# The Beauty of Mathematical Functions - Impact Modifiers in u-PVC - Part I - Acrylic Impact Modier

Michael Schiller (HMS Concept e.U., Arnoldstein; Austria), Hitesh K. Singh, Padmaja Samal (Platinum Industries Ltd. Mumbai, India)

Abstract: Impact strength is the ability of a material or structure to withstand the application of a sudden, substantial load without failure. PVC is a polymer that already has a relatively high impact strength but there are applications which requires an increased impact strength by adding an impact modifier. The impact strength does not linearly depend on the dosage of impact modifier. It is a more complex dependency. We found a mathematical description for the dependency of Charpy impact strength on the modifier dosage. This paper will show several mathematical arguments which supports our hypothesis.

Keywords: Polyvinyl chloride, PVC, acrylic impact modifier, impact strength, Charpy test

## 1. Introduction

Impact strength is defined as “the ability of a material or structure to withstand the application of a sudden, substantial load without failure” [1].
Impact strength depends on various parameters:

- Type of plastic
- Structure of the plastic
- Type of impact stress
- Rate of impact stress
- Temperature
- Type of additives and their dosages
- …

PVC is a polymer that already has a relatively high impact strength. However, there are applications where it is necessary to increase the impact strength by adding an impact modifier.
In principle, impact modifiers can divide gates into two groups:

- Modifiers with a core-shell structure such as MBS (methacrylate butadiene styrene), AIM (acrylic impact modifiers, acrylate-based impact modifiers), ABS (acrylonitrile butadiene styrene), etc.
- Modifiers with semi-compatible network structures such as CPE (chlorinated PE), EVA (ethylene vinyl acetate), NBR (acrylonitrile butadiene rubber), etc.

„Core-shell acrylic impact modifiers … are produced by emulsion polymerization with radical initiators… Suitable monomers are combined and polymerized in several steps. Crosslinking agents are added to form the cross-linked rubbery phase of the core, which generally has a glass transition temperature of −45 to −60 °C… a benefit of this core technology is that it prevents the product from being destroyed under shear during processing. The disadvantage of the rubber core is its stickiness. In order to reduce the stickiness, different monomers are grafted onto the surface of the core. This grafted shell serves two functions: It prevents the AIM particles from sticking to each other and also supports a better dispersion and compatibility in the PVC matrix“ [2].
Several chemical and physical parameters of the AIM influence its final performance in PVC. „Takaki et al. found an optimum impact resistance when the modifier has a particle

size of about 200 nm… The 200 nm size seems to comprise the borderlines between various mechanisms that are happening during impact. Takaki et al. also found that at a lower particle size (< 200 nm) crazing dominates the energy absorption. At larger particle sizes shear yielding becomes the main absorption mechanism. Wu reported that the interparticle distance of the modifier particles is more important than the particle size itself… Wu observed that the same impact toughness could be achieved by using the identical type of modifier with different particle sizes as long as the interparticle distance stayed the same“ [2]. „…the thickness of the shell turns out to be very critical. If it is too thin, there is the risk that it will not completely encase the core and the resulting AIM particles will stick to each other. If the shell layer is too thick, a relatively lower percentage of rubber core will be in the final product, causing the impact strength to decrease. X. Chen et al. … published that the shell of an MBS impact modifier should best have a thickness of 4.2 to 9.8 nm, depending on the type of monomer used“ [2].

Schiller „investigated the influence of the shell thickness on the impact strength for an AIM of constant particle size. The impact strength was determined using Charpy and Gardner impact tests… Charpy impact strength improved with decreasing shell thickness to the lower level limits investigated… The Gardner impact values behaved totally different, though… The maximum impact energy was reached at a higher shell thickness compared to the Charpy… With a thinner as well as a thicker shell the Gardner impact energy decreased“ [2].

Accordingly, the performance of an AIM depends on its particle size, the chemical composition and the glass transition temperature Tg of its core plus the thickness and closeness of its shell.

„The addition level of impact modifiers influences several parameters… Increasing the dosage will result in:

- a small increase in Charpy and Izod impact strengths at low dosages,
- a rapid increase in Charpy and Izod impact strengths at slightly higher dosages,
- again a small improvement of impact strengths when the amount of modifier is further increased…“ [2]; Figure 1.

The addition of the impact modifier and its dosage affect both impact strength and tensile strength (Figure 1) but also melt viscosity, as well as the costs [3]. An increase in the percentage initially causes a slight increase in impact strength (measured according to Charpy and Izod) at low dosages. If the dosage is further increased, the impact strength increases very rapidly up to a certain point. If the dosage is further increased, the impact strength improves only slowly and then even decreases again. The tensile strength decreases continuously with increasing modifier dosage. Melt viscosity and costs increase with dosage [4].

The definition of impact strength/shock strength is simple in itself, but it can be determined using different methods. The Izod impact test described by E.G. Izod in [5]. It is a method which is standardized in several systems like ASTM [6], ISO [7] and others. With this method, a pendulum hammer hits the non-notched back of the sample with a certain potential energy (Fig. 4). When hitting the sample, part of the kinetic energy of the pendulum hammer is absorbed by deformation processes in the sample. The impact energy is calculated from this energy absorbed by the sample. The Charpy impact test works similarly (Fig. 4). G. Charpy suggested it as a standardized method in 1901 [8]. Similar to Izod test the conditions of testing a standardized in ASTM, ISO etc.

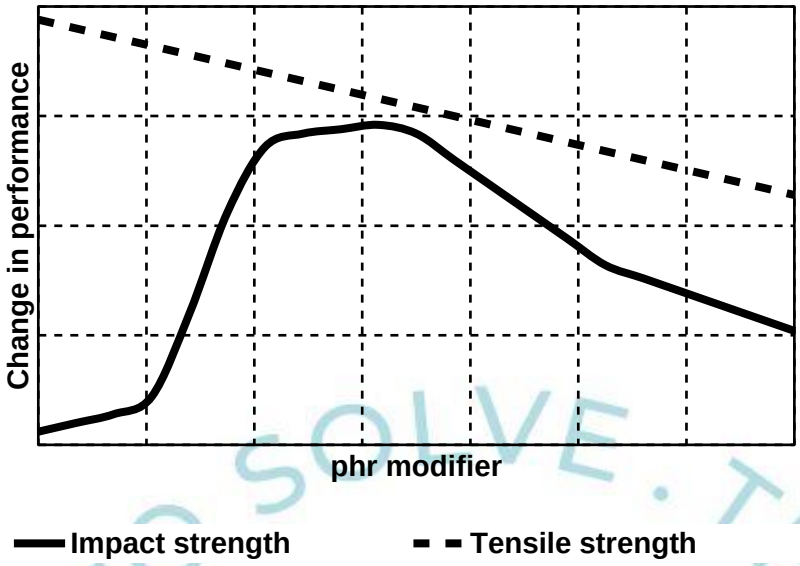



Figure 1 Influence of increasing modifier dosage in phr on the PVC properties [4]

The "Gardner Free Falling Dart Impact Test" works according to a different principle and is an established method for determining the impact strength of plastic materials. The plastic sample is placed on a base plate with an opening in the middle. Then an impact body is placed in the middle of the test body. The impact body is located in a drop tube in which a drop weight can be raised to a predetermined height. If the drop weight is released, it hits the impact body in free fall, which penetrates the test body with its torpedo-like tip. The drop height, drop weight and test result (pass or fail) are recorded. In addition, the "mean failure energy" (MFE) can be determined using the "Bruceton Staircase" method [9].
There is currently agreement that it is impossible to draw conclusions about the results of one test method from the other. A possible explanation is that both the Izod and Charpy methods measure the impact strength of a profile after mechanical damage, while the Gardner method measures the impact strength before mechanical damage.
In 2017 Schiller et al. tried in "Theoretical and practical aspects of the influence of acrylic impact modifiers and calcium carbonate on the impact strength" [10] to find a mathematical relationship between the impact strength determined according to Charpy and that determined according to Gardner (Figure 2). They assumed that Figure 2 shows the 1st mathematical derivative of Figure 2. However, the authors failed to provide the mathematical proof.

