# The Beauty of Mathematical Functions - Impact Modifiers in u-PVC - Part III - Non-acrylic Impact Modifier.pages

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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. The previous paper supports the 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. The recent paper focuses on non-acrylica modifiers and Izod impact strength.

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

## 1. Introduction

Polyvinyl chloride (PVC) is a plastic that a priori has good impact strength. However, for some applications such as profiles for window and door frames, for compact panels, tubes in special applications... this is not necessarily sufficient. Therefore, additives, so-called impact modifiers, are added to increase the impact strength. 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. ; Figure 1 [1].

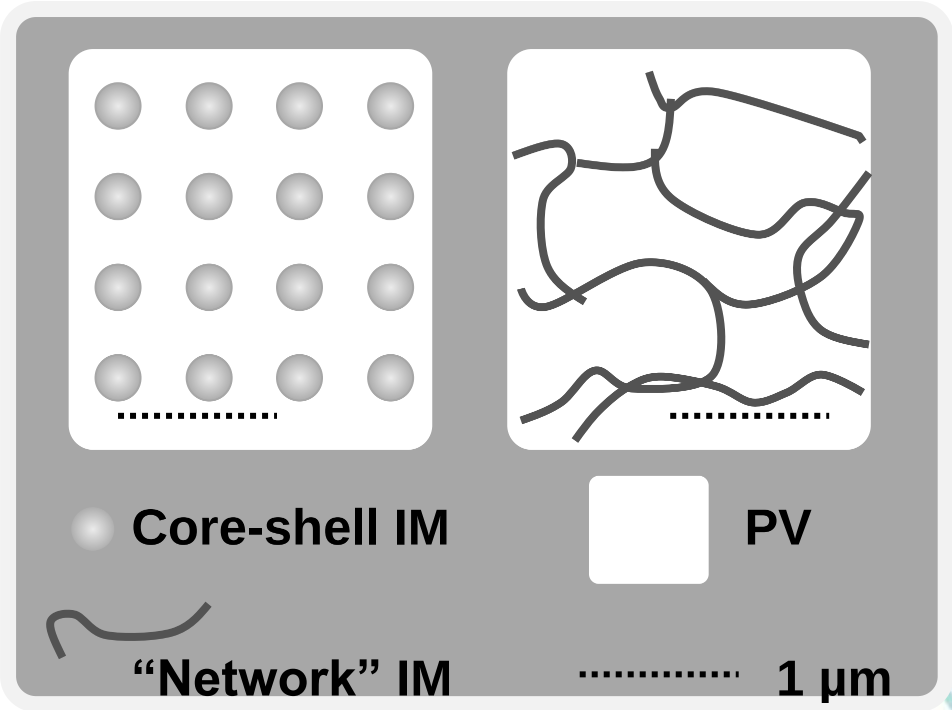



Figure 1 Differences between impact modifiers with defined particle structure and those which form network structures [1]

"Of the impact modifiers that form network structures within the PVC, the CPE modifiers are the commercially most important representative. CPE has been used as impact modifier in PVC for more than 40 years. It is produced by chlorination of high-density polyethylene (HDPE). During this process the HDPE loses some of its crystallinity. The resulting chlorine content of the CPE is between 25 and 50% chlorine. The typical and probably optimal chlorine content is at about 35% (PVC has a theoretical chlorine content of 56%). A high chlorine content improves the compatibility with PVC but reduces the impact modifying properties. At a rather low chlorine content the compatibility with PVC as well as the impact modifying properties is reduced. The Tg of CPE is at about −16 °C…

Ethylene-vinylacetate polymers (EVA) are synthesized by copolymerization of ethylene and vinylacetate under pressure. They are perfectly suited for transparent applications but only to a limited extent for applications which require outdoor weathering. In production the chain length of the EVA is controlled via process conditions and the concentration of the initiators. Short-chain EVAs can be utilized as lubricants in PVC extrusion whereas the long-chain copolymers act as impact modifiers. The content of vinyl acetate controls the compatibility, crystallinity and glass transition temperature of the EVA copolymer. If the vinyl acetate content is higher 60%, no more crystallinity can be detected. The glass transition temperature Tg and the compatibility also increase with increasing vinyl acetate concentration. A perfect EVA-based modifier would have a good compatibility in PVC and preferably a low Tg and crystallinity. Due to the opposing influences of the two monomer components with regard to these properties, any EVA modifier represents an ultimate compromise: A high amount of ethylene results in a low Tg, a high level of crystallinity and a lower compatibility in PVC. A high vinyl acetate proportion improves the compatibility with PVC and lowers the crystallinity but increases the glass transition temperature Tg.“ [2]

Acrylic impact modifiers (AIM) belong to the core-shell modifiers and are most commonly used in PVC applications. "MMA-butadiene-styrene (MBS) modifiers also have a core-shell structure. As the name implies, they are produced by copolymerization of styrene, butadiene, and MMA, which is present in the shell analog to the AIMs. The glass transition temperature Tg of MBS types is significantly lower than those of AIMs. They are at −55 °C... and lower (down to −70 °C...) and the MBS modifiers therefore perfectly suited for low temperature applications. However, they do have a negative influence on transparency and have only limited suitability for outdoor applications...

