The Beauty of Mathematical Functions - Impact Modifiers in u-PVC - Part II - Different Acrylic Modifier at Constant Dosages of Filler

Michael Schiller (HMS Concept e.U., Arnoldstein; Austria), Hitesh K. Singh (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. Polyvinyl chloride (VC) is a polymer that already has a relatively high impact strength. However, 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. On one hand we found a mathematical description for the dependency of Charpy impact strength on the modifier dosage. On the other hand we assume a mathematical relationship between Charpy impact strength and Gardner impact strength. This paper supports previously found mathematical descriptions but it also shows how the macromolecular structure of the core has an influence on the dependency of Charpy impact strength on the dosage and its mathematical function.

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

1. Introduction

„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 „[1].

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; Figure 1), 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. [2].

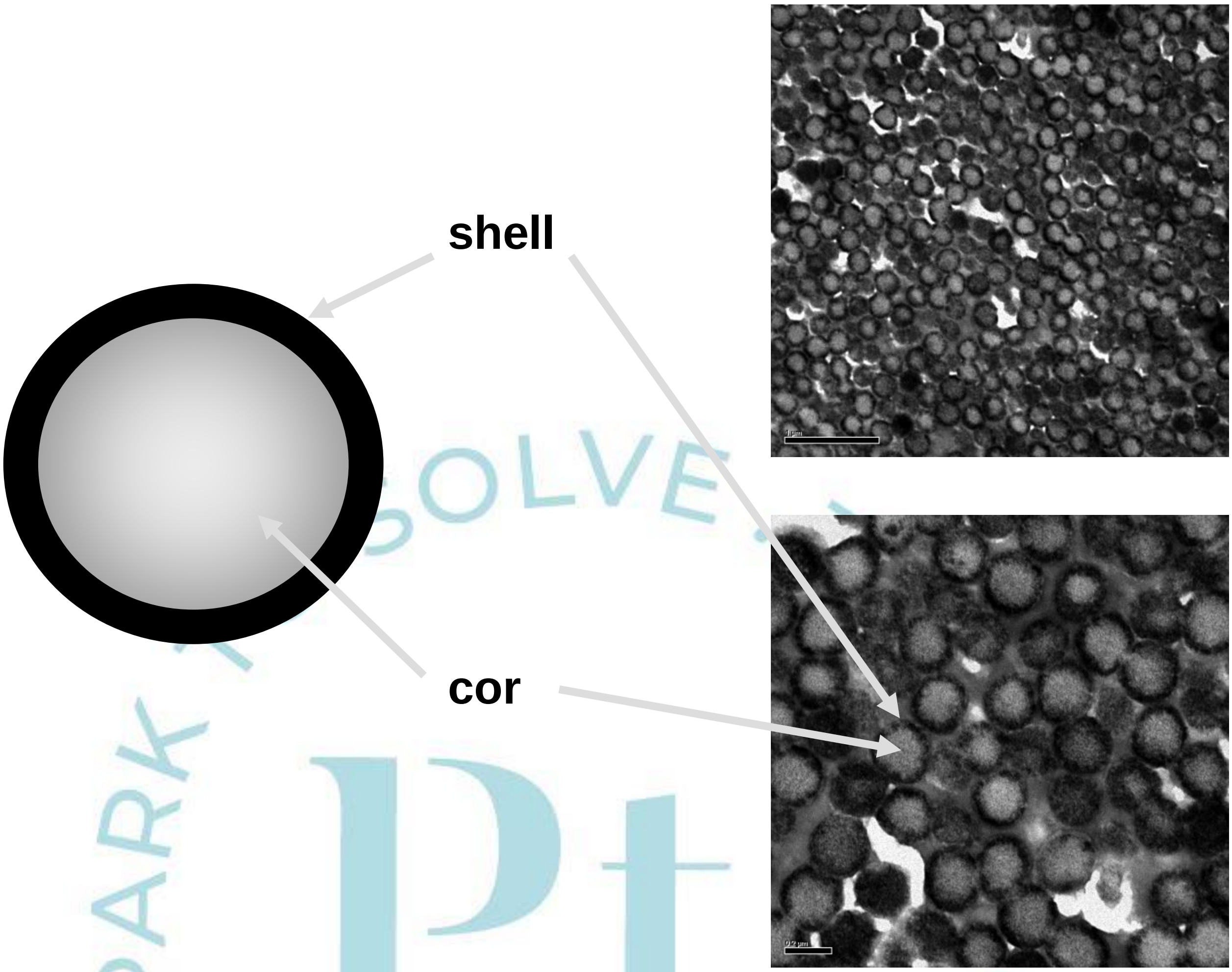

Figure 1 Core-shell modifier structure [2]

„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 gra☐fted onto the surface of the core. This graft☐ed 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“ [3].
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“ [3].
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 2 [3].

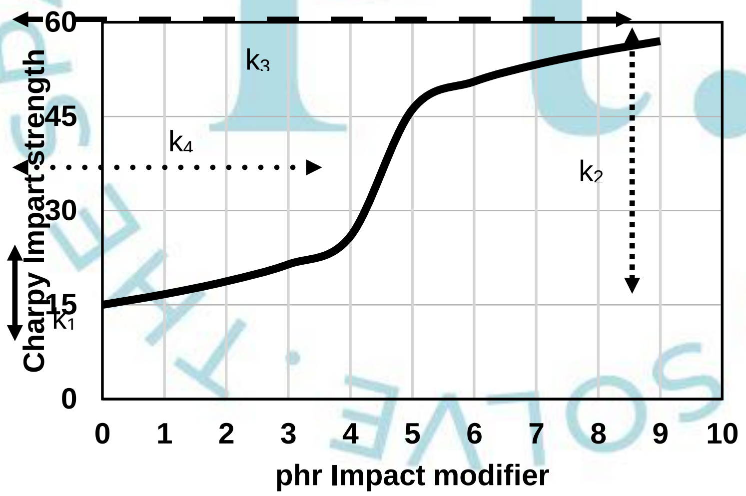

Figure 2 Cube root function according to Eq. 1 [3]

$$y = \left[\sqrt[3]{(k_3 \cdot x) - (k_4)^3} + k_4 \right] \cdot k_2 + k_1 \qquad (1)$$

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 2.

The material constants k_1 to k_4 are functions of the impact strength which depends on many factors [4]:

- 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

Schiller and Singh [3] „…have succeeded in mathematically describing the influence of the dosage of an acrylate-based core-shell modifier on the Charpy[1] impact strength in a range from 0 to 8 phr modifier. The basis for this is provided by a cube root function. This contains four 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. At the moment we cannot postulate where the influence of the constant k_3 comes from. The constant k4 was assumed to be constant with the value 3 for all tests. It is highly probable that this mathematical model can also be applied to Izod[2] for the impact strength…“
The target of this project is to confirm the previous findings and hopefully to find an explanation for the constant k_3.

[1] Remark by the authors [5]
[2] Remark by the authors [6]

2. Experimental of synthesis of AIM 10 to AIM 12

Three different AIM (10-12) were prepared by applying the method of Goertz and Oschmann [7]. The composition and process details are not disclosed because of commercial reasons. The main properties of AIM 10-12 are summarized in Table 1.

Table 1 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. Experimental of testing 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 [8]. The results are summarized in Table 2.