## 2. Attempt at a mathematical description of the impact strength tests

We used the data reported in [10] as a kind of Design of Experiments (DoE) and treated these with the software ECHIP [11]. There wasn't any correlation with any mathematical model inside this software. So, we concluded that the dependency of the impact strength on the dosage of modifier (Figure 2 bottom) cannot be described by a polynomial function. We searched in literature but there wasn't any paper about the mathematical correlation of impact strength and dosage of impact modifier. That's why we thought about it. There are several option which could be applied. The course of the dependence of the impact strength according to Charpy in Figure 2 is strongly reminiscent of the course of the cube root function; Figure 3. It is possible to shift the cube root function to the positive quadrant of the graph; Figure 3.

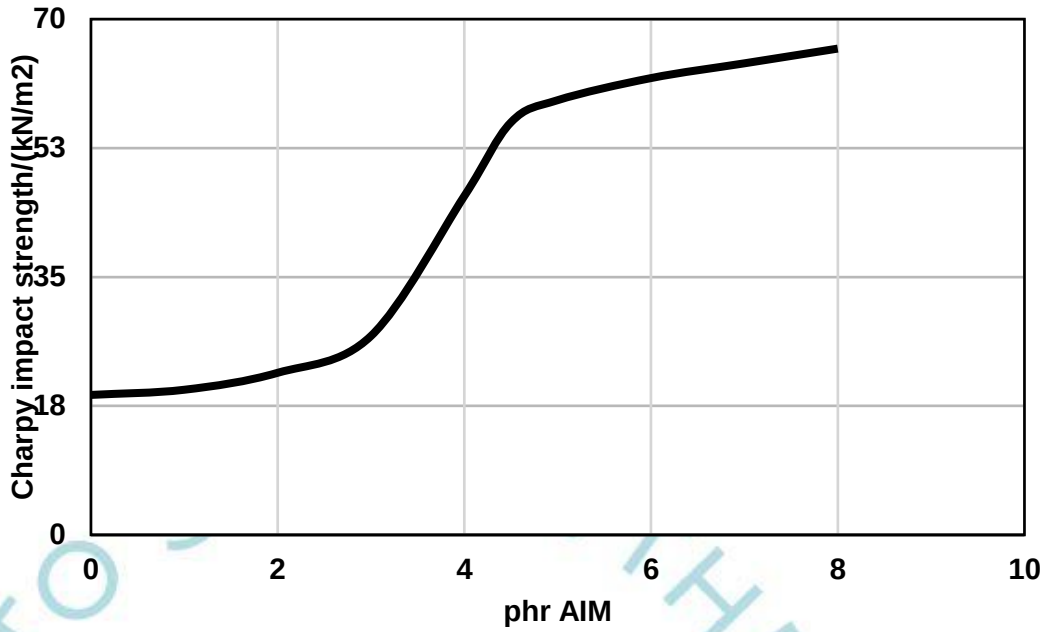
In principle, the x-axis now corresponds to the dosage of the impact modifiers and the y-

$$y = \left[\sqrt[3]{(k_3 \cdot x)-(k_4)^3} + k_4\right] \cdot k_2 + k_1$$

axis to the impact strength according to Charpy. It enables us to adapt the Equation 1: wherein is:
y : Charpy impact strength in $kN/m^2$
x : dosage of impact modifier in phr
$k_1$ : a material constant probably it is the Charpy impact strength without modifier
$k_2$ : a material constant related to modifier (and maybe to dryblend composition)
$k_3$ : a material constant related to modifier (and maybe to dryblend composition)
$k_4$ : a material constant related to modifier (and maybe to dryblend composition)
to the experimental values by compressing, stretching and shifting it on the x and y axes, Figure 4.

The material constants $k_1$ to $k_4$ are functions of the impact strength which depends on many factors [12]:

- Formulation of dryblend:
  - K-value of the PVC (the higher the K-value is the higher the impact strength will be)
  - Type, dosage and quality of the impact modifier
  - Type and dosage of the filler
- Processing the product:
  - Optimal melting temperature
  - Degree of gelation
  - The "free volume" between PVC chains - tension build-up
- Impact test itself:
  - The load condition at the point of impact (flat or edged, notch radius)
  - Test temperature
  - Strain rate
  - Relaxation time and conditions




- Product design, especially wall thickness

Figure 2 Influence of AIM 11 dosage on the Charpy test in kJ/m$^2$ [3]

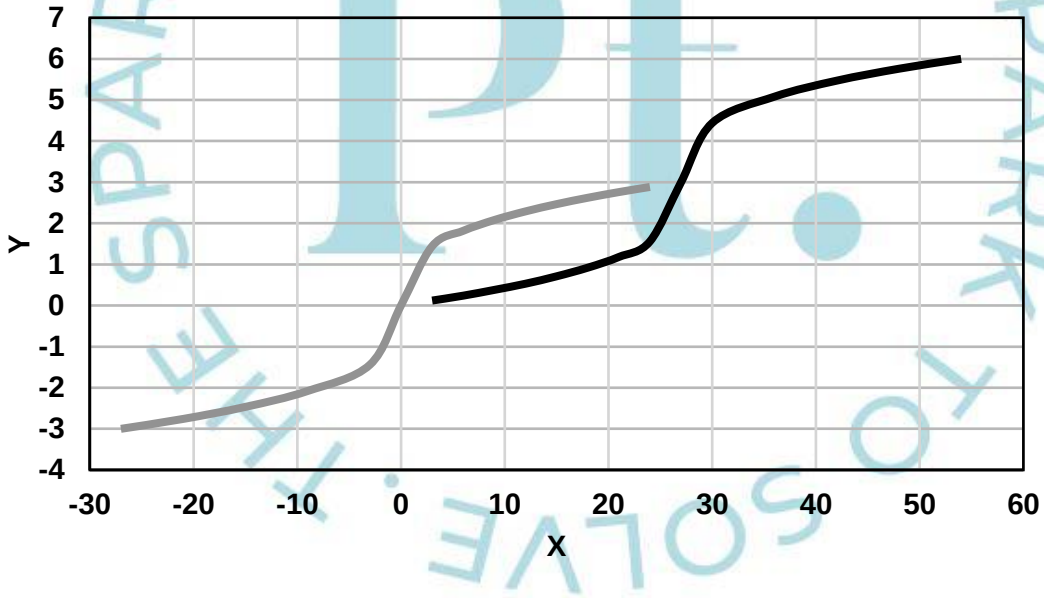


Figure 3 Cube root function $y=x^{1/3}$ for $-27<x<27$ and $y=((x-27)^{1/3}+3)$ for $0<x<54$