Acrylonitrile-butadiene-styrene (remark by the authors: ABS) terpolymers may also be classified as core-shell modifiers. During their production acrylonitrile and styrene are grafted onto butadiene rubber or acrylonitrile is grafted onto styrene-butadiene copolymers. Due to their low glass transition temperature (down to −70 °C) they are well suited for low temperature applications..." [2].

"There are several methods and standards for testing impact strength, as already briefly mentioned previously: The Izod impact strength testing, initially described by E. G. Izod…, is today an ASTM method… The testing equipment consists of a pendulum with a hammer that is released from a specific height, therefore having a specific potential energy. The test specimen with a single notch is clamped into a solid block, ready for “the hammer to fall”… Once the hammer is released it hits the sample on the side with the notch and breaks it... Based on the energy absorbed by the sample, the impact energy is calculated. A similar procedure is the Charpy impact test... G. Charpy proposed it as a standardized method in 1901… The absorbed impact energy can once again be correlated to the notch toughness. The Charpy test can also be used as a tool to study the temperature-dependent ductile-brittle transition...

A different principle is used in Gardner’s Free-Falling Dart Impact Testing, which is a common method for evaluating the impact strength of plastic materials. The plastic specimen is placed on a base plate over an opening. An impactor sits on the top of the specimen and is in contact with the unsupported center of the specimen. A specific weight is raised inside a guide tube to a predetermined height and then released to drop onto the impactor, which forces the impactor nose through the test sample. The drop height, drop weight, and the test result (pass/fail) are recorded. (A variation of this method, useful for a quick test, is to drop a weight from a defined height onto a (window) profile at room temperature or at minus temperatures. The resulting pass/fail allows for a rapid qualitative assessment of the impact resistance of the tested PVC product.) Furthermore, it is possible to calculate the mean failure energy by using the Bruceton Staircase method.“ [3].“ The addition of the impact modifier and its dosage affect the impact strength (Figure 2).

Schiller and Singh [4] 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; Equation 1 and Figure 3. 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.

