https://doi.org/10.3311/PPch.20991

Periodica Polytechnica Chemical Engineering, 67(2), pp. 232–241, 2023

Robustness Study of a Tensile Modulus Prediction Model for Semicrystalline Polymers

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Received: 11 August 2022, Accepted: 10 January 2023, Published online: 16 March 2023

Abstract

This work presents a robustness study of a previously developed empirical model that links Young's modulus to two key parameters of crystalline structure; crystallinity and lamellae thickness. The reliability of this modulus prediction model was tested by using different calorimeters and different polypropylene grades as well. Small samples were fabricated from injection-molded bars from different locations of the specimens in order to check the effect of structural inhomogeneity originated by the dynamic processing conditions. In addition, the standard deviation and consequently the accuracy of the prediction was tested by repeated calorimetric measurements. The crystalline structure and melting characteristics were measured by differential scanning calorimetry (DSC). The tensile properties of studied specimens were evaluated by standardized tensile tests. Although, the accuracy and reliability of the prediction model is dependent on the instrument used for thermal analysis, reasonably good agreement was found between the predicted and measured values in most cases. However, we may note that only well-calibrated calorimeters are suitable for reliable prediction of the modulus.

Keywords

mechanical properties, prediction model, crystalline structure, melting curve, semicrystalline polymer

1 Introduction

Better understanding and consequently optimization of mechanical properties of semicrystalline polymers have always been in the focus of extensive research [1–9]. Relying on the earlier studies, it is well established that a solid basis to estimate the mechanical properties of materials is grounded on the understanding and interpretation of their complex microstructure [10–15]. It should be highlighted, that prediction mechanical properties should be separated into two basic cases according to the mechanism of deformation in the polymer part. The first case is the elastic deformation, which can be characterized by the tensile modulus, for example. In this case, the deformation is energy elastic, and the elongation of the specimen is very small. However, at larger deformations, if the segmental movement is liberated in the material, conformational changes appear also, and plastic deformation develops. The two cases should be separated, and the predictive models should be matched to these two crucially different deformation mechanisms. The handling of elastic behavior is simpler since the mathematical treatment of conformational changes is very complicated and requires mostly statistical approaches. In addition, other parameters need to be considered, such as the number of tie molecules, chain entanglements etc. [13]. Despite of the simpler nature of elastic behavior, it still remained a challenge to predict elastic modulus of semicrystalline polymers accurately due to several complex influencing factors, including their molecular architecture and processing conditions. Our work also aims the prediction of the tensile modulus, thus we will summarize the previous pioneering researches in this area only.

The results of many empirical approaches are convincing enough to reveal a qualitative relationship between crystalline structure and mechanical properties of semicrystalline thermoplastic polymers; basic end-use elastic behavior is highly affected by microscopic architecture. Nevertheless, it is also worth noting that, in literature, theoretical or mathematical clarification of this correlation

Cite this article as: Zarbali, A., Pinke, B., Menyhárd, A. "Robustness Study of a Tensile Modulus Prediction Model for Semicrystalline Polymers", Periodica Polytechnica Chemical Engineering, 67(2), pp. 232–241, 2023. https://doi.org/10.3311/PPch.20991

between density or crystallinity and modulus from a quantitative point of view is relatively insufficient [3, 12, 16–18].

Several micromechanical models and multiscale simulations have been developed and applied to predict elastic properties of semicrystalline polymers [19–24]. In different models the semi-crystalline morphology is approached by holding different assumptions. Mostly, the reported models are based on Mori–Tanaka type model and its generalized form [25, 26], Self-consistent model [27] and Double Inclusion model [28]. In a study concerning comparison of micromechanical prediction models, it was concluded that Generalized Mori–Tanaka model and the Self-Consistent Composite-Inclusion model presented comparably accurate outcomes [29]. In another report, by comparing the estimated results to experimentally obtained data, it was stated that three-phase models show more precision than two-phase models [30]. The main disadvantage of some of these approaches is that they are only valid in case of volume fractions (of crystalline phase) up to 30%, which is not relevant for most of the semicrystalline materials, since the crystallinity usually reaches up to 70% [24].