Table 2 Formulation and impact strength according to Charpy

Trial	phr AIM	AIM	Charpy/(kN/sqm)	
			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

4. Results and discussion

We used the data in Table 2 to check the plausibility of Eq. 1 and to determine the values of the material constants k_1 to k_3. Material constant k_4 was assumed as 3. Figure 3 to Figure 5 show the correlation of simulated graphs and the experimental impact strength depending on the dosage of the different AIM in phr. The material constants k_1 to k_4 are summarized in Table 3 and plotted in Figure 6. The squared 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 3 to 5 are excellent. Combined with the results from our previously reported series in Table 4 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 3 don't contradict the results of AIM 10 in Table 4 at about 10 phr calcium carbonate.
- The constant k_1 characterizes the impact strength of the material without an impact modifier [3]. This is confirmed in the previous set of trials.
- The constant k_2 very probably describes the influence of the filler on the Charpy impact strength [3]. This is confirmed in the previous set of trials.
- Regarding constant k_3 we could not postulate any influence in the previous investigations [3]. According the results in Table 3 and in Figure 6 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. According to Schiller and Singh [3] 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 3 to Figure 5; Table 3. There also might be also a dependency of it on the glass transition temperature Tg of the impact modifier at constant filler content; Figure 7.
- 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.

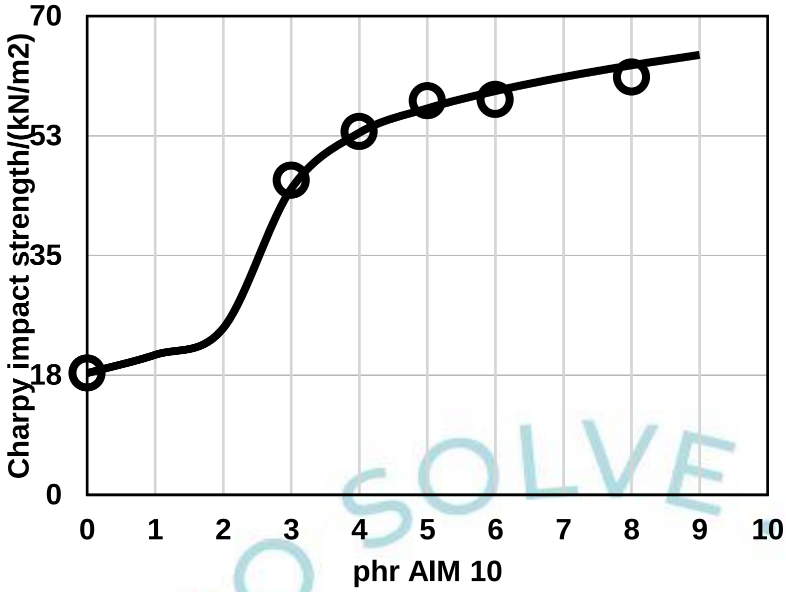

Figure 3 Dependency of Charpy impact strength on the dosage of AIM 10; experimental values (o) from Table 1 and calculated values (line) based on Eq. 1; k_1=17.8, k_2=6.8, k_3=9.3

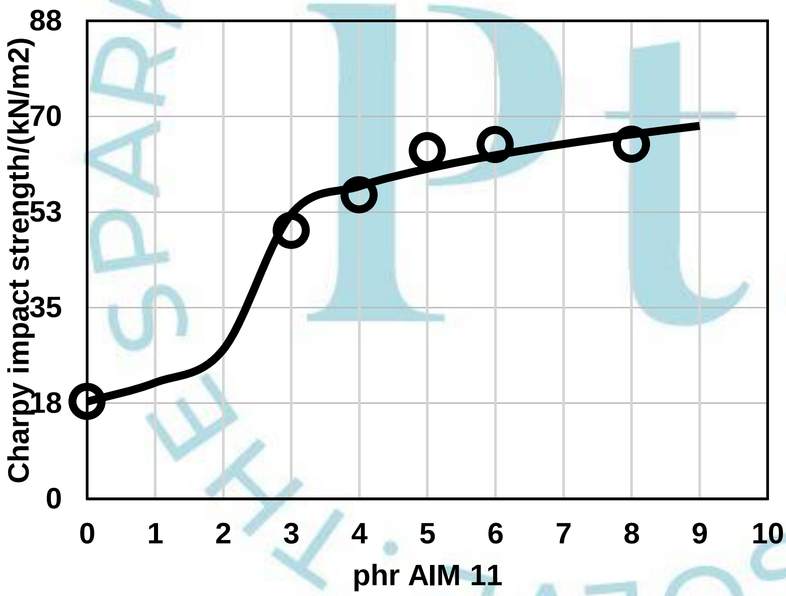

Figure 4 Dependency of Charpy impact strength on the dosage of AIM 11; experimental values (o) from Table 1 and calculated values (line) based on Eq. 1; k_1=17.8, k_2=7.0, k_3=11.3

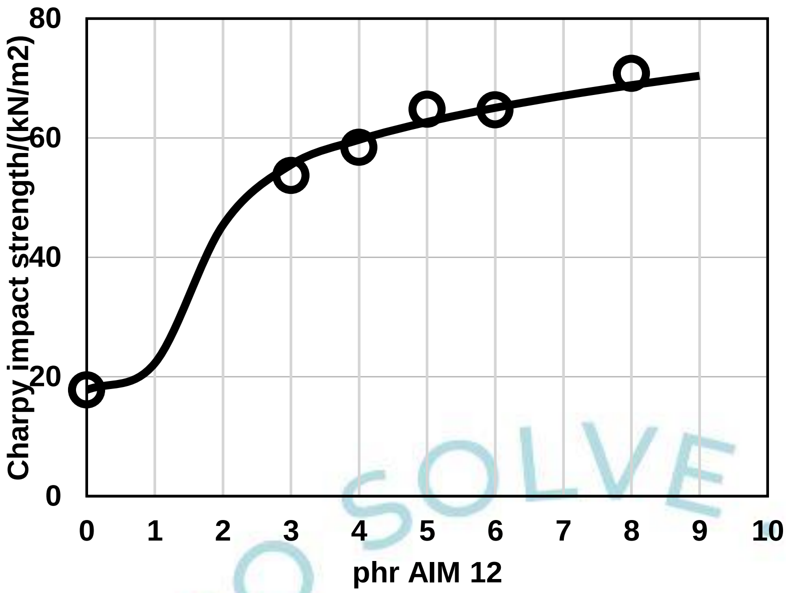

Figure 5 Dependency of Charpy impact strength on the dosage of AIM 12; experimental values (o) from Table 1 and calculated values (line) based on Eq. 1; k_1=17.8, k_2=6.9, k_3=14.0

Table 3 Material constants k_1 to k_4 and squared deviation of observations from the calculations F based on the simulations in Figures 3 to 5

AIM	phr $CaCO_3$	Tg/°C	k_1	k_2	k_3	k_4	F	Inflection point/phr
10	8	-45,1	17,8	6,8	9,3	3,0	7,2	2,90
11	8	-46,7	17,8	7,0	11,3	3,0	29,4	2,39
12	8	-55,4	17,8	6,9	14,0	3,0	13,5	1,93

Table 4 Material constants k_1 to k_4 and squared deviation of observations from the calculations F based on the simulations in the previous series [3]

Trials	phr $CaCO_3$	phr Lubricant	k_1	k_2	k_3	k_4	F
1- 6	5	0.0	13.4	7.9	6.7	3.0	50.0
7-12	10	0.0	17.1	7.0	8.9	3.0	9.4
13-18	15	0.6	17.5	6.7	9.0	3.0	25.0
19-24	20	1.2	15.9	2.5	5.9	3.0	20.1
25-30	25	1.8	13.7	2.0	5.3	3.0	0.8

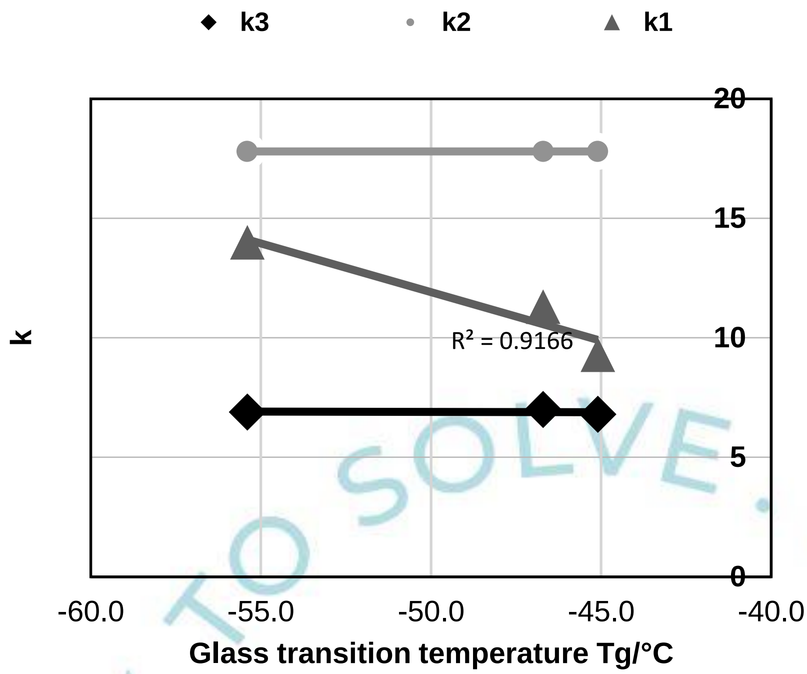

Figure 6 Dependency of k_1, k_2 and k_3 on the glass transition temperature Tg

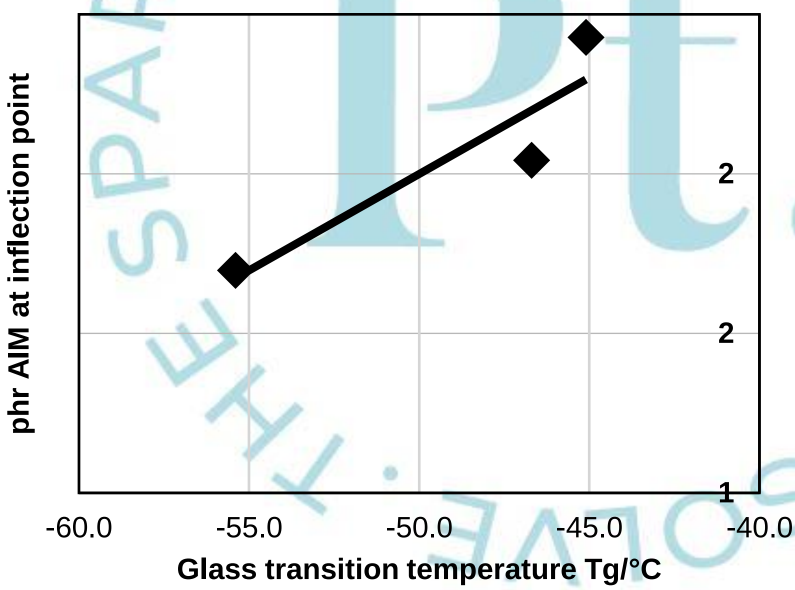

Figure 7 Dependency of phr AIM at inflection point on the glass transition temperature Tg

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 1. 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 [9]; Eq. 2.

$$Tg = Tg_1 \cdot w_1 + Tg_2 \cdot w_2 \quad (2)$$

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.

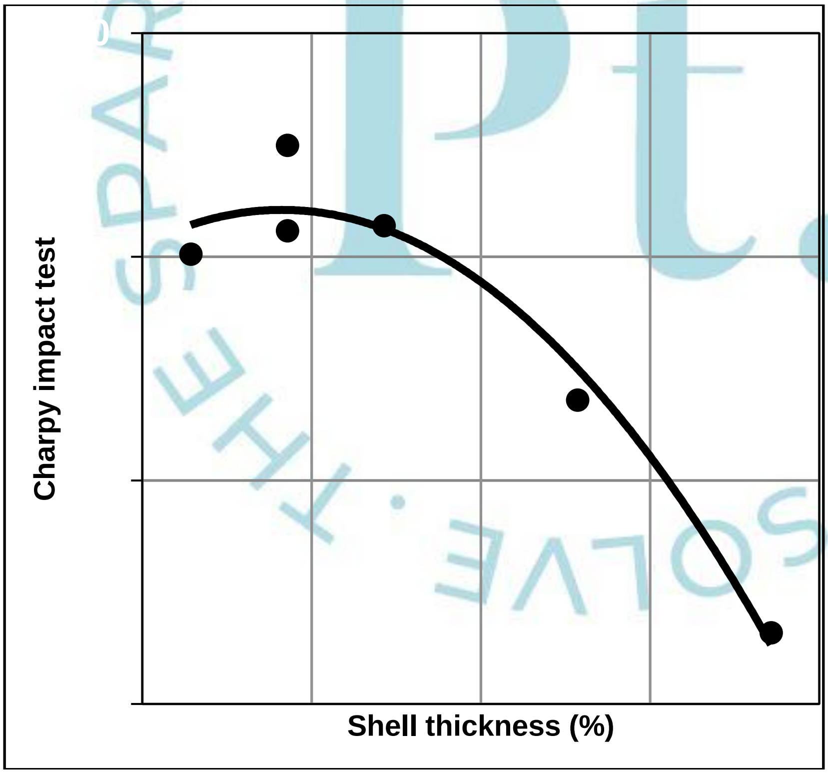

Figure 8 Impact strength (Charpy in kN/m^2) as a function of relative shell thickness of an AIM at constant particle size [2]

- 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 a 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 shall 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

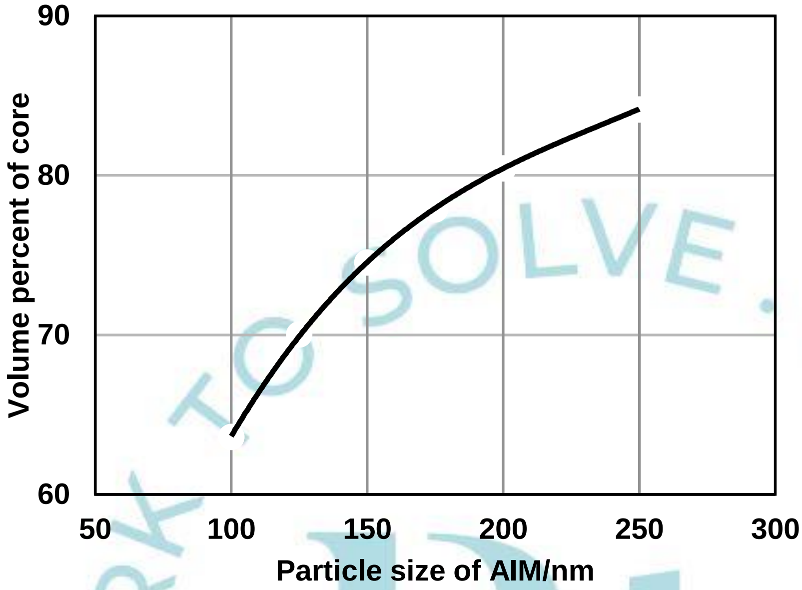

Figure 9 Dependency of volume percentage of rubber core in an AIM depending of the primary particle size

5. Summary and conclusion

The correlations between the calculated Charpy graphs and the experimental observations in Figures 3 to 5 are excellent. Combined with the results from our previously reported series we are absolutely convinced that Equation 1 is a useful tool to describe the impact strength of PVC product containing a corse-shell modifier. The material constant k_1 characterizes the impact strength of the material without an impact modifier [3]. The material constant k_2 very probably describes the influence of the filler on the Charpy impact strength [3]. This is confirmed in the previous set of trials. Regarding constant k_3 we could not postulate any influence in the previous investigations. According the recent results in Table 3 and in Figure 6 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 Schiller and Singh [3] 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.

6. Literature

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