

# ENHANCING POLYOLEFINS PRODUCT DEVELOPMENT THROUGH SMALL SCALE PROCESSING AND TESTING

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## Abstract

This paper presents a new methodology combining up-to date small scale processing capabilities, representative sample preparation and small scale and accelerated mechanical and rheological properties measurements aiming at rapid delivery of new product development options

## Introduction

Accelerating the development and design of new polymeric materials remains a key objective for polymer manufacturers who wants to decrease time to market as well as development costs<sup>1,2</sup>.

Therefore, capabilities of performing a larger amount of lab scale experiments instead of pilot plant trials, together with a proper use of design of experiments and statistical analysis of the results has been strongly developed in recent years.

In contrast to the relatively simple active / not active diagnostic in new catalysts discovery (first screening), secondary screening of catalytic species or appraisal of new resins structures will require minimum amounts of some grams of polymers to investigate several properties<sup>3,4</sup>.

In the case of high throughput production of polyolefins, their basic structural characteristics can be evaluated with high throughput and small scale techniques derived from classical GPC, FTIR and DSC techniques. Most of these techniques are not directly dependant on native solid state structure as they require a solubilization or an initial melting of the material.

Generally, that combination of techniques gives a good indication of future end-use properties of the materials, especially through appropriate structure-properties models and is well suited for the first screening of the different options. Nevertheless, appropriate structure/property models do not always exist and need to be built, especially for some end-use properties that have to be guaranteed on the final product and are strongly dependant on the solidification conditions of the sample. This last point is of particular importance for HDPE applications where long term properties like creep and stress crack resistance, or rapid crack propagation resistance, are usually appraised on the final product (pipe, bottle, ...). Based on the growing opportunity to access rapidly to a higher number of molecular designs, eventually emerging from H.T.E tools, the purpose of this paper is to illustrate how it is possible to adapt processing and testing methods to appraise some key mechanical end-use properties at a very small scale.

## Experimental Procedure

Polymer samples have been produced either on conventional pilot plant, bench scale laboratory facilities or in our High Throughput facility, located in the Ineos-Polyolefins Research laboratory in Brussels. This comprises 8 fully automated parallel reactors that operate at commercial conditions and polymerization rates and is able to produce 10 to 15 g of polymer per reactor<sup>5</sup>.

A Micro-Compounder, developed by DSM Xplore<sup>6</sup> has been used to homogenize the samples or to prepare blends.

This apparatus is a micro-scale, conical, twin-screw compounder, which has been designed to process 10-15 cc of polymer, mimicking the mixing behavior of large twin-screw compounding machines, while offering precise control of the mixing temperature and speed.

The pellets obtained are compression molded with an adapted mould to give a 10 g plate. This initial plate is then cut to form a number of test specimens of the required dimensions. For the remaining unused material, we have found a process suitable for preparing molded polymer samples for physical testing like Charpy or FNCT (notched samples) which uses a reduced amount but still enables the polymer to be tested using standard methods. This method is currently under a patentability examination process and will therefore not be disclosed here.

A number of the tests we need to perform are subject to international standards, often including both ISO and ASTM. These standards can also require defined sample sizes.

In order to ensure uniform results and derived structure/properties models interpretation, our aim all along in this work has been to use standard methods and sample sizes whenever possible.

## Results

Within the framework of that Conference, we will only focus on four key properties of HDPE pipe grades :

- Processability through rheological properties
- Resistance against aging (slow crack growth)
- Resistance against rapid crack propagation
- Long term pressure resistance (creep behavior)

## Rheological properties

Dynamic rheometry can provide a good indication of general processability potential. Moreover, very slow relaxation mechanisms can be highlighted by a specific look at the curve  $\tan \delta = f(\omega/\omega_c)$  around  $\omega = 0.01$  rad/s . A simple compression moulded disk of 20 mm diameter and 2mm thickness (less than 1 g) is needed for such a measurement.

Fig 1 and Fig 2 illustrate respectively the similarity of the general properties and rheological curves obtained for the same HDPE blend produced either on pilot scale or with the micro-scale (DSM) extruder.

To get more detail on the nature of the chains responsible for these relaxations (presence of long chain branching or UHMWPE), it is also possible to perform elongational rheometry. The Universal Testing Platform adaptor, called "SER-HV-A01" and commercialized by Xpansion Instruments<sup>7</sup> can be accommodated onto an existing classical dynamic rheometer (e.g., ARES) and give access to transient extensional viscosity curves by using only a 100 mg compression molded specimen.

## Mechanical properties

Slow Crack Growth resistance : The full-notch creep test (FNCT) is now well accepted and used in our laboratories, according to ISO 16770, to predict long-term properties of resins , and resistance to slow crack growth. The principle of the test is to apply a static tensile load to notched specimens immersed in an active solution (environment) held at a specified temperature, and to measure their time to failure.

