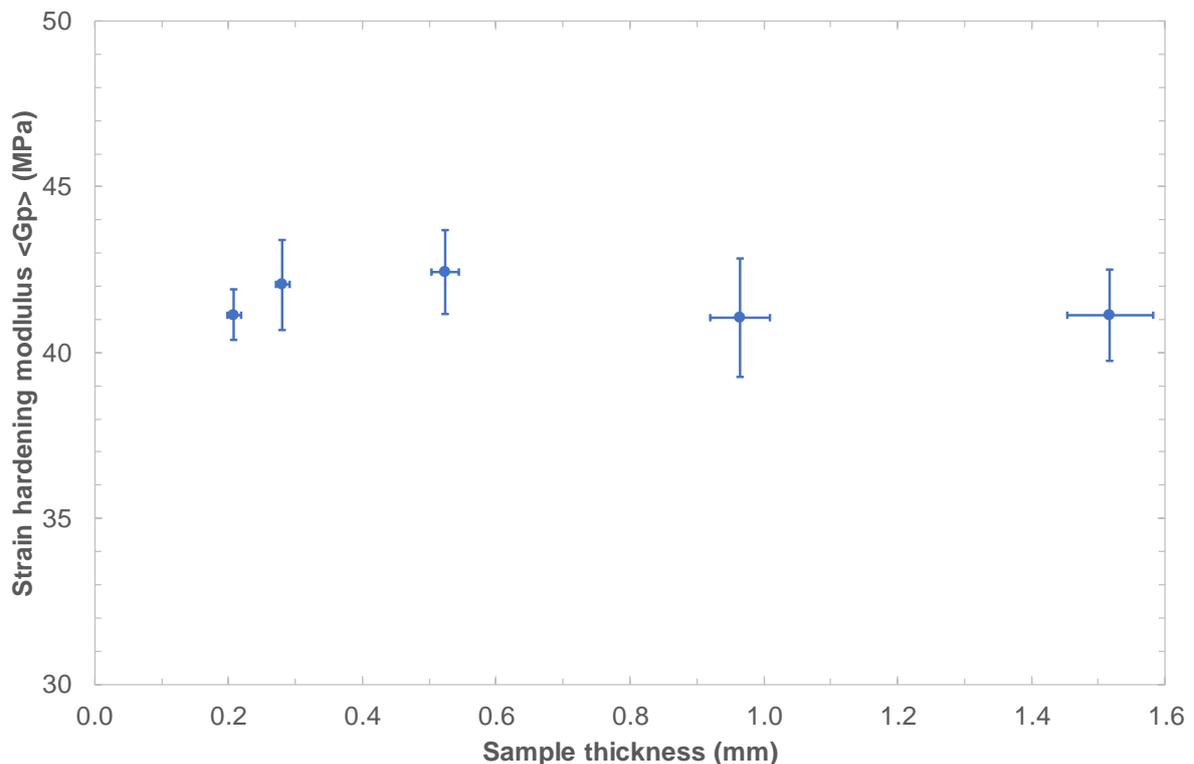


Figure 8. The strain hardening modulus at 80°C as a function of sample thickness using the one-factor-at-a-time method [11].

CONCLUSIONS

The Design of Experiments statistical method proved to be a suitable tool for rapid screening of the effect of various test parameters on the strain hardening modulus. It was found that a 2°C temperature variation may introduce a statistical deviation of up to 3.8 MPa. This study also demonstrates that the deviation for PE100-RC is greater than for first-generation PE. Furthermore, some of the test parameters related to the test setup were of statistical significance, which highlights the importance of proper preparation. Very fast cooling after

annealing has a statistically significant effect on the strain hardening modulus of about -2.7 MPa compared to slow cooling as required by the standard. This shows the effect of crystallinity in the PE molecular structure. It was also found that, although the tensile drawing speed on its own is not statistically significant, the interaction between “tensile drawing speed” and “test temperature” is. Finally, it was found that higher <Gp> values resulted in more scatter (also relatively). This is possibly caused by the lower draw ratio at break compared to materials with a low resistance to SCG.

ACKNOWLEDGMENTS

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