Inaccuracies of some of the developed models stem from the fact that these methods treat modulus as the function of crystallinity only, which means that only the volume fraction of the crystalline phase is considered, but its regularity or level of perfection is not. In fact, the stiffness of semicrystalline polymers can be altered by just rearrangement of lamellas, even if overall crystallinity remains unchanged [31]. Additionally, another issue in most of the reported models is that they require independent structural variables and different material-specific constants. The required parameters and constants, which are not identified for most of the polymers, make these approaches difficult to apply widely.

In a pioneering study, an empirical model equation reported by Pukánszky et al. [32] connecting the stiffness of polypropylene with crystallization characteristics: enthalpy and peak temperature of crystallization. The major advantage of this simple empirical approach was that it considered crystallinity proportional to the enthalpy and lamella thickness proportional to crystallization temperature as independent variables. This empirical method makes the approximate estimation of tensile modulus possible based on a simple calorimetric curve and shows that the principal structural parameters which influence the stiffness are crystallinity and lamella thickness. Despite of its reasonably good accuracy, this approach can be used only in a limited crystallinity range within 30 and 60%, which range overlaps completely the crystallinity range of iPP samples in the industrial practice.

Based on the findings of Pukánszky et al. [32] an improved approach was introduced which also predicts tensile stiffness using experimental values proportional to crystallinity and lamellar thickness. This improved model equation is applicable in entire crystallinity range [33]. Considering the difficult and time-consuming aspect of the evaluation of lamellar thickness, later the equation was simplified by replacing lamellar thickness with a temperature value (average melting temperature), which can be determined easily from a simple melting curve, and which is strictly proportional to lamella thickness. This approach can be easily applied for polymers with less known thermodynamic constants [34]. According to these results the improved prediction equation was successfully applied to predict the modulus of polyamide-6 and poly(lactic-acid) as well [34, 35].

Our present work aims to validate the robustness of our newest modulus prediction model [34], which was developed in our previous studies. This method was optimized to predict tensile stiffness of ISO 527-1:2019 injection-molded dumbbell shaped specimens [36]. Furthermore, in this work, we focus on improving the model equation further by transforming it into logistic function which can predict the modulus values in very high crystallinity range more precisely and consequently, it can be better used for prediction of stiffness of unique crystalline structure prepared by annealing, for example.

2 Experimental

2.1 Materials and sample preparation

Three different grades of polypropylene were tested during the reliability study of this prediction model, one of which was homopolymer and the two other random copolymers. Their characteristics are shown in the Table 1. It can be

Table 1 The iPP grades used in the study

Notation in article	Trade names	PP grade	MFR values (g/10 min)	Supplier
H1	TIPPLEN H649FH	Homopolymer	2.5	MOL Petrochemicals Co. Ltd.
R1	TIPPLEN R351F	Random copolymer	8.5	MOL Petrochemicals Co. Ltd.
R2	BorPure RG466MO	Random copolymer	30	Borealis AG

seen that the selected polymers differ in their molecular structure as well as in their molecular mass and they are obtained from different producers either. We have selected these samples in order to demonstrate that how much the robustness depends on the selection of the material grade.

Standard dumbbell shaped specimens (ISO 527-1:2019 [36]) were prepared by using DEMAG IntElect 560/330-100 type electronic injection molding machine. The temperature profile of the process was 180–190–200–210 °C and mold temperature was 40 °C. Injection pressure was set to 1600 bar with holding pressure of 420 bar. Holding and cooling times were 35 s and 15 s, respectively. Due to the physical ageing, in the newly produced specimens, modulus changes may occur during the first few days of fabrication. Therefore, the ready materials were set aside for a week to avoid the potential post crystallization effects.

For the calorimetric measurements, small pieces were cut from the core of the injection molded bars. The sample mass was kept between 3 and 5 mg and hermetically sealed aluminum crucibles were used as sample holder. We may note that the small pieces of the samples were cut from the core of the products, since in these ISO 527-1:2019 dumbbell shaped specimens [36] with 4 mm thickness, the elastic properties are governed by the core structure, not by the skin. This fact will be revealed in the further section concerning the microscopic studies.