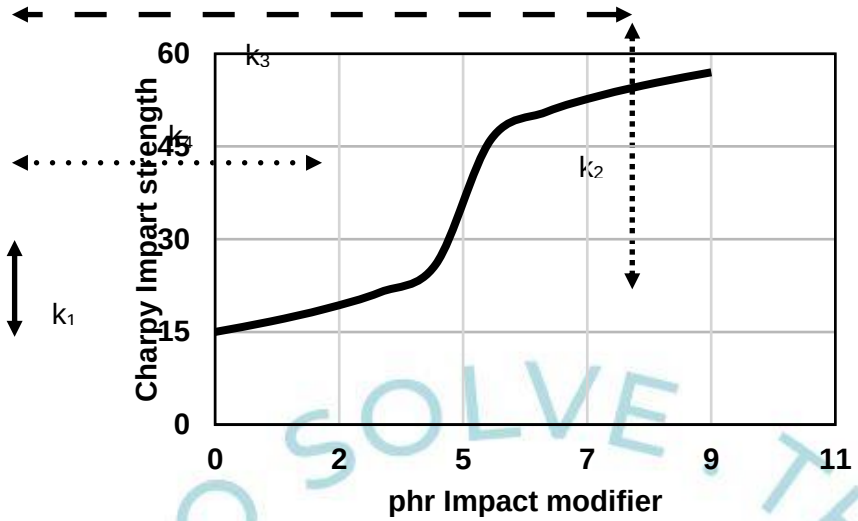



Figure 4 Cube root function according to Eq. 1

Another option is to apply a a sigmoid function. A sigmoid function is a mathematical function having a characteristic "S"-shaped curve or sigmoid curve similar to Figure 2. In general, a sigmoid function is a bounded and differentiable real function with an all-positive or all-negative first derivative and exactly one inflection point. The integral of any continuous, positive function with exactly one local maximum and no local minimum, e.g. B. the Gaussian bell curve, is also a sigmoid function. Therefore, many cumulative distribution functions are sigmoidal. In addition to the logistic function, the set of sigmoid functions contains the arctangent, the hyperbolic tangent and the error function, all of which are transcendental, as well as simple algebraic functions such as Equation 2:

$$y = x/(1+x^2)^{0.5}$$

We have chosen to use the logistic function [13]; Equation 3:

$$y = \frac{L}{1+e^{-c(x-x_0)}}$$

wherein is:

L : the supremum of the values of the function
$x_0$: value of the sigmoid's midpoint/inflection point
c : the logistic growth rate or steepness of the curve
e : Euler's constant (≈ 2.718)

We have slightly to change Equation 3 for the consideration of the relationship of impact strength to Equation 4:

$$y = \frac{IS_{max}-IS_{min}}{1+e^{-c(x-x_0)}} + IS_{min}$$

wherein is:
y : Charpy impact strength in kN/m$^2$
x : dosage of impact modifier in phr
$IS_{max}$ : the maximum of impact strength
$IS_{min}$ : the impact strength without modifier
$x_0$: value of the sigmoid's midpoint/inflection point
c : the logistic growth rate or steepness of the curve
e : Euler's constant (≈ 2.718)

## 3. Results and discussion

### 3.1. One acrylic impact modifier at different dosages and with different amounts of calcium carbonate

We used the data published by Schiller etal. [10] in Table 1 to check the plausibility of Eq. 1 and to determine the values of the material constants $k_1$ to $k_4$. We varied the material constants and calculated the difference to calculated and experimental values. Due to the fact that the difference can be a negative or a positive number we multiplied it with itself. We sum the 6 values up, divide it by 6 (because of six experimental values) and calculated the square root F. This was repeated until we found a minimum. The square root F in Table 2a gives an indication of the average difference between experimental and calculated values. Figure 5a shows the correlation of simulated graphs and the experimental impact strength depending on the dosage of AIM 11 in phr. The material constants $k_1$ to $k_4$ are summarized in Table 2a and plotted in Figure 6a.
The correlations of the calculated Charpy graphs with the experimental values in Figure 5a are already good to very good in most cases. The deviation of observations from the calculations F support the observations. We assume that with such a mathematical description of the impact strength according to Charpy depending on the modifier dosage in the range of up to 10 phr, we have taken a first step towards further understanding of modifiers and their properties. However, we need to find more data and treat these mathematically to get confirmation of this hypothesis.
In Figure 6a we tried to gain information about the mechanical background of the constants $k_1$ to $k_3$. A very few if any scientifically backed conclusions are possible. Only with regard to the constant $k_2$ does it seem that it describes the influence of the chalk content (possibly also the content of other finely divided, non-melting additives such as titanium dioxide). As a trend, we can state that the constant $k_2$ seems to decrease with increasing chalk content. Here, too, further investigations and calculations are necessary to scientifically back up this hypothesis.
We repeated the procedure based on Equation 4; Table 2b, Figure 5b and Figure 6b.

Table 1 Formulation, rheology parameters, L* a* b* values and impact strength according to Charpy and Gardner (100 phr S-PVC [k=67], 5 phr Titanium dioxide [Rutile], 4 phr calcium-zinc stabilizer, modifier: AIM 11)[1]

[1] There is not any standard deviation given for the Charpy impact strength by the authors. We assume according to our experience that the standard deviation is in a range of 0.8 to 3.7; see Table 4

| Trial | phr AIM 11 | phr CaCarbonate | phr lubricant | tgel/sec | Torque/Nm | Pressure/bar | Gloss/% | L* | a* | b* | Charpy/(kN/sqm) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | |
| 1 | 0.0 | 5 | 0 | 66 | 127.0 | 99.0 | 42 | 90.3 | -1.1 | 2.3 | 13.4 |
| 2 | 3.0 | 5 | 0 | 50 | 134.5 | 97.5 | 51 | 91.0 | -1.1 | 2.6 | 24.5 |
| 3 | 4.0 | 5 | 0 | 42 | 137.5 | 97.5 | 48 | 91.4 | -1.1 | 2.7 | 35.0 |
| 4 | 4.5 | 5 | 0 | 38 | 140.0 | 96.0 | 48 | 91.4 | -1.2 | 2.8 | 46.8 |
| 5 | 5.0 | 5 | 0 | 42 | 143.0 | 97.5 | 48 | 91.0 | -1.2 | 2.7 | 47.6 |
| 6 | 8.0 | 5 | 0 | 32 | 150.1 | 99.0 | 47 | 91.9 | -1.2 | 3.1 | 64.7 |
| 7 | 0.0 | 10 | 0 | 64 | 126.0 | 93.5 | 34 | 90.4 | -1.2 | 2.4 | 17.1 |
| 8 | 3.0 | 10 | 0 | 50 | 134.0 | 96.0 | 34 | 90.8 | -1.2 | 2.7 | 35.1 |
| 9 | 4.0 | 10 | 0 | 44 | 144.0 | 95.5 | 32 | 91.1 | -1.3 | 3.1 | 52.0 |
| 10 | 4.5 | 10 | 0 | 44 | 142.5 | 95.5 | 34 | 90.6 | -1.2 | 2.7 | 52.4 |
| 11 | 5.0 | 10 | 0 | 42 | 141.5 | 96.5 | 36 | 91.1 | -1.2 | 2.8 | 56.1 |
| 12 | 8.0 | 10 | 0 | 36 | 152.0 | 97.5 | 23 | 91.3 | -1.3 | 3.1 | 64.1 |
| 13 | 0.0 | 15 | 0.6 | 104 | 119.5 | 92.5 | 28 | 90.3 | -1.2 | 2.5 | 17.5 |
| 14 | 3.0 | 15 | 0.6 | 58 | 126.0 | 91.5 | 27 | 91.0 | -1.2 | 2.9 | 39.7 |
| 15 | 4.0 | 15 | 0.6 | 58 | 129.0 | 92.5 | 28 | 91.0 | -1.3 | 3.1 | 53.2 |
| 16 | 4.5 | 15 | 0.6 | 54 | 135.0 | 93.0 | 28 | 91.0 | -1.3 | 3.1 | 57.5 |
| 17 | 5.0 | 15 | 0.6 | 54 | 138.0 | 94.0 | 28 | 90.9 | -1.3 | 3.2 | 55.5 |
| 18 | 8.0 | 15 | 0.6 | 42 | 153.5 | 96.0 | 27 | 91.4 | -1.4 | 3.5 | 58.8 |
| 19 | 0.0 | 20 | 1.2 | 54 | 63.0 | 93.5 | 24 | 90.8 | -1.2 | 2.6 | 15.9 |
| 20 | 3.0 | 20 | 1.2 | 42 | 61.5 | 92.0 | 27 | 90.8 | -1.2 | 2.7 | 21.2 |
| 21 | 4.0 | 20 | 1.2 | 36 | 61.0 | 91.5 | 24 | 91.0 | -1.2 | 2.9 | 22.6 |
| 22 | 4.5 | 20 | 1.2 | 38 | 61.5 | 91.5 | 25 | 91.3 | -1.3 | 3.2 | 21.0 |
| 23 | 5.0 | 20 | 1.2 | 30 | 62.0 | 91.5 | 20 | 91.3 | -1.3 | 3.2 | 23.7 |
| 24 | 8.0 | 20 | 1.2 | 24 | 64.5 | 92.5 | 24 | 91.5 | -1.3 | 3.1 | 31.3 |
| 25 | 0.0 | 25 | 1.8 | 58 | 57.5 | 90.0 | 21 | 91.1 | -1.3 | 3.2 | 13.7 |
| 26 | 3.0 | 25 | 1.8 | 48 | 58.5 | 90.0 | 22 | 91.1 | -1.3 | 3.4 | 15.5 |
| 27 | 4.0 | 25 | 1.8 | 42 | 57.0 | 89.0 | 24 | 91.0 | -1.3 | 3.3 | 16.1 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 28 | 4.5 | 25 | 1.8 | 38 | 57.5 | 89.5 | 23 | 91.4 | -1.4 | 3.6 | 17.5 |
| 29 | 5.0 | 25 | 1.8 | 40 | 58.5 | 89.5 | 22 | 91.6 | -1.4 | 3.9 | 18.1 |
| 30 | 8.0 | 25 | 1.8 | 32 | 60.5 | 90.5 | 22 | 91.9 | -1.4 | 4.3 | 24.2 |

Table 2a Material constants $k_1$ to $k_4$, deviation of observations from the calculations F and inflection point of the curve based on the simulations in Figure 5a (according to Equation 1)

| Trials | phr CaCarbonate | phr lubricant | $k_1$ | $k_2$ | $k_3$ | $k_4$ | Inflection point | F |
|---|---|---|---|---|---|---|---|---|
| 1-6 | 5 | 0,0 | 13,4 | 7,9 | 6,7 | 3,0 | 4,0 | 2,89 |
| 7-12 | 10 | 0,0 | 17,1 | 7,0 | 8,9 | 3,0 | 3,0 | 1,25 |
| 13-18 | 15 | 0,6 | 17,5 | 6,7 | 9,2 | 3,0 | 3,0 | 2,04 |
| 19-24 | 20 | 1,2 | 15,9 | 2,9 | 5,4 | 3,0 | 5,0 | 1,83 |
| 25-30 | 25 | 1,8 | 13,7 | 2,0 | 5,3 | 3,0 | 5,1 | 0,37 |
| Total | | | | | | | | 8,38 |

Table 2b Material constants $IS_{max}$-$IS_{min}$, $IS_{min}$, c, $x_0$ (inflection point) and deviation of observations from the calculations F and inflection point of the curve based on the simulations in Figure 5b (according to Equation 4)

| Trials | phr CaCarbonate | phr lubricant | $IS_{min}$ | $IS_{max}$-$IS_{min}$ | c | | $x_0$ | F |
|---|---|---|---|---|---|---|---|---|
| 1-6 | 5 | 0,0 | 13,4 | 51,3 | 1,2 | | 4,0 | 2,73 |
| 7-12 | 10 | 0,0 | 17,1 | 47,0 | 1,0 | | 3,2 | 2,00 |
| 13-18 | 15 | 0,6 | 17,5 | 41,3 | 1,8 | | 3,0 | 1,18 |
| 19-24 | 20 | 1,2 | 15,9 | 15,4 | 0,7 | | 4,8 | 1,33 |
| 25-30 | 25 | 1,8 | 13,7 | 10,5 | 0,9 | | 5,2 | 0,47 |
| Total | | | | | | | | 7,72 |

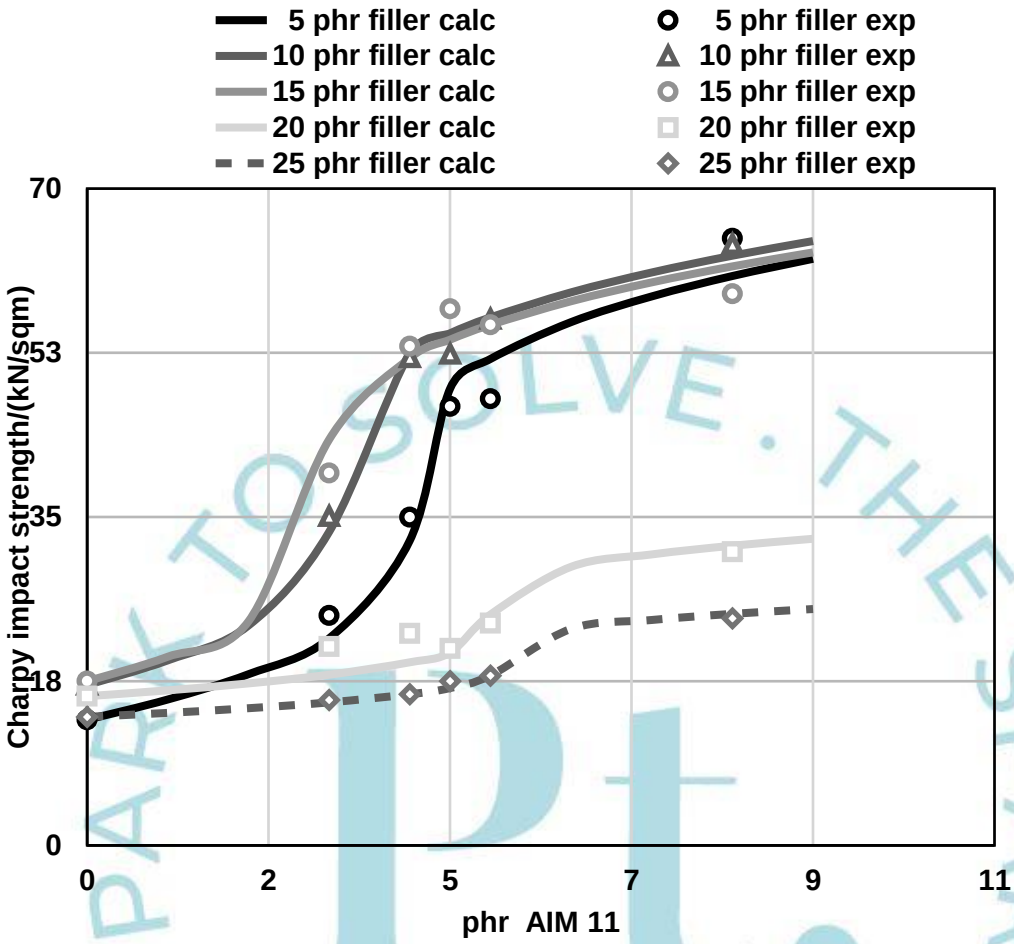



Figure 5a Dependency of Charpy impact strength on the dosage of AIM 11; experimental values (symbols) from Table 1 and calculated values (lines) based on Eq. 1; $k_1$ to $k_4$ (Table 2a)





+91-9321052537 www.platinumindustriesltd.com

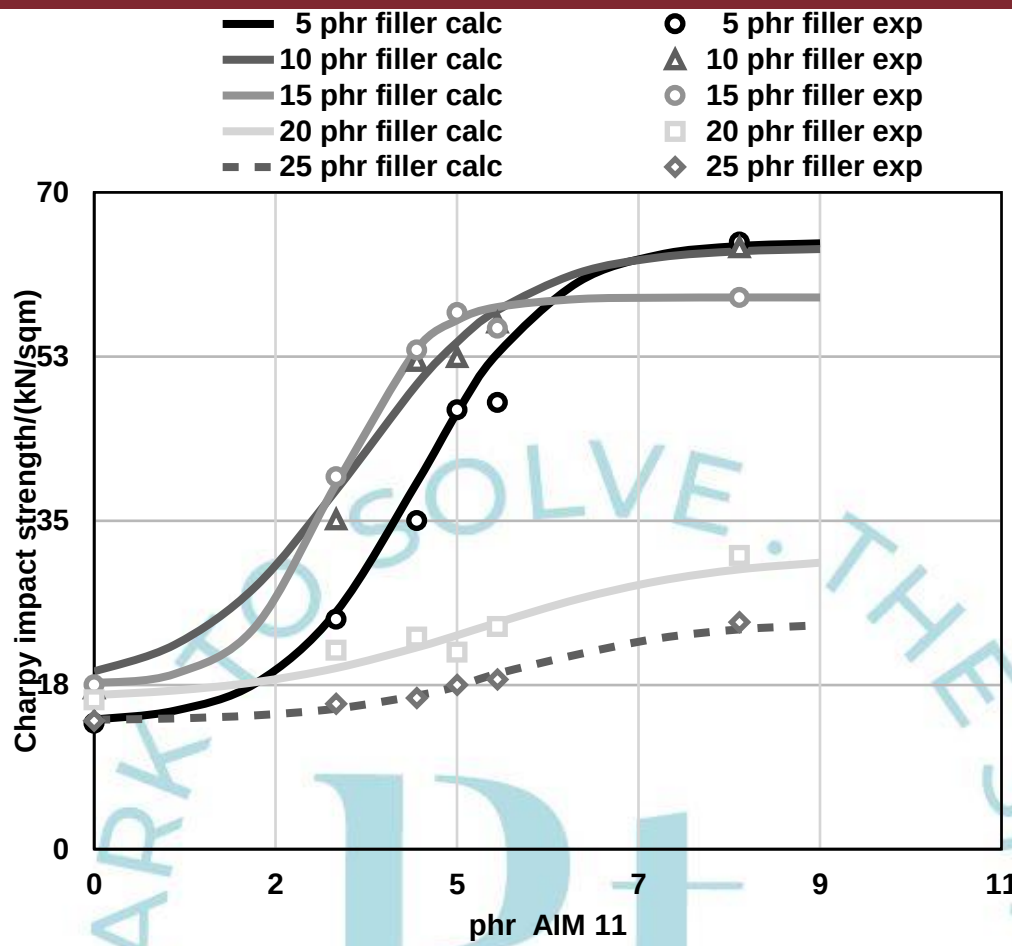



Figure 5b Dependency of Charpy impact strength on the dosage of AIM 11; experimental values (symbols) from Table 1 and calculated values (lines) based on Eq. 4; $IS_{max}$, $IS_{min}$, c and $x_0$ (Table 2b)

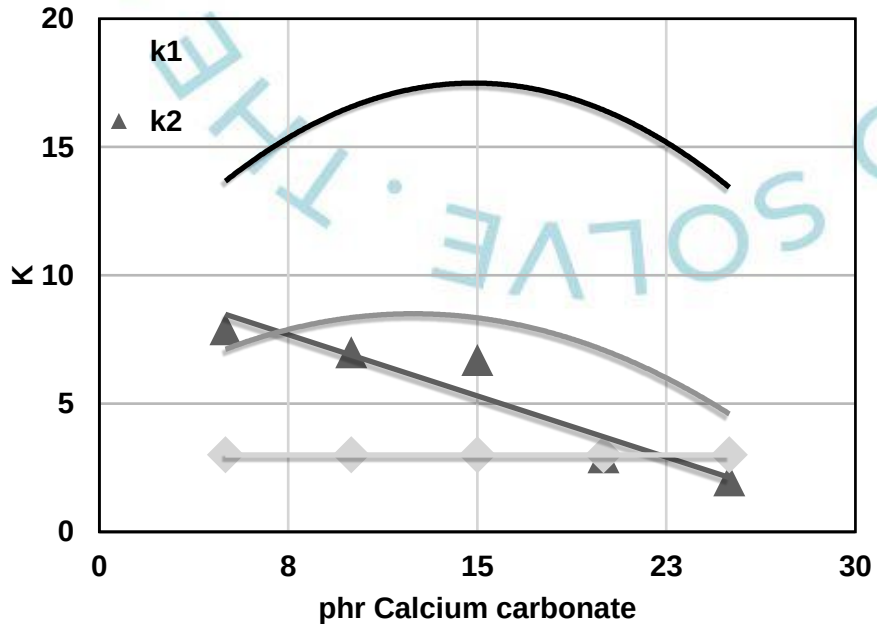



Figure 6a Dependency of $k_1$, $k_2$, $k_3$ and $k_4$ (Table 2a) on the content of calcium carbonate

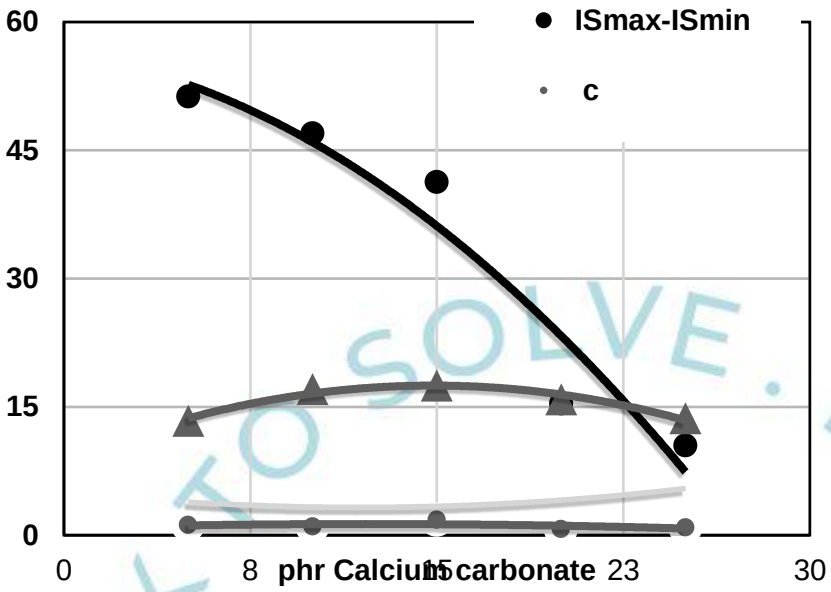



Figure 6b Material constants $IS_{max}$, $IS_{min}$, c and $x_0$ (Table 2b) on the content of calcium carbonate

**3.2. Different acrylic impact modifier at constant dosage of filler**

3.2.1. Data of AIM 10 to AIM 12

Three different AIM (10-12) were prepared by applying the method of Goertz and Oschmann [14]. The composition and process details are not disclosed because of commercial reasons. The main properties of AIM 10-12 are summarized in Table 3.

Table 3 AIM 10 to AIM 12 and their physical properties and differences to each other

| AIM | Particle size | Characterisation of shell | | Glass transition temperature |
|---|---|---|---|---|
| | range in nm | thickness in nm | Type | °C |
| 10 | 200-250 | ~6-10 | PMMA-copolymer | -45.1 |
| 11 | 200-250 | ~6-10 | PMMA | -46.7 |
| 12 | 200-250 | ~6-10 | PMMA | -55.4 |

3.2.2. Dryblend composition and testing of AIM 10 to AIM 12 in PVC

The AIMs were mixed at different dosages in a dryblend (100 phr S-PVC [k = 65-67], 8 phr surface treaded calcium carbonate D50 = 1 micron, 5 phr titanium dioxide, rutile, window profile grade, 4 phr calcium-zinc stabiliser, window profile grade) up to 120°C. The dryblends were discharged, cooled to <45°C and stored overnight. The dryblends were

extruded with a Brabender twin screw extruder. The specimen for Charpy impact test were prepared according to ISO 179 [15]. The results are summarized in Table 4.

Table 4 Formulation and impact strength according to Charpy

| Trial | phr AIM | AIM | Charpy/(kN/m$^2$) | |
|---|---|---|---|---|
| | | | average | Standard deviation |
| 1 | 0 | None | 17.8 | 0.8 |
| 2 | 3 | 10 | 49.1 | 1.7 |
| 3 | 4 | 10 | 55.9 | 2.0 |
| 4 | 5 | 10 | 60.4 | 2.0 |
| 5 | 6 | 10 | 60.9 | 1.8 |
| 6 | 8 | 10 | 63.6 | 1.1 |
| 7 | 3 | 11 | 51.8 | 1.4 |
| 8 | 4 | 11 | 58.6 | 2.6 |
| 9 | 5 | 11 | 63.1 | 2.2 |
| 10 | 6 | 11 | 65.1 | 1.4 |
| 11 | 8 | 11 | 68.5 | 1.3 |
| 12 | 3 | 12 | 60.6 | 3.7 |
| 13 | 4 | 12 | 59.6 | 0.9 |
| 14 | 5 | 12 | 67.8 | 1.4 |
| 15 | 6 | 12 | 70.2 | 2.9 |
| 16 | 8 | 12 | 72.5 | 1.1 |

3.2.3. Test results of AIM 10 to AIM 12 in PVC

We used the data in Table 4 to check the plausibility of Equation 1 resp. Equation 4. Figure 7 shows the correlation of simulated graphs regarding Equation 1, regarding Equation 4 and the experimental impact strength depending on the dosage of the different AIM in phr. The material constants $k_1$ to $k_4$ resp. $IS_{max}$, $IS_{min}$, c, $x_0$ (inflection point) are summarized in Table 5. The deviation of observations from the calculations F are small and support the observations. The correlations between the calculated Charpy graphs and the experimental observations in Figures 7 are very good to excellent. Combined with the results from our previously reported series in Table 2a we are absolutely convinced that Equation 1 is a useful tool to describe the impact strength of PVC product containing a corse-shell modifier. We can conclude:

- The results regarding the material constants of AIM in Table 5 don't contradict the results of AIM 10 in Table 2a at about 10 phr calcium carbonate.
- The constant $k_1$ characterizes the impact strength of the material without an impact modifier. This is confirmed in the previous set of trials in section 3.1.
- The constant $k_2$ very probably describes the influence of the filler on the Charpy impact strength. This is confirmed in the previous set of trials in section 3.1.
- Regarding constant $k_3$ we could not postulate any influence in section 3.1. According the results in Table 5 there are some indications that constant $k_3$ might depend on the performance/property of the AIM probably on the glass transition temperature Tg at the same filler content. The constant $k_3$ might be also influenced by the filler content if it changes.
- Furthermore, we calculated the inflection points of the graphs in Figure 7a; Table 5. There also might be also a dependency of it on the glass transition temperature Tg of the impact modifier at constant filler content.
- It seems that a decrease in Tg shifts the inflection point of the graphs to lower dosages in phr and increases the constant $k_3$ respectively the maximal Charpy impact strength in the case of modifiers with the same particle size, the same thickness of shell and the same filler dosage.; Table 5 Simplified, the impact modifier becomes more effective and might be used at lower dosages.
- The logistic Equation 4 can be also used to correlate the experimental values. The material constant $k_1$ from Equation 1 and the material constant $IS_{min}$ from Equation 4 are the same and representing the impact strength without (acrylic) impact modifier. However, even if the simulation with Equation 4 might optically look better compared to that with Equation 1 we will not can any new information because the material constants $IS_{max}$-$IS_{min}$, $IS_{min}$, c and $x_0$ are either known from the experiments or can be manually determined.

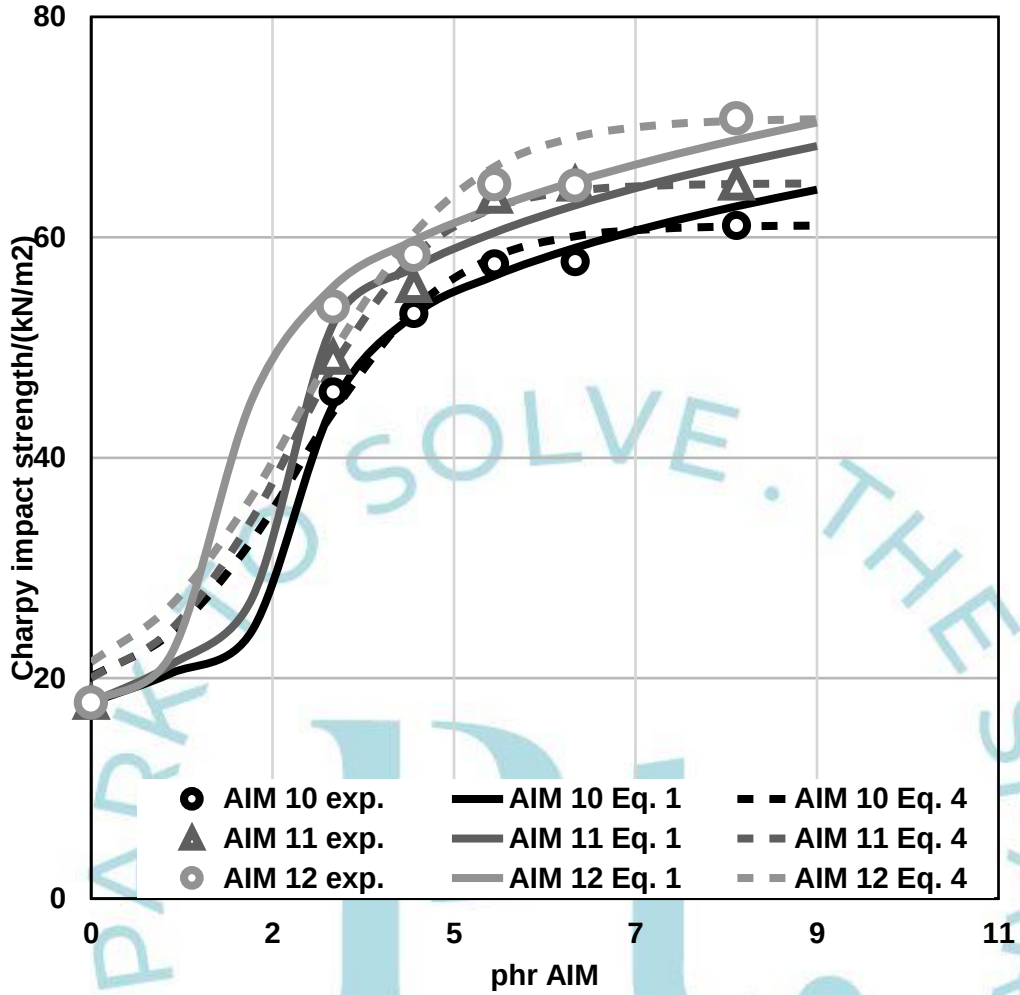



Figure 7 Dependency of Charpy impact strength on the dosage of AIM 10 to AIM 12; experimental values (symbols) from Table 4, calculated values based on Equation 1 (lines) and calculated values based on Equation 4 (dashed lines)

Table 5 Material constants $k_1$ to $k_4$ resp. $IS_{max}$-$IS_{min}$, $IS_{min}$, c, $x_0$ (inflection point) and squared deviation of observations from the calculations F based on the simulations in Figure 7

| AIM | phr $CaCO_3$ | Tg/°C | $k_1$ | $k_2$ | $k_3$ | $k_4$ | Inflection point/phr | F |
|---|---|---|---|---|---|---|---|---|
| 10 | 8 | -45,1 | 17,8 | 6,8 | 9,3 | 3,0 | 2,90 | 1,10 |
| 11 | 8 | -46,7 | 17,8 | 7,0 | 11,3 | 3,0 | 2,39 | 2,21 |
| 12 | 8 | -55,4 | 17,8 | 6,9 | 14,0 | 3,0 | 1,93 | 1,50 |

| AIM | phr $CaCO_3$ | Tg/°C | $IS_{min}$ | $IS_{max}$-$IS_{min}$ | c | | $x_0$ | F |
|---|---|---|---|---|---|---|---|---|

| AIM | phr $CaCO_3$ | Tg/°C | $k_1$ | $k_2$ | $k_3$ | $k_4$ | Inflection point/phr | F |
|---|---|---|---|---|---|---|---|---|
| 10 | 8 | -45,1 | 17,8 | 43,3 | 1,1 | | 2,6 | 1,57 |
| 11 | 8 | -46,7 | 17,8 | 47,1 | 1,2 | | 2,5 | 1,53 |
| 12 | 8 | -55,4 | 17,8 | 53,0 | 1,0 | | 2,6 | 3,06 |

If these findings match with reality and if we go and follow this idea further, we can either compare different impact modifiers at the same dosage to the glass transition temperature Tg or vice versa from the Tg values of the modifiers to the impact strength at the same dosage (assuming a comparable particle size and thickness of the shell. This means, if we want to improve an existing impact modifier in terms of its performance, we have various options:

- We can optimize the thickness of the shell. „Chen et al… published that the shell of an MBS impact modifier should best have a thickness of 4.2 to 9.8 nm, depending on the type of monomer used“ [2]. The thicknesses of the modifiers in our study are in a similar range; Table 3. Schiller published „…the influence of the shell thickness on the impact strength for an AIM of constant particle size. The impact strength was determined using Charpy …impact tests… Charpy impact strength improved with decreasing shell thickness to the lower level limits investigated; see Figure 8 [2].
- We can optimize respectively lower the Tg of the modifier by using the Fox equation. The Fox equation is an equation describing the glass transition temperature of two-component mixtures as a function of their respective mass fractions. The Fox equation was published by Thomas G. Fox in 1956 [16]; Equation 5:

$$Tg = Tg_1 \cdot w_1 + Tg_2 \cdot w_2$$

wherein
Tg is the glass transition temperature in Kelvin (K) of the mixture
$Tg_1$ and $Tg_2$ are the glass transition temperatures (K) of the pure polymers inside the mixture
$w_1$ and $w_2$ are the mass fractions of the components 1 and 2.

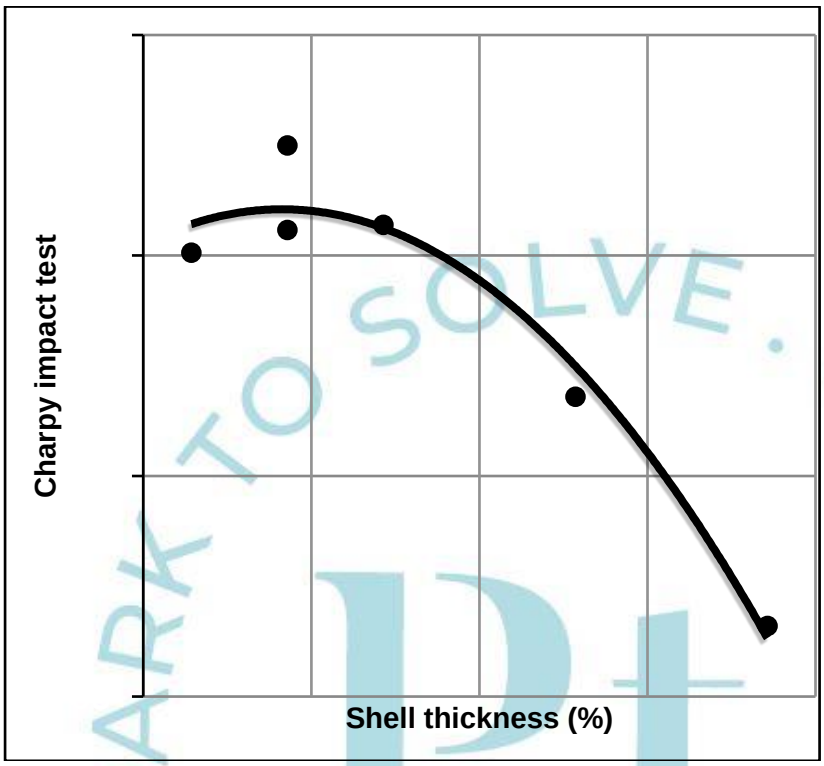



Figure 8 Impact strength (Charpy in kN/m$^2$) as a function of relative shell thickness of an AIM at constant particle size [2]

- Furthermore, we can assume that a particle size of 200-250 nm might be optimal. Why? - The core gives the impact strength due to its rubber nature. The shell must have a thickness of >4-10 nm and even more important it must be closed. Otherwise, modifier particle can stick to each other and the impact strength will be reduced. If we consider AIM 10 to AIM 12 with an assumed uniform particle size of 250 nm and a shell thickness of 6-7 nm the core will have 84 vol-% of the particle and the shell only 16 vol-%. If we keep the thickness of the shell and reducing the particle size the volume of core will drop; Figure 9. However, less percent core will reduce the impact

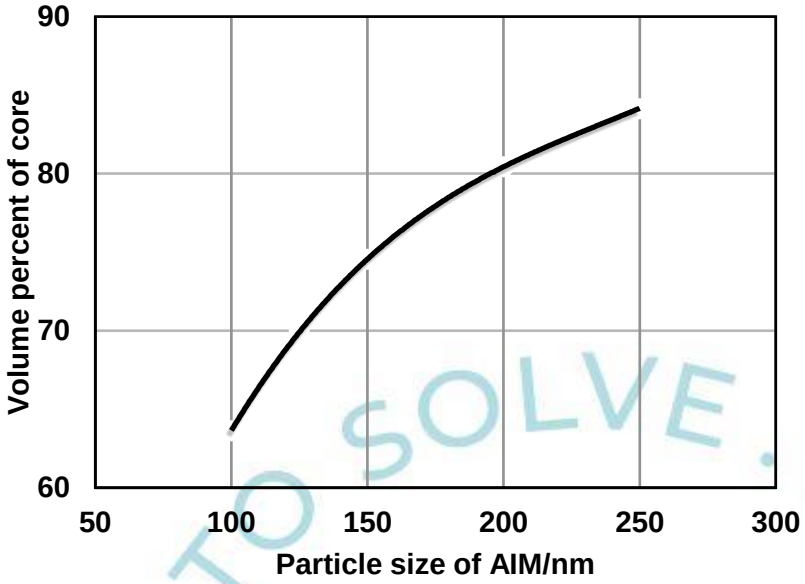



Figure 9 Dependency of volume percentage of rubber core in an AIM depending of the primary particle size

## 4. Summary and conclusion

We have succeeded in mathematically describing the influence of the dosage of an acrylate-based core-shell modifier on the Charpy impact strength in a range from 0 to 8 phr modifier. The basis for this is provided by a cube root function. The correlation with a logistic function was also successful but it did not result in any new conclusion. The cubic root function contains four material constants ($k_1$ to $k_4$). The constant $k_1$ characterizes the impact strength of the material without an impact modifier. The constant $k_2$ probably describes the influence of the filler on the Charpy impact strength.

According the recent results in Table 5 there are some indications that constant $k_3$ might depend on the performance/property of the AIM probably on the glass transition temperature Tg at the same filler content. However, according to section 3.1 the material constant $k_3$ might be also influenced by the filler content if it changes. It seems that a decrease in Tg shifts the inflection point of the graphs to lower dosages in phr and increases the constant $k_3$ respectively the maximal Charpy impact strength in the case of modifiers with the same particle size, the same thickness of shell and the same filler dosage. Simplified, the impact modifier becomes more effective and might be used at lower dosages.

If these findings match with reality it will be relatively easy to design a new modifier by:

- Optimization of the thickness of the shell to about 10 nm.
- Optimization respectively decrease of Tg of the modifier by using the Fox equation; Eq. 2.
- Optimization of the particle size of 200-250 nm.

The constant $k_4$ was constant with the value of 3 for all tests. It is highly probable that this mathematical model can also be applied to Izod for the impact strength.

## 5. Literature

[1] A. F. Yee, “Impact resistance” in “Encyclopedia of Polymer Science and Engineering”, J. Wiley & Sons, 36 (1987)
[2] M. Schiller, „PVC Additives“, 2nd Edition, C. Hanser Publisher Munich/Germany (2022) pp. 268-274 (and the cited literature inside)
[3] M. Schiller, M. Basalp, A. Sahin, B. Aldanmaz, E. Alyamaç, The 12th International PVC Conference, Brighton/U.K. (2014)
[4] C. E. Wilkes, J. W. Summers and C. A. Daniels (Eds.), “PVC Handbook”, C. Hanser Publisher Munich/Germany, (2005) p. 230
[5] E. G. Izod, Engineering, 431 (1903)
[6] ASTM D256
[7] ISO 180
[8] G. Charpy, Mémoire et compte-rendus de la Société des ingénieurs civils de France (1901)
[9] http://www.ptli.com/testlopedia/tests/Gardner-D5420.asp, (accessed on 18.11.2022)
[10] M. Schiller, A. Sahin, B. Aldanmaz, A. Elitez, Rubber Fibers Plastics RFP (03/2017) p.188
[11] http://echip.com/; accessed on 16.11.2022
[12] B. Cora, “The effect of compliant rubber particles on the rheology and mechanical properties of PVC profiles” at PVC Formulation 2014, Düsseldorf/Germany (2014).
[13] P.-F. Verhulst; "Notice sur la loi que la population poursuit dans son accroissement", Correspondance Mathématique et Physique. 10 (1838) pp. 113–121
[14] H.-H. Goertz, W. Oschmann (inventors), EP 0 486 906 A1, priority 23.11.1990
[15] ISO 179
[16] T. G. Fox: „Influence of Diluent and of Copolymer Composition on the Glass Temperature of a Polymer System“. Bull. Am. Phys. Soc., Vol. 1 (1956) p. 123