Fig 3 illustrates the very good agreement between results obtained on conventional samples and with our small scale new method. The dispersion for 3 samples was very low (< 10 %); only one can be used for the first screening. Then, depending on the resistance of the resin (respectively blow-moulding or pipe grade),

either 1.5 or 2.5 g of material are needed to appraise slow crack growth resistance.

While this test is well suited for the current generation of HDPE including common bimodal pipe grades, more recently developed compositions can have a time to failure greater than one year. Other options are currently used to overcome that drawback.

Rapid crack propagation : The method to appraise Rapid Crack Propagation (RCP) properties is based on the determination of the critical strain energy release rate ( $G_c$ ) as described in Appendix A of reference 8. The  $G_c$  value is extracted from resilience measurements on five Charpy type samples with notches of different depth.

A very good agreement is shown in Figure 4 between classical (according to ISO 179) and small scale Charpy notched sample results.

Figure 5 shows very good agreement between  $G_c$  values extrapolated from classical or “small scale” samples. In the latter case, only 2.5 g of material is needed to perform the 5 tests.

Finally, Figure 6 illustrates that such a test allows us, at least, to discriminate between well known families of pipe resins and can identify products with an even better behavior. This has been confirmed with classical large scale S4 testing on the corresponding pipes.

Long term pressure resistance :

In the development and approval of HDPE pipe products, failure under constant internal pressure is a key property. This is characterized by tests such as ISO 9080 where a pipe section is subjected to a constant nominal stress and the time to failure is recorded for a given  $T^\circ$ .

We have developed an internal testing methodology for predicting pipe hydrostatic strength performance from creep experiments performed on small laboratory samples. As shown in the Figure 7, creep experiments at a maximum of 3 different loads (which means 3 samples of 1.5 g) allow us to extrapolate the 50 year Long Term Hoop Stress (LTHS) value, consistent with standard pipe tests.

## Summary

We have shown that it is possible to provide a comprehensive appraisal of key end-use properties of HDPE pipe-type structures by using only 10-15 g of material. This is compatible with typical H.T.E polymer production levels for secondary screening and product development purposes.

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**Key Words** : Small scale testing, H.T.E, RCP, FNCT, HDPE

Samples	Micro-extruder (10 g)			Lab scale (500g)		
	HLMI g/10 min	MI 5 g/10 min	MVS kg/m <sup>3</sup>	HLMI g/10 min	MI 5 g/10 min	MVS kg/m <sup>3</sup>
RS1854/1861_55/45	11.6	0.4	955.0	9.9	0.4	955.1
RS1854/1861_40/60	2.8	0.2	948.1	2.5	0.1	948.8
RS1857/1863_50/50	28.0	1.0	953.2	25.5	1.0	953.2
RS1857/1863_35/65	6.1	0.3	945.9	6.1	0.3	946.4
RS1855/1871_50/50	12.2	0.3	950.3	11.3	0.4	950.1
RS1855/1871_45/55	6.8	0.2	947.3	6.2	0.2	947.2

Figure 1. Comparison of general properties of blends obtained at pilot scale or with micro-extruder

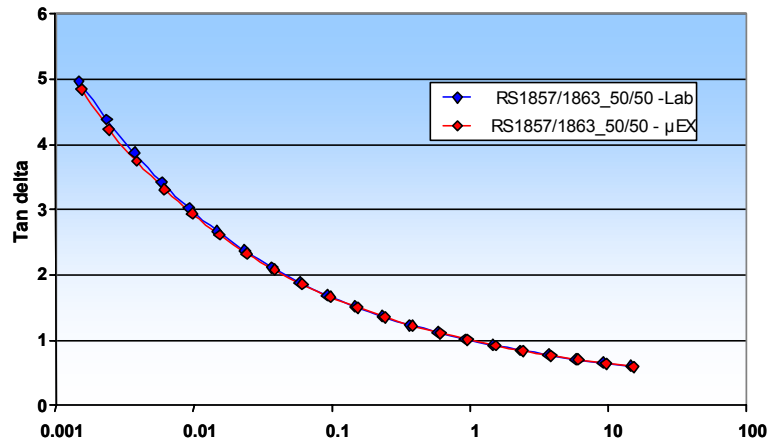


Figure 2. Comparison of rheological curves of blends obtained at pilot scale or with micro-extruder

Conditions test	Grade	Failure time (h)	
		Standard sample	Small scale sample
A	BM 1	4.3 ± 0.3	4.3 ± 0.4
A	BM 2	22.2 ± 0.2	21.2 ± 1.6
A	BM 3	57.7 ± 2.1	59.1 ± 1.3
B	PE80	94 ± 8	107 ± 9
B	PE100	414 ± 33	400 ± 27
B	PE n.g.	> 2500	> 2500

A : Sample section: 6X6 mm, Temperature: 50°C, Notch depth: 1.0 mm,

B : Sample section: 10X10 mm, Temperature: 80°C, Notch depth: 1.6 mm

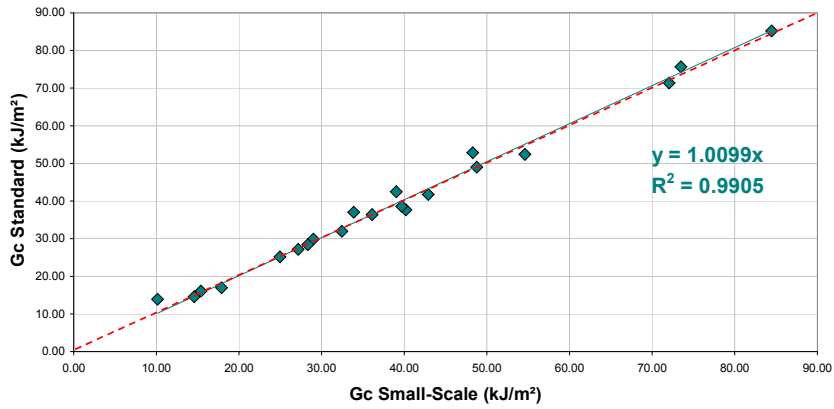
PE n.g. = PE new generation

Figure 3. Small scale approach validation for FNCT Test (Tensio active: 2%w Arkopal N100®)

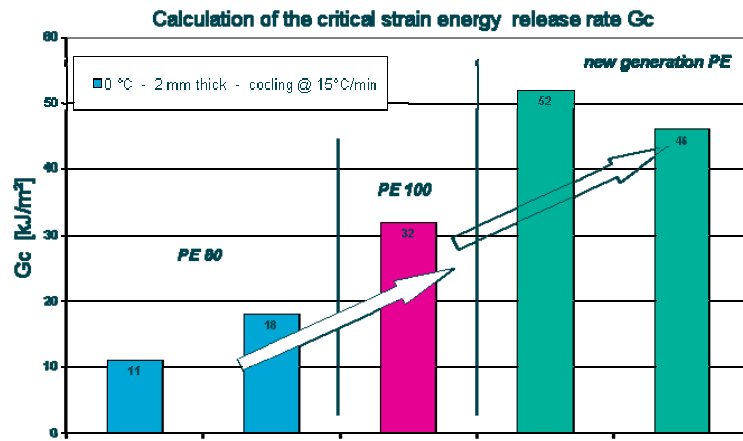
Grade	Resilience (kJ/m <sup>2</sup> )		Small scale specimen
	Specimen out of		
	Standard plate	Small plate	
Injection	2,31 ± 0.08	2.52 ± 0.06	2.64
Blowmolding	6,01 ± 0.59	6.09 ± 0.27	6.47
Rotomolding	9,38 ± 0.36	10.35 ± 0.35	9.77
Injection	10,76 ± 1.03	10.08 ± 0.91	10.21
Pipe	16,04 ± 0.57	17.09 ± 0.05	17.18
Nb of specimen	10	3	1

Figure 4. Small Scale approach validation for Charpy test

**Critical strain energy release rate (Gc) @ 0 °C**  
Gc standard vs. Gc small-scale

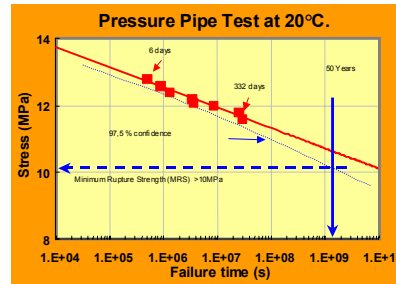


**Figure 5. Small Scale approach validation for Gc test**



**Figure 6. Relative ranking of HDPE pipe resins obtained with Gc test**

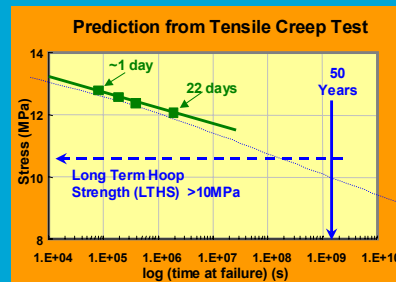
**Conventional pipe testing**



0.005 kg



14 – 21 days



**Rapid & Small Scale Testing**

**Figure 7. Small Scale test to appraise Long Term Pressure resistance**