For the microscopic studies thin slices with 70 microns were cut from the standard bars to present the skin-core structure of these cross sections. The cuts were prepared using Reichert-Jung Polycut Sliding Microtome machine with automatic cutting sequence.

2.2 Characterization techniques

Young's modulus values were evaluated by Instron 5566 type tensile testing machine (Instron, Germany) with ISO 527-1:2019 [36]. Gauge length was 115 mm and crosshead speed of 0.5 mm/min was applied until 0.3% deformation occurs, in which range the modulus values were measured.

Melting characteristics were analyzed by DSC. Five different differential scanning calorimeters were implemented where three out of them were power compensation types: Perkin Elmer DSC 7, Perkin Elmer Diamond DSC-IC, Perkin Elmer DSC-8500, and the remaining two were heat-flux instruments: Q2000 DSC, Perkin Elmer STA6000. All the instruments were calibrated by high purity gallium, indium and tin reference standard materials. In all measurements, single heating run from 30 to 220 °C was performed with heating rate of 10 °C min^{-1}. As purge gas, high purity nitrogen atmosphere (20 mL min^{-1}) was applied. We have to highlight here that the single heating run deviates from the usual calorimetric protocol from the study of melting and crystallization of polymeric materials, because polymers are usually studied after elimination of the thermal and mechanical prehistory. However, in our case we are interested in the crystalline structure of the injection molded specimen, so we must use the first heating run for evaluation.

Moreover, it is necessary to add that to obtain accurate experimental results the temperature and heat flow calibration of the calorimeters were checked as well. Indium Calibration Standard is used to re-check the calibration of all DSC instruments. Indium has a transition point (onset temperature) of 156.60 °C and its enthalpy of fusion is 28.45 ± 0.2 J g^{-1}. Accordingly, the onset temperature and fusion enthalpy results of each calorimeter ($T_{\text{onset,av.}}$ = 156.88 ± 0.21 °C and $\Delta H_{\text{fusion,av.}}$ = 28.57 ± 0.1 J g^{-1}) were compared to these reference values and based on the displayed results it was concluded that our DSC apparatuses are well-calibrated.

Supermolecular structure of the injection molded bars was characterized by polarized light microscopy (PLM) using a Zeiss Axisocope equipped by a Leica DMC 320 digital camera. The images were recorded using Leica IM50 software. All thin films were placed between crossed polarizers and an additional λ-plate located diagonally was used to enhance the contrast of the image.

2.3 Estimation methods of modulus

As it is mentioned before, our approach calculates modulus values from crystallinity and lamellar thickness data obtained from calorimetric measurements, similarly to the pioneering model of Pukánszky et al. [32]. The mathematical form our empirical equation is an exponential function [34] given in Eq. (1):

$$E = E_a + \left(E_c - E_a\right) e^{-\left(\left(\frac{1-X}{X}\right)^{\alpha} + \left(\frac{T_m^0 - T_{av}}{T_m^0}\right)^{\beta}\right)^{\gamma}}, \tag{1}$$

where E_a and E_c are the tensile modulus values for completely amorphous and perfectly crystalline polymer, respectively. T_{av} is the average melting temperature, X is the crystallinity, T_m^0 is the equilibrium melting temperature and α, β, γ are iterative constants.

E_a, the minimum stiffness or the stiffness of the amorphous iPP is in between 0.01–0.02 GPa and 0.01 GPa is used in this study, since we always used this value during our previous works [33, 34].

All constants used for the calculations are summarized in the Table 2 [34, 37]. We have to consider that these constants are material-specific, however, by following an estimation protocol [34], these constants can be obtained for other polymers as well. In the previous studies concerning this model, the constants were calculated for iPP, PA6 and PLA [34, 35].

