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UHMWPE Selection Based on Properties Balance

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1 Introduction

There is a paradigm on the UHMWPE end-users market which says that the properties of such a material can be directly correlated to its Molecular Weight (MW). This is not completely true.

In fact, the higher the molecular weight, the higher the abrasion resistance and the lower the impact strength of a UHMWPE molded article. However, the correlation among those properties depends on other polymer intrinsic properties such as molecular structure and weight distribution among the chains, which are on their turn dependent on the polymer production technology used to produce it.

In a more mathematical approach, the correlation curve between MW and a mechanical property can have different slopes if the polymer production technology is different. In other words, in the correlation equation $y = ax + b$, both the constants "a" and "b" can show distinct values if the way to produce the polymer varies.

In the present Technical Bulletin, a comparison between two technologies to produce UHMWPE is carried out. It's clear to notice that, for one determined property value, the materials show different molecular weights. And because performance is what really matters on the application, which means mechanical properties, the conclusion of this Bulletin is that the final end-user selects a UHMWPE material based on its performance, not on the molecular weight itself.

2 The Molecular Weight of UHMWPE – An Indirect Measurement

Commercial synthetic polymers are characterized by having molecules not of the same molecular weight, but a distribution of molecular weights. It's therefore necessary to report an average molecular weight when characterizing a sample. There are three important molecular weight averages: number average (M_n), weight average (M_w) and **z** average (M_z). Absolute values of M_n, M_w and M_z can be obtained by primary characterization methods of osmometry, light-scattering, and sedimentation, respectively. These are accurate but time-consuming techniques.

For practical purposes in the industry, there are some secondary – or indirect – methods by which average molecular weights can be determined provided that standard polymer samples are available for reference and calibration. In those cases, some property is measured and then correlated to the MW using some boundary conditions, which can be different when more than one production process technologies are used. This can explain why, for example, two materials may show the same MW when measured by method "A" and different values when measured by method "B".

In order to understand the influence of the boundary conditions on the MW values, it's taken for example the MW values calculated from Intrinsic Viscosity (IV) measurements. Depending on the equation used to calculate MW, absolute numbers can be very different.

Figure 1 depicts the correlation between IV and Molecular Weight using Margolies' Equation[1] (blue) and ASTM Equation[2] (red). For the same IV, the absolute MW value is different. In this particular case, the difference increases as the IV value increases.

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[1] Margolies' Equation: $MW = 53{,}700 \times [IV]^{1.49}$
[2] ASTM Equation: $MW = 53{,}700 \times [IV]^{1.37}$

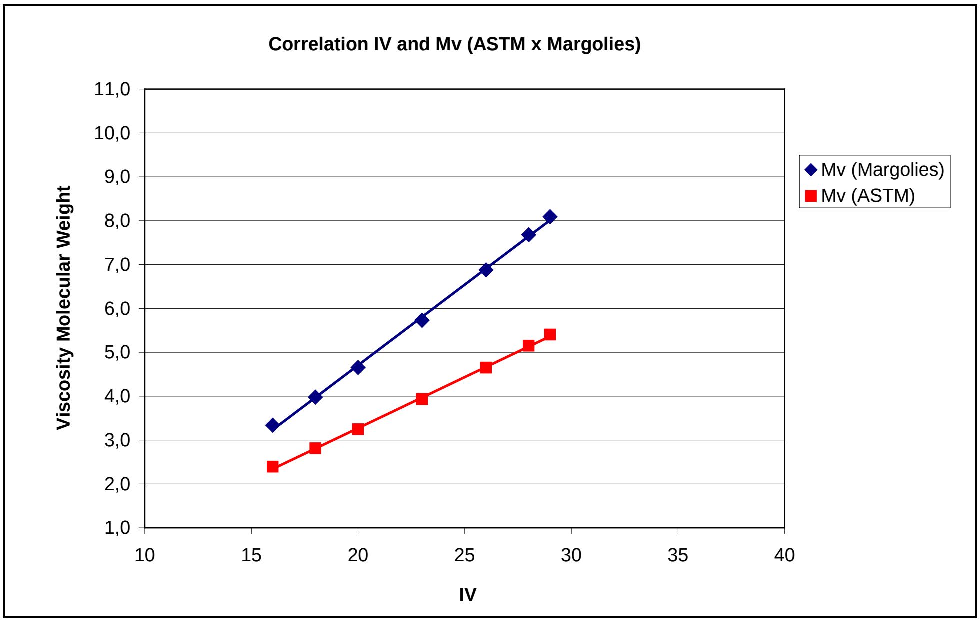


Figure 1 – Correlation between IV and Molecular Weight using Margolies' Equation (blue) and ASTM Equation (red).

Another important indirect method to determine the molecular weight of a UHMWPE resin is the Gel Permeation Chromatography, or GPC. From this technique, two polymers with the same IV but produced with different technologies can present different values of number-average molecular weight (M_n) and weight-average molecular weight (M_w). This happens because GPC measurements are more sensitive to polymer molecular structure differences – such as molecular weight fractions and branching degree – than viscosimetry.

Figure 2 presents the correlation between the MW obtained from viscosimetry, or simply Mv (calculated from Margolies' Equation), and M_w calculated from GPC curves. Note that the production technology influences the numerical result.

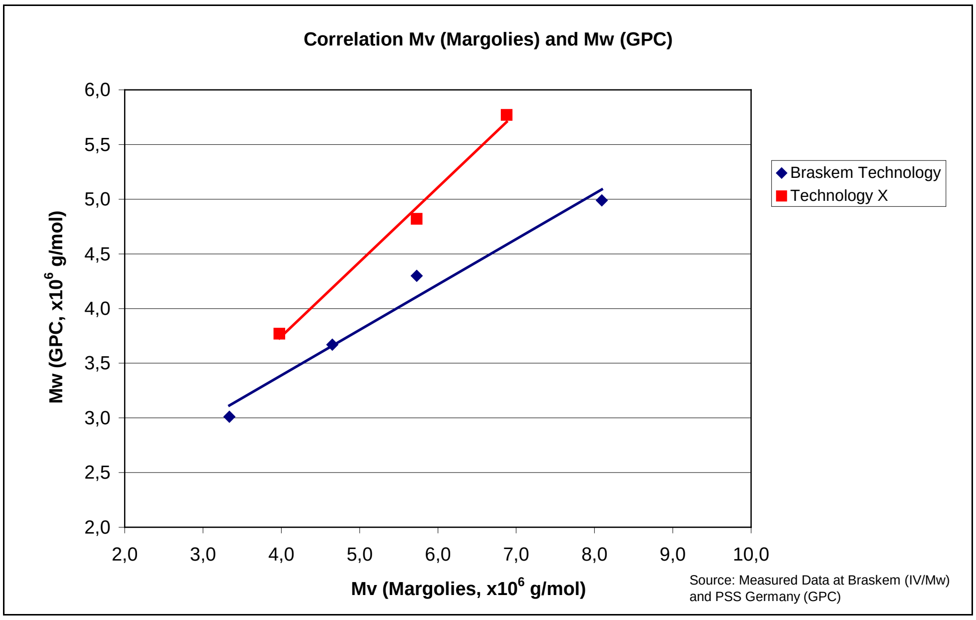


Figure 2 – Correlation between Mv (Margolies) and Mw (GPC) using Braskem production technology (blue) and a different technology (red).

The UHMWPE industry uses a third indirect measurement to access the molecular weight of a sample – the Elongational Stress, or ZST. In this case the correlation between two technologies is close but still not the same. The data can be seen on figure 3.

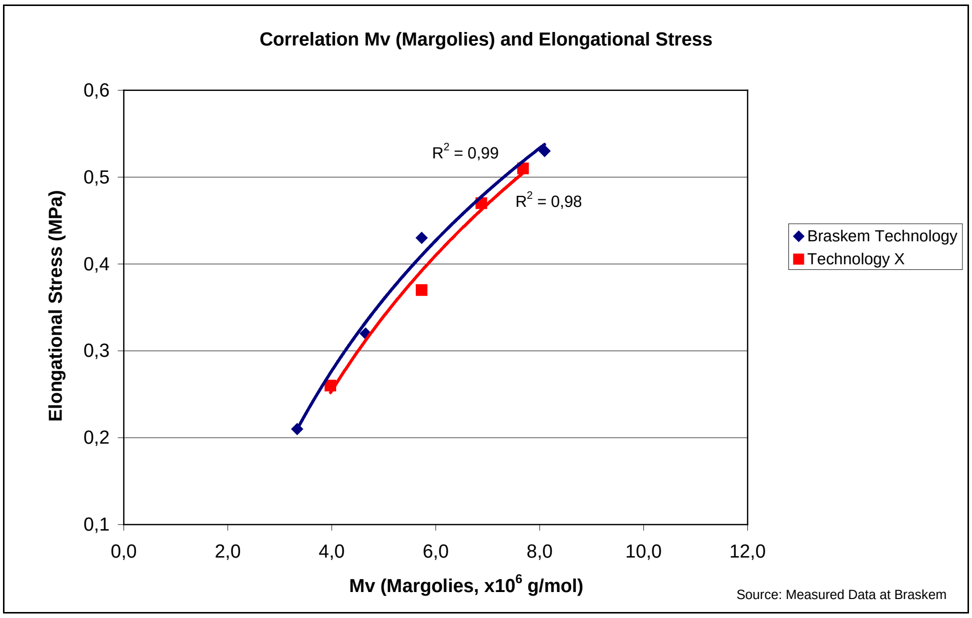


Figure 3 – Correlation between Mv (Margolies) and Elongational Stress using Braskem production technology (blue) and a different technology (red).

From the shown above, it's clear that the molecular weight numerical value of a given polymer depends on the technique used to measure a primary parameter, on the mathematical approach to correlate such parameter with MW, and on the polymer production technology from which such a material was produced.

In practice, two given polymer samples can have the same molecular weights or totally different ones. It's just a matter on how the results were calculated.

3 Correlations between Mechanical Properties and Molecular Weight

It's found below some figures showing how the pair molecular weight + production technology correlates to the most common mechanical properties of UHMWPE – Charpy Impact Strength and Abrasion Index.

Charpy Impact Strength was measured at Braskem's UTEC Technology Center according to ISO 11542-2.

The abrasion index was conducted in a sand slurry testing equipment based on an internal method, whose testing conditions are detailed on table 1.

Figure 4 brings the correlation between MW measured from viscosimetry (Mv) and the abrasion index, for products produced using both Braskem and some other methodology.

It is well described on the literature that the abrasion wear decreases as the molecular weight increases. One of the possible mechanisms for this phenomenon is that longer chains promote more physical bonds among the molecules (the number of tie molecules is higher), which makes it more difficult to remove material apart due to abrasion.

Table 1 – Testing conditions for Abrasion Index measurements – Braskem Method

Characteristic	Braskem Method (NBR 14922)
Unit	% lost mass in relation to the lost mass of a standard UHMWPE material defined at ISO 15527
Abrasive Media	Water + Sand or Glass Beads (50/50)
Equipment	Height: 370 mm Diameter: 290 mm Stick Length: 9.5 mm
Specimen Dimensions	Length: 76.2 mm Width: 25.4 mm Thickness: 6.35 mm
Test Duration	24 h

An interesting point on figure 4 is the numerical discrepancy in the correlation between MW and Abrasion. Speaking of absolute numbers, the same molecular weight leads to different abrasion indexes if different technologies are used, as seen below.

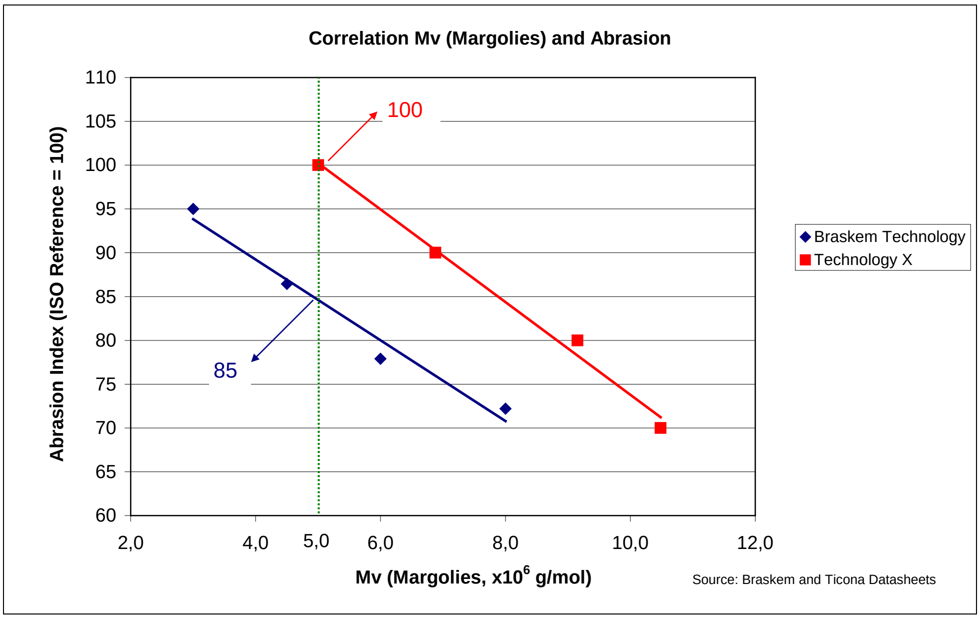
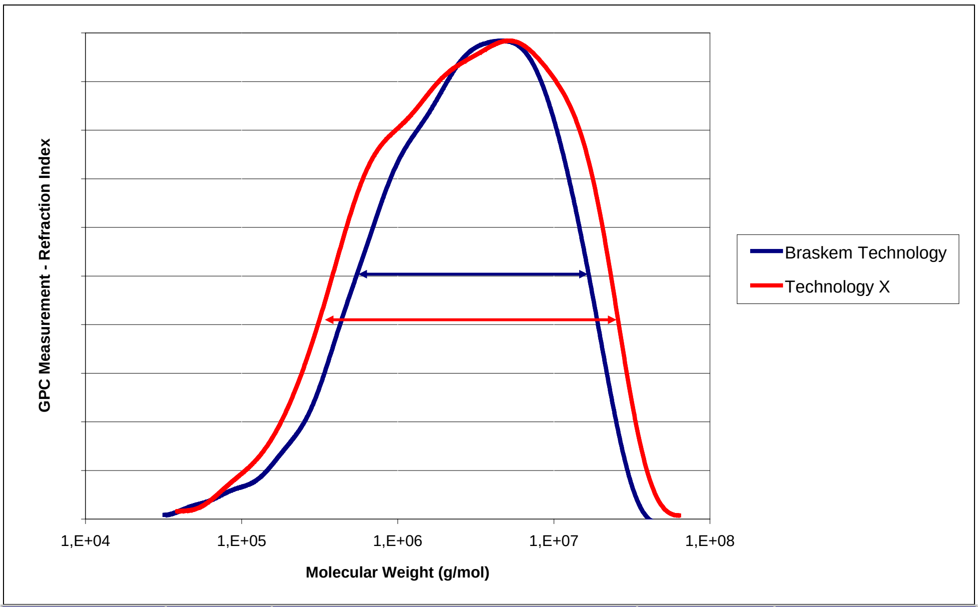


Figure 4 – Correlation between Mv (Margolies) and Abrasion Index using Braskem production technology (blue) and a different technology (red).

From the figure above, a UHMWPE with molecular weight of 5.0 million g/mol has an abrasion index of 85 if produced with Braskem technology, and 100 if produced with some other technology. Again, it's clear that the molecular weight value is not enough to be fully correlated to a mechanical property.

Some more deep analysis on materials produced with those two production technologies give some indication on the reason for such a difference in behavior. Below it's shown a GPC curve of two samples with similar molecular weights but produced with different technologies.



Technology	IV (dl/g)	Mv, Margolies ($x10^6$ g/mol)	Mw (GPC)	Polydispersity (Mw/Mn)
Braskem	29,2	8,2	4,6	5,0
Competitor	27,4	7,6	5,5	7,5

Figure 5 – Molecular weight distribution obtained from GPC for UHMWPE samples produced using Braskem production technology (blue) and a different technology (red).

From the above, it's noticed that Braskem technology produces narrower molecular weight distribution UHMWPE than some other technology. The polydispersity (M_w/M_n) difference in the two technologies is about 50%. Such difference could be able to explain the mechanical property difference between materials.

It's possible to extract from GPC data both the low and high molecular weight fractions of the samples. On table 2 below there's a comparison of two groups of materials, one with MW in the range of 3-5 million g/mol and another in the range of 8-9 million g/mol. In both cases, the higher amount of low molecular chains seems to be responsible for the lower abrasion resistance of the respective samples.

Table 2 – Correlation between molecular weight and molecular weight fractions and abrasion index for samples produced from different technologies

Technology	Mv ($x10^6$ g/mol)	PDI*	GPC Fraction (%) < 100.000 g/mol	GPC Fraction (%) 100,000 - 10,000,000 g/mol	GPC Fraction (%) > 10,000,000 g/mol	Abrasion Index DIN 15527 (%)
Braskem	3.0	3.9	1.0	92.1	6.8	95
X	5.0	7.9	3.9	85.9	10.2	100
Braskem	8.0	5,0	1.1	83.6	15.3	76
X	9.2	7.5	1.9	78.9	19.2	80

* Polydispersity Index

In terms of Charpy Impact Strength, it's shown on figure 6 the correlation of this property with molecular weight, again for two different technologies. The behavior of the curve is similar to the one observed for abrasion wear. In both technologies the impact strength value decreases with the increase of molecular weight. But again the absolute values in the correlation MW x Charpy are different.

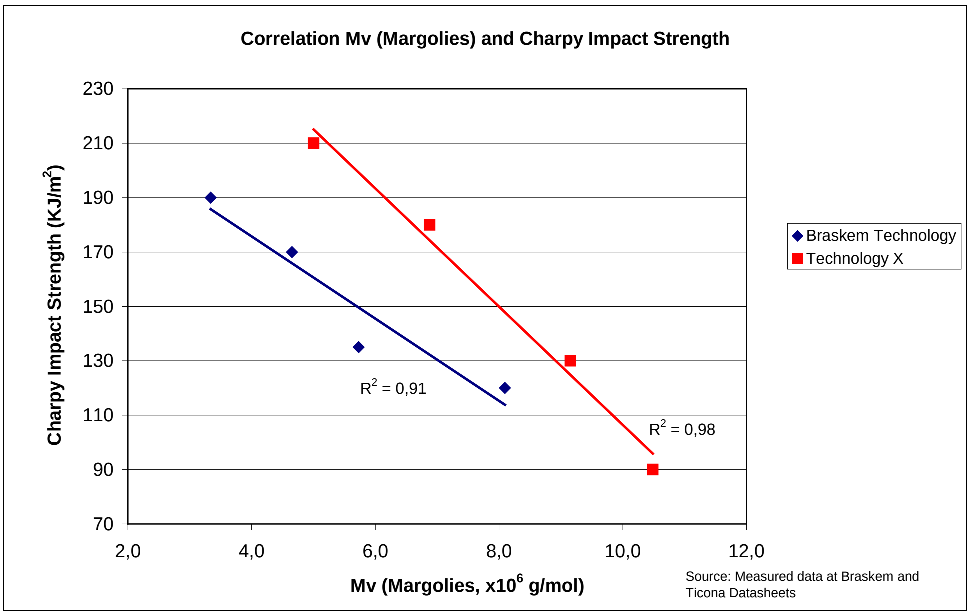


Figure 6 – Correlation between Mv (Margolies) and Charpy Impact Strength using Braskem production technology (blue) and a different technology (red).

Another interesting point to be extracted from figure 6 is the slope of the two curves. Braskem technology seems to lead to a smoother decrease in Charpy as the molecular weight increases.

The numerical difference between the two materials/technologies may also be explained by molecular structure. It appears that the presence of low molecular weight fractions aid the process of energy absorption required when the material is subjected to an impact hit. In fact, Braskem technology leads to a narrower molecular weight distribution, which in its turn makes the material have less low molecular weight chains if compared to another one of same average molecular weight produced with a different technology. This is shown on figure 5 and table 2 above.

Rheology and thermal characterization are also interesting tools to help understand the difference in the correlation between MW and Charpy when two UHMWPE production technologies are used.

From the data obtained by cone and plate rheometry (figure 7), it’s seen that Braskem products show higher shear viscosity (η) and elastic modulus (G’) when compared to a material produced from other technology at the same MW level measured from IV. These parameters are related to molecular motion, that is, the higher the shear viscosity and G’, the more difficult it is for the molecules to move. This motion ability is also related to the energy absorption capacity as described above.

The thermal behavior evaluated by a heating curve obtained from DSC shows that crystalline morphologies of the products produced from the two technologies are different (figure 8). The crystal melt of the product obtained by Braskem technology begins at higher temperature, which may be the effect of different crystal size and perfection.

Crystalline structure is also an important parameter to explain a material's Impact Strength behavior.

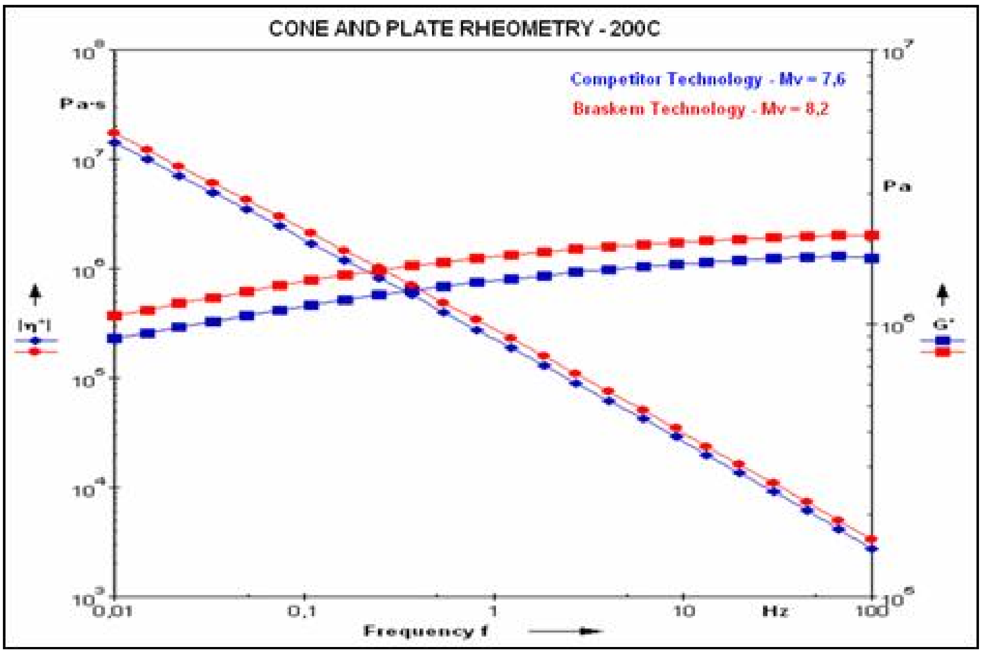
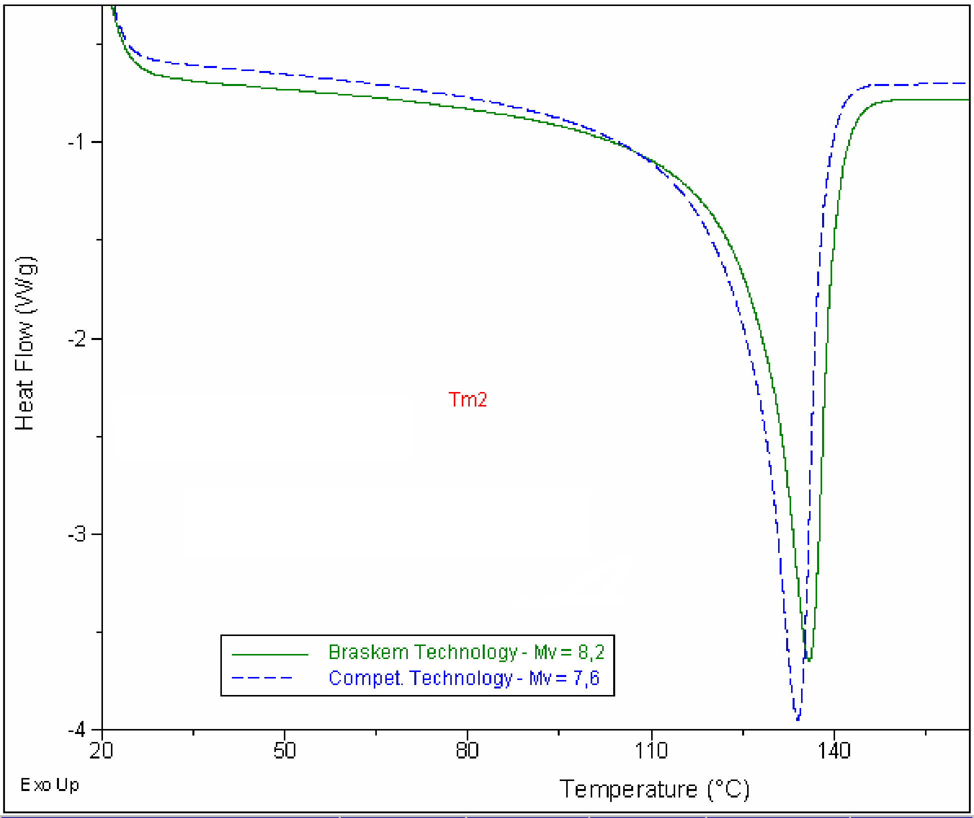


Figure 7 – Shear viscosity (η, [Pa.s]) and storage modulus (G', [Pa]) obtained from cone and plate rheometry for UHMWPE samples produced using Braskem production technology (red) and a different technology (blue).



Product	Tm (°C)	Xc_1 (%)	Tc (°C)	Tm_2 (°C)	Xc_2 (%)
Braskem Technology	145,3	57	118,5	135,9	42
Competitor Technology	145,2	64	118,7	134,0	48

Figure 8 – Heating curve (2nd melt) and thermal data obtained from DSC for UHMWPE samples produced using Braskem production technology (green) and a different technology (blue).

In summary, the data above represent consistent arguments for the understanding that the molecular weight alone shall not be directly correlated to the polymer mechanical properties. Those properties are influenced by molecular weight distribution, crystalline degree and kinetics, crystalline morphology, rheological properties, among others. These polymer characteristics are surely dependent on the polymerization technology used to produce the polymer.

When selecting a product for a specific application, the correlation between properties shall be more relevant than the correlation between a property and the molecular weight of that product.

4 Correlation between Abrasion Index and Charpy Impact Strength

An interesting and valuable way to select a UHMWPE grade for a certain application is based on the correlation of some of its properties. When the application requirements are known, this kind of selection will always search for the best material, independent on its properties which are not relevant to the application such as molecular weight.

On figure 9 this exercise is made by comparing Abrasion Index and Charpy Impact Strength of two UHMWPE materials produced from different technologies. The two technologies studied produce very similar materials in terms of property balance between Charpy and Abrasion in the molecular weight range studied.

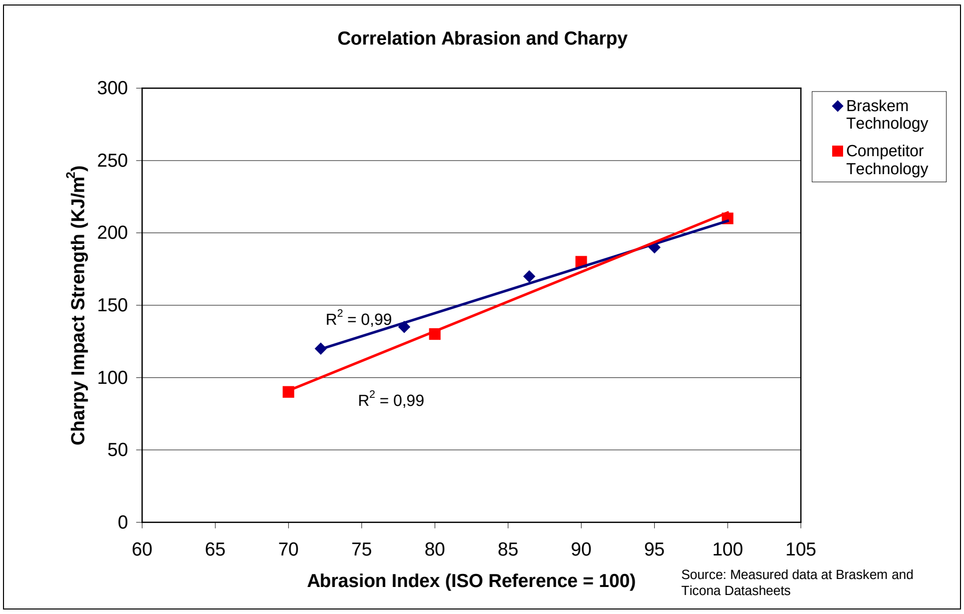


Figure 9 – Correlation between Abrasion Index and Charpy Impact Strength using Braskem production technology (blue) and a different technology (red).

A hypothetical extrapolation to the left side of Braskem technology curve above would show a trend that possibly materials of lower abrasion wear could have higher Charpy in comparison to some other technology. Nonetheless there are no data yet to ratify that hypothesis.

5 Conclusions

For UHMWPE materials, the correlation between molecular weight and properties is dependent on the production technology used to produce such a polymer. The paradigm that knowing the material molecular weight is enough to predict its properties should be definitely reviewed.

The wise way to select a UHMWPE material is by its balance of properties, instead of picking a determined molecular weight.

UHMWPE references used in Standards such as ISO and ASTM should not be selected based on its molecular weight, once different technologies may lead to similar molecular weights but different mechanical properties.

6 References

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