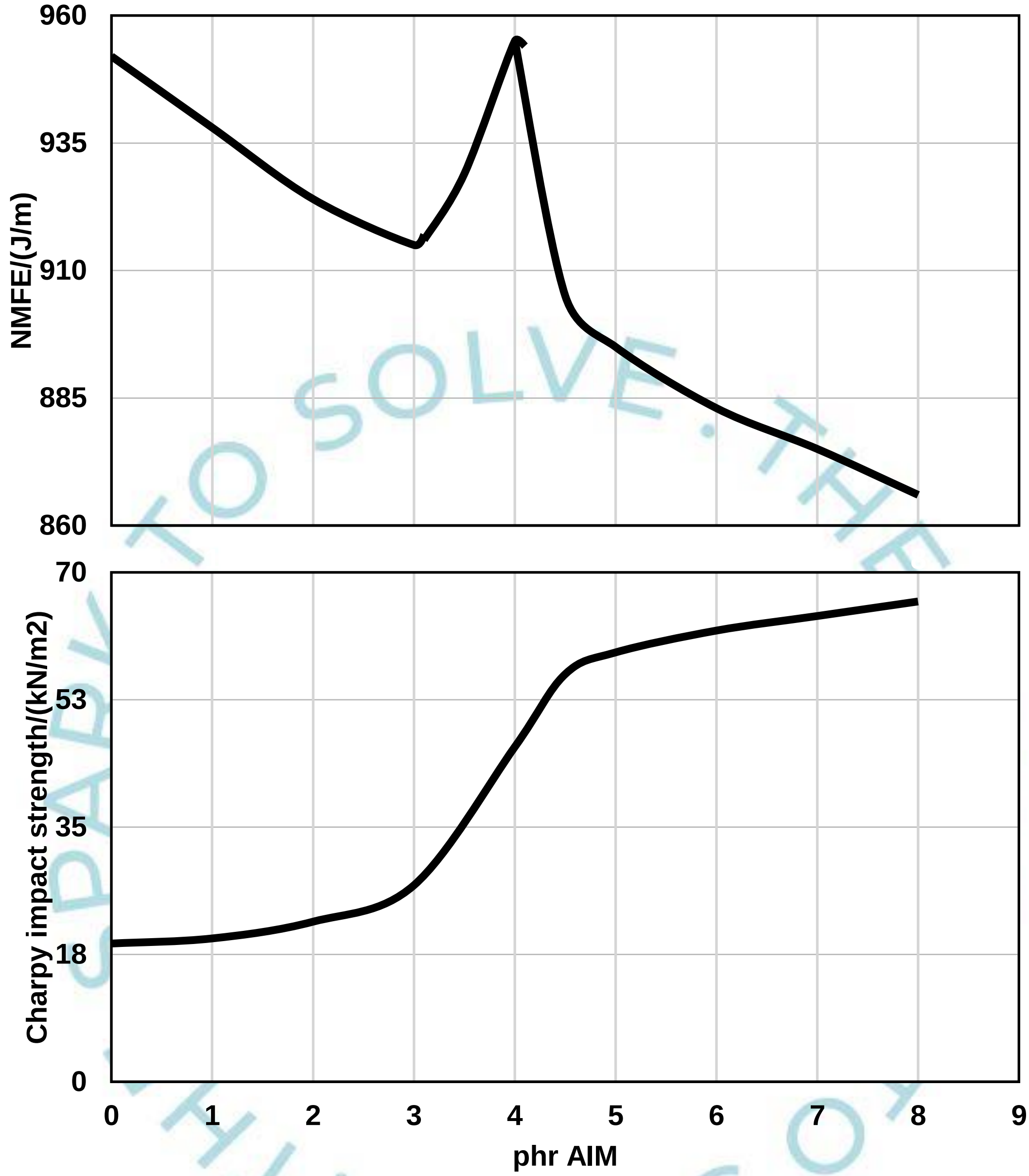



Figure 2 Influence of AIM 11 dosage on the Charpy test in $kJ/m^2$ and on the impact energy (Normalized Mean Failure Energy; NMFE) measured according to Gardner in J per m test specimen cross-section [5]

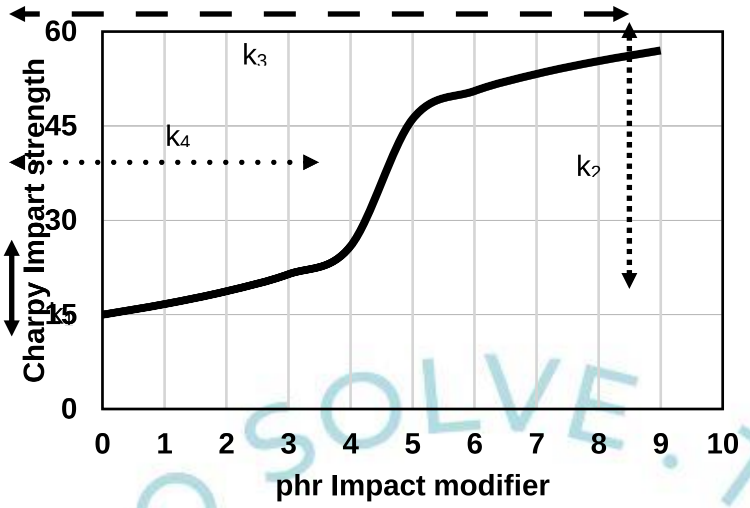



Figure 3 Cube root function according to Eq. 1 [4]

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

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 3.

Regarding constant $k_3$ Schiller and Singh [6] found 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 [4] 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. The constant $k_4$ 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 for the impact strength and also to other impact modifiers like CPE, EVA, ABS and MBS.

## 2. Results and discussion

Mitsui Polychemical published in 1992 [7] a comparison of Izod impact strength of CPE, EVA, ABS and MBS in dependence of their dosage; Figure 4. We have digitized the data (Figure 4). We used the data from Figure 4 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 5 show the correlation of simulated graphs and the experimental impact strength depending on the dosage of the different modifier in phr. The material constants $k_1$ to $k_4$ are summarized in Table 1. On one hand, it is obvious that Equation 1 also applies to the impact strength measured according to Izod. On the other hand, Figure 5 shows that Equation 1 mathematically describes the dependency of the impact strength for non-acrylic impact modifiers too. Unfortunately, the authors do not have access to the original [8], despite extensive research and personal inquiries from the authors of [7], which, on top of that, may have been incorrectly quoted [9]. Therefore, the following conclusions are pure speculation.

The authors are aware that the glass transition temperature Tg of (co)polymers depends on the molecular weight of the polymer, the monomers, their molar fraction in copolymers and the degree of crystallinity. Since the original literature [8] is not available to us, we have to resort to data from probably similar polymers. Agroul et al. [10] found in his DSC experiments of EVA a glass transition at about −33.1 °C (exothermic, characteristic of crystalline phase) and an endothermic peak at 55 °C (characteristic of amorphous phase).

Schepers [11] reports that the glass transition temperature Tg of CPE depends on the degree of chlorination on the one hand and the degree of crystallinity on the other. Therefore Tg can vary between -25 and +1°C. In [2] -16°C is given as Tg for CPE.

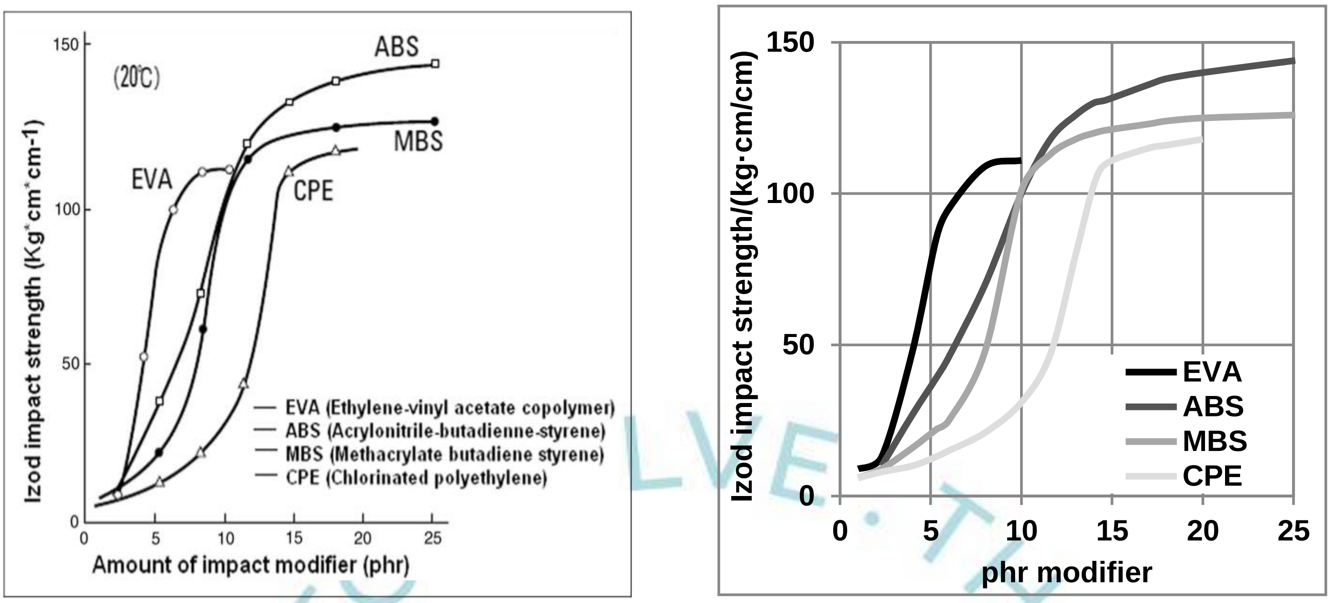
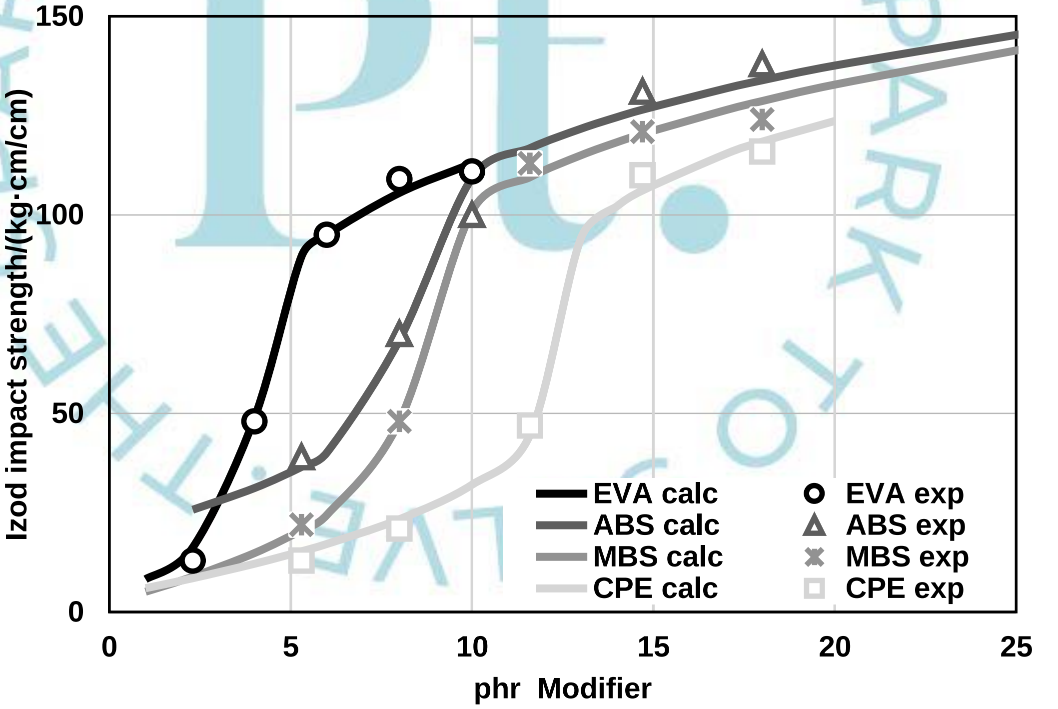



Figure 4 Izod impact strength of CPE, EVA, ABS and MBS in dependence of their dosage at 20°C (left: original [7]; right: digitized by the authors)

Figure 5 Dependency of Izod impact strength on the dosage of modifier reported




by Mitsui [7] and calculated by Equation 1.

Table 1 Material constants $k_1$ to $k_4$ and squared deviation of observations from the calculations F based on the simulations in Figure 5

| Modifier | Modifier type (assumptions) | | k1 | k2 | k3 | k4 | F | Inflection point |
|---|---|---|---|---|---|---|---|---|
| | | Tg/°C | | | | | | |
| EVA | Net work | -31 & 55 [10] | 3,6 | 17,0 | 6,74 | 3 | 27 | 4,0 |
| CPE | | -25 to +1 [11] | 4,2 | 21,4 | 2,21 | 3 | 37 | 12,2 |
| ABS | Core-shell | -70 to -55 [2] | 19,9 | 18,3 | 3,37 | 3 | 134 | 8,0 |
| MBS | | >-70 [2] | 2,5 | 20,4 | 3,32 | 3 | 36 | 8,1 |

Lutz and Dunkelberger [12] reported in 1992 similar about impact modifiers and the Izod impact strength depending on the dosage of modifiers in a tin stabilized dryblend[1]; Figure 6.Unfortunately, we don't really know which modifiers were tested, aside from Tyrin. And unfortunately the modifiers were only tested up to a dosage of 12 phr, although it has been known since Mitsui [7] that the maximum is reached above 12 phr (Figure 5). However, here too, the values we simulated correlate quite well with the experimental values. The material constants $k_1$ to $k_4$ are summarized in Table 2.

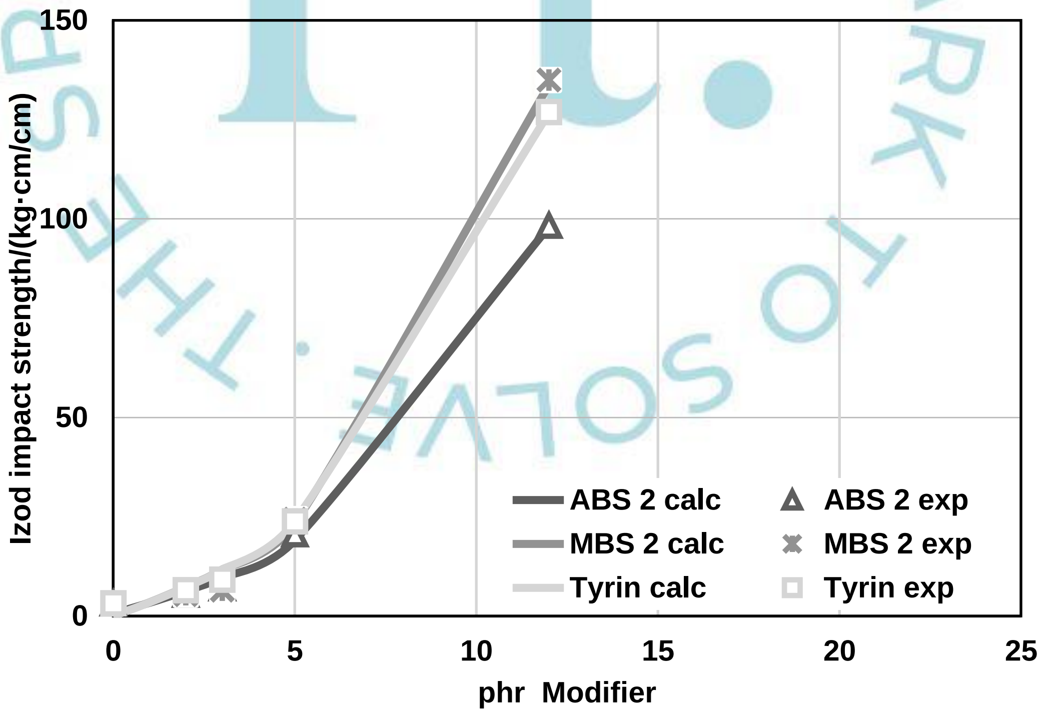



Figure 6 Dependency of Izod impact strength on the dosage of modifier reported by Lutz und Dunkelberger [12] and calculated by Equation 1.

[1] 100 phr PVC (k=68, 2 phr tin stabilizer, 2 phr lubricants, x phr modifier as indicated

Table 2 Material constants $k_1$ to $k_4$ and squared deviation of observations from the calculations F based on the simulations in Figure 6

| Modifier | Modifier type (assumptions) | k1 | k2 | k3 | k4 | F | Inflection point |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| **ABS 2** | Core-shell | 0,7 | 16,9 | 4,00 | 3 | 17,0 | 6,80 |
| **MBS 2** | Core-shell | 0,0 | 23,8 | 3,75 | 3 | 44,6 | 7,20 |
| **Tyrin** | Net work | 0,0 | 22,0 | 4,00 | 3 | 17,7 | 6,80 |

Of course, we cannot compare the data in Table 1 and Table 2 because we do not have enough information. But overall we can state that our hypothesis that the impact strength can be calculated using Equation 1 as a function of the dosage of the modifier. This applies regardless of whether the impact strength is measured according to Charpy or Izod.
In 1993, Lutz [13] published another comparison of the impact strength's dependency on the dosage of the impact modifier. Lutz compares PVCs with different k values. Since we only had the image (Figure 7), we also had to digitize it (Figure 7). Figure 7 „depicts typical response to modifier concentration in PVC having various *MW* (remark by the authors of this paper: molecular weight). The absolute values and placement of the curves will vary with the specific impact modifier, but the relative positions will remain. It is obvious from these curves that one cannot achieve maximum impact by using more modifier in lower *MW* PVC.“ [13]

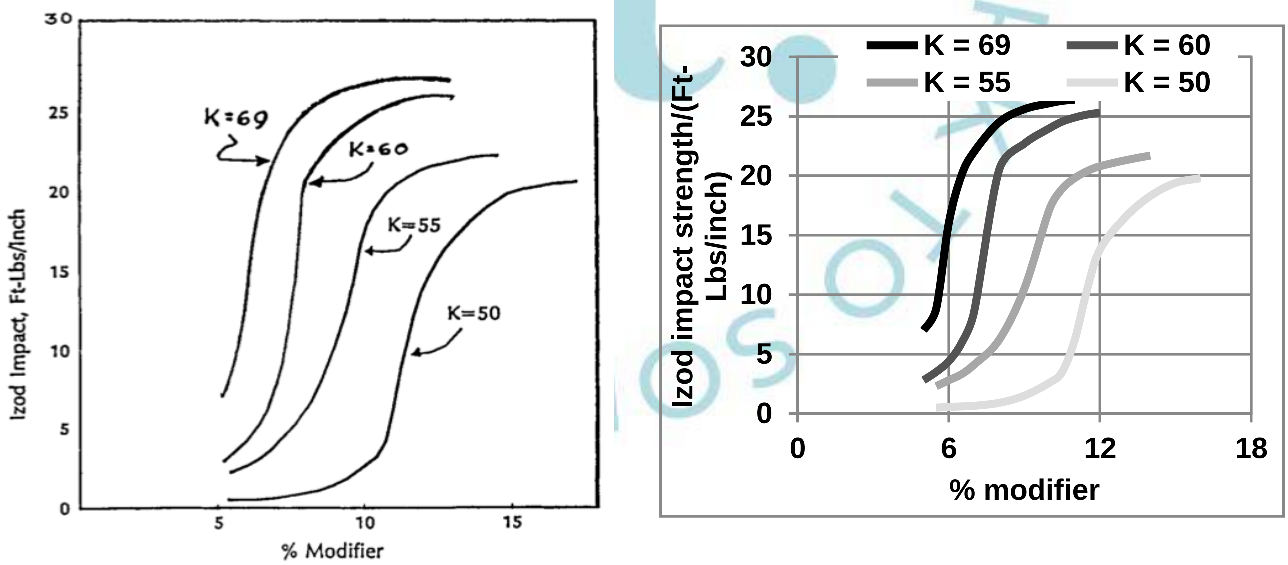



Figure 7 Izod impact strength[2] of an undefined impact modifier in dependence of their dosage at PVC with different k values (top: original [13]; bottom: digitized by the authors)

[2] Please keep in mind that in Figure 7 the impact strength is in Ft·Lbs/inch and the dosage in percent while in Figure 4 it's kg·cm/cm and phr.

Based on the digitized value from Figur 7 we tried to correlate the curves with Equation 1. The results are summarized in Figure 8 and Table 3. Before discussing the results we have to keep in mind that

- the units in Figure 4 and Figure 7 are different
- we have curves drawn with a curve ruler but no real experimental values
- the modifier is not specified.

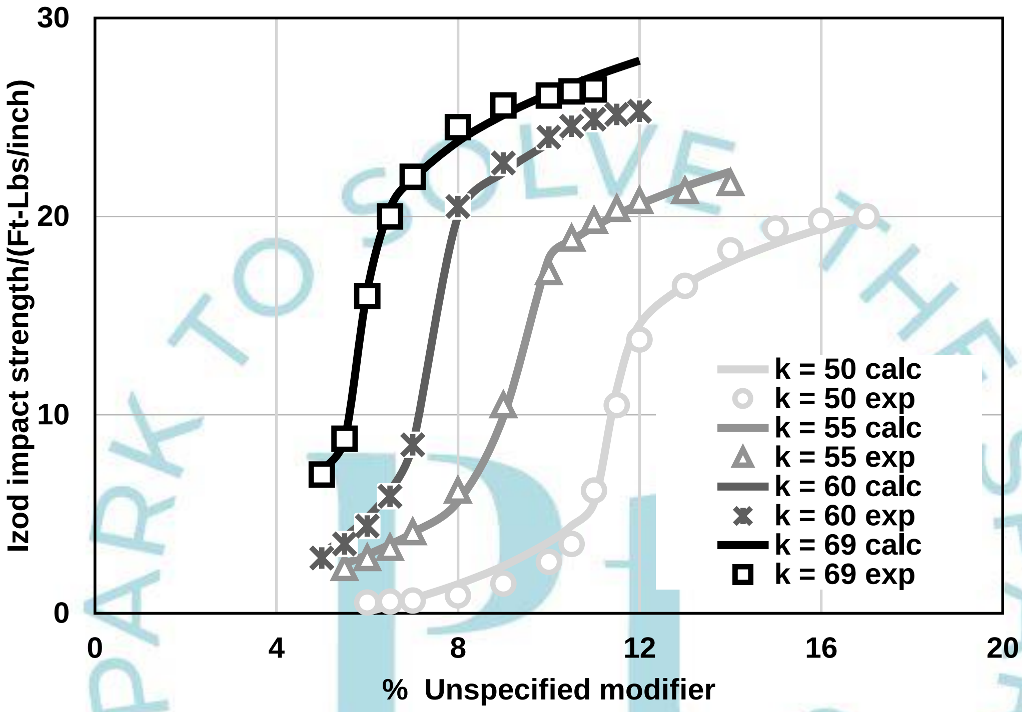



Figure 8 Dependency of Izod impact strength on the dosage of modifier and the k values of used PVC reported by Lutz [13] and calculated by Equation 1.

Table 3 Material constants $k_1$ to $k_4$ and squared deviation of observations from the calculations F based on the simulations in Figure 8

| K value of PVC | k1 | k2 | k3 | k4 | F | Inflection point |
|---|---|---|---|---|---|---|
| | | | | | | |
| 50 | -2,7 | 4,25 | 2,35 | 3 | 6,4 | 11,50 |
| 55 | -0,9 | 4,25 | 2,99 | 3 | 1,8 | 9,10 |
| 60 | -1,8 | 4,91 | 3,75 | 3 | 1,3 | 7,20 |
| 69 | 1,2 | 4,44 | 4,51 | 3 | 1,6 | 5,90 |

The correlation between the experimental data and the calculated vales is reasonable good because the squared deviation of observations from the

calculations F is very low. A small flaw is that negative values were calculated for some of the material constant $k_1$. This is probably because:
- the impact strength was not measured without the impact modifier and/or
- the curves were drawn with a curve ruler.

Based on the data published by Lutz and Dunkelberger [12, 14], values of 0.50 to 0.65 ft lbs/inch should be expected.
In Figure 9 we have plotted the dependency of the material constants and in Figure 10 the dependency of the inflection point on the k value of the PVC.
As we know from previous investigations and calculations, the material constant $k_1$ tells us something about the impact strength without a modifier. Even though we have partially calculated negative values here, one can at least guess the trend that the impact strength of PVC increases with increasing k value. This correlates with literature [15]. In Figure 10 it is obvious that the inflection point of the curve moves to lower values of the dosage of the modifier as the k value of the PVC increases. In other words, the higher the k value of the PVC, the lower the impact modifier dosage will be to achieve the same impact strength.
The constant $k_2$ probably describes the influence of the filler on the Charpy impact strength. In Figure 2 we can see that the trend line of $k_2$ for is nearly parallel to the x axis. So, we can conclude that $k_2$ describes also the influence of filler on Izod impact strength.
Regarding constant $k_3$ Schiller and Singh [6] found 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 Figure 9 $k_3$ will be also influenced by the k value of PVC.

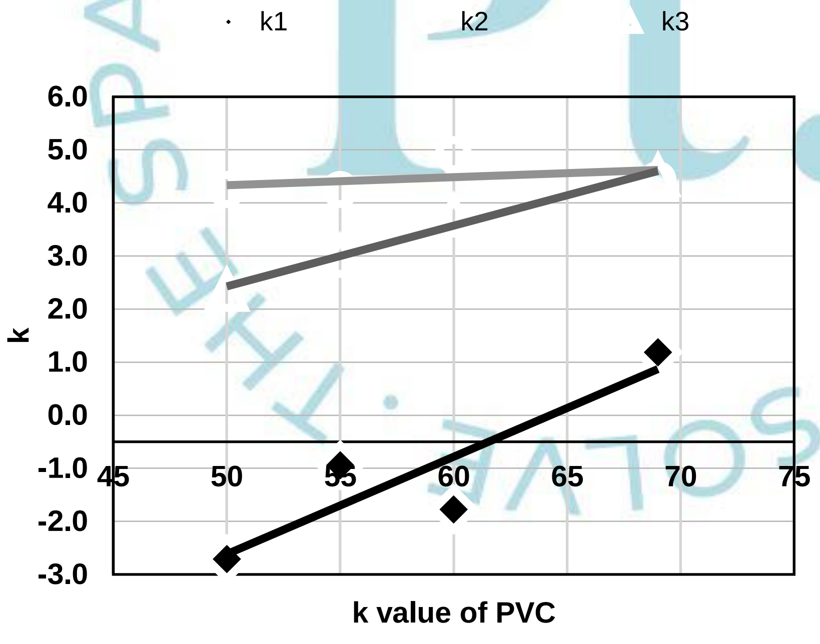



Figure 9 Dependency of k1, k2 and k3 in Table 3 on k value of PVC

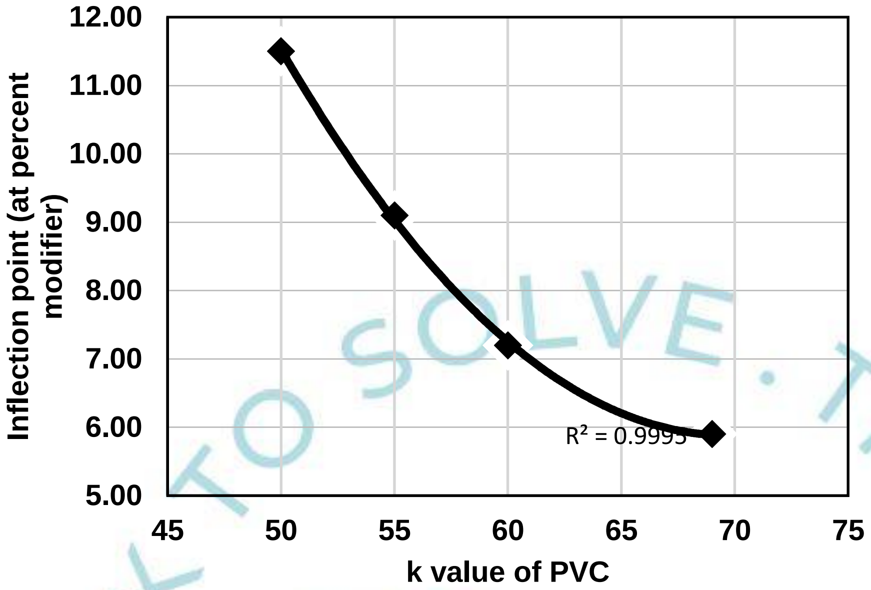



Figure 10 Dependency of the inflection point in Table 3 on k value of PVC

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## 3. Summary and conclusion

In the previous reports, we were able to prove that equation 1 is valid for the dependence of the impact strength on the dosage of the impact modifier. With the available investigations we can prove the same for the Izod impact test.
For both different test methods we can summarize that the material constant:

- $k_1$ describes the impact strength of a PVC specimen without an impact modifier
- $k_2$ probably describes the influence of the filler dosage on the impact strength
- $k_3$ describes the influence of the impact modifier (glass transition temperature but also probably particle size, shell thickness…) and the k value of PVC
- $k_4$ was assumed and proofed to be 3 without any idea about the „mechanical“ background of this material constant.

Beside the finding regarding PVC and impact modifiers Equation 1 seems to comprise something philosophical too namely namely the law of the conversion of quantity into quality and vice versa [16]. With the addition of the impact modifier, the behavior changes from "brittle" to "ductile" in a relatively narrow range.

## 4. Literature

[1] M. Schiller, „PVC Additives", 2nd Edition, C. Hanser Publisher Munich/Germany (2022) p. 268 (and the cited literature inside)

[2] M. Schiller, „PVC Additives", 2nd Edition, C. Hanser Publisher Munich/Germany (2022) pp. 275-276 (and the cited literature inside)

[3] M. Schiller, „PVC Additives", 2nd Edition, C. Hanser Publisher Munich/Germany (2022) pp. 281-283 (and the cited literature inside)

[4] M. Schiller, H. K. Singh, „The Beauty of Mathematical Functions - Impact Modifiers in u-PVC - Part I - One Modifier at Different Dosages of Filler" under publication

[5] M. Schiller, M. Basalp, A. Sahin, B. Aldanmaz, E. Alyamaç, The 12th International PVC Conference, Brighton/U.K. (2014)

[6] M. Schiller, H. K. Singh, „The Beauty of Mathematical Functions - Impact Modifiers in u-PVC - Part II - Different Acrylic Modifier at Constant Dosages of Filler " under publication

[7] H. P. S. A. Khalil, M. Tehrani, Y. Davoudpour, A.H. Bhat, M. Jawaid, A. Hassan; Journal of Reinforced Plastics and Composites (2012); DOI: 10.1177/0731684412458553) which shows [8] with 1992

[8] Mitsui Polychemical (1979) PVC and Polymers. 19 (12), 26 or Mitsui Polychemical (1992) PVC and Polymers. 19 (12), 26; see also [7] and [9]

[9] https://pvc.org/about-pvc/pvcs-physical-properties/property-modification-of-pvc-products/ (accessed on 14.10.2022) which shows [8] with 1979

[10| K. Agroul, G. Collins, J Farenc; Renewable Energy 43 (07/2021) pp. 218-223, DOI:10.1016/j.renene.2011.11.015

[11] H. A. J. Schepers; US 4,341,885 (1981), table 2

[12] J. T. Lutz jr, D. L. Dunkelberger; Impact Modifiers for PVC - The History and Practice; John Wiley &Sons, Inc. New York, Chichester, Brisbane, Toronto, Singapore (1992) p.108

[13] J. T. Lutz jr; J. Vinyl Technology, Vol. 15 (06/1993) pp. 82-99

[14] J. T. Lutz jr, D. L. Dunkelberger; Impact Modifiers for PVC - The History and Practice; John Wiley &Sons, Inc. New York, Chichester, Brisbane, Toronto, Singapore (1992) p.104

[15] M. Schiller; „PVC Additives"; C. Hanser Publisher Munich/Germany, 1st Ed. (2015) p. 206 (and the cited literature inside)

[16] http://www.mlwerke.de/me/me20/me20_348.htm; accessed on 10.11.2022