Since the necessary constants are already known, only two parameters are required to evaluate from calorimetric curves: crystallinity and average melting temperature. Crystallinity values can be calculated from the enthalpy of fusion data by Eq. (2):

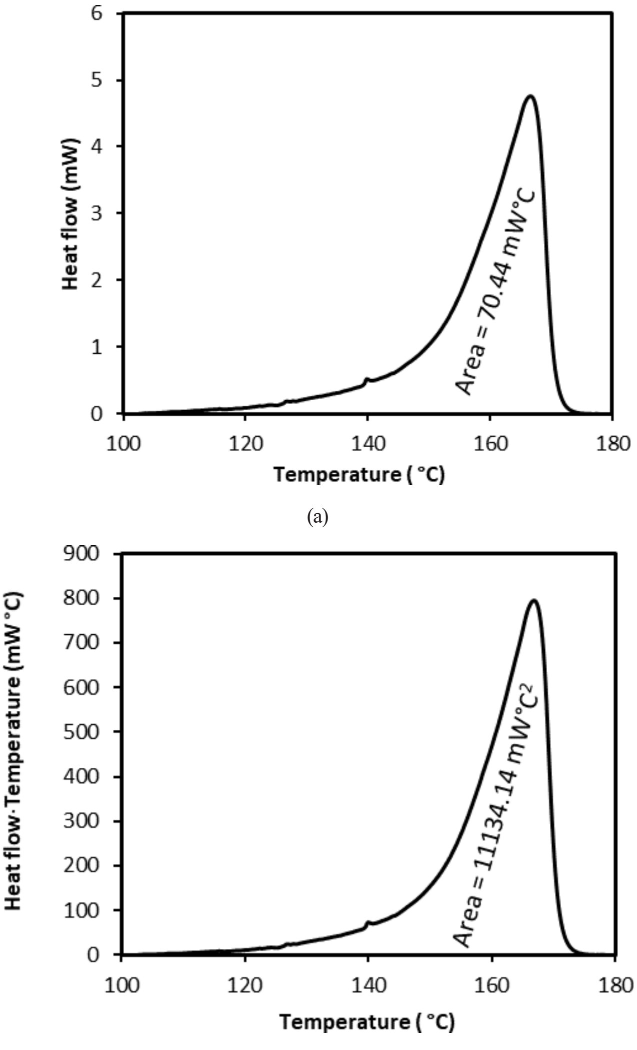
$$X = \frac{\Delta H_m}{\Delta H_m^0}. \tag{2}$$

ΔH_m is the experimentally obtained enthalpy of fusion based on the melting curve and ΔH_m^0 is the equilibrium enthalpy of fusion. ΔH_m^0 is taken from the literature, which is 148 J/g [37].

The other parameter to be determined is average melting temperature and it can be calculated directly from the melting curve by using the Eq. (3):

$$T_{av} = \frac{\int \dot{Q} T dT}{\int \dot{Q} dT}. \tag{3}$$

As it seems from Eq. (3), the average melting point can be evaluated in two simple steps. The temperature is multiplied with the heat flow curve generated by calorimetry and the area under the curve should be determined. Then the computed value needs to be divided by the area under heat flow curve. Examples of the aforementioned curves are given in Fig. 1.



(a)

(b)

Fig. 1 Heat flow curve (a), Heat flow · Temperature curve (b)

3 Results and discussion

3.1 Estimation of raw data for modulus calculations

Evaluation of E_c value for iPP by simple tensile experiments is not possible. According to van Krevelen and te Nijenhuis [38], estimation of the stiffness of perfectly crystalline polymer can be achieved theoretically by measuring the propagation velocity of longitudinal sound waves in the material. The advantage of this method is that it handles the polymer as a polycrystalline material instead being a single crystal. The single crystals usually have direction dependent properties due to the symmetry and geometry of their unit cell. However, polycrystalline polymers contain supermolecular units (spherulites for example) and they have random orientation without any external shearing force. Consequently, the properties of the polycrystalline materials are uniform in every direction, and this is much closer to the reality in practice. Although, structures formed in injection molding cannot be handled as polycrystalline structure without any orientation, its properties (modulus for example) are mainly deterned by the core structure, in which no pronounced orientation develops and usually can be treated as non-oriented polycrystalline structure. Therefore, to use sound wave propagation was the most accurate approach to model the theoretical mechanical properties of injection molded structure in a realistic way, because the propagation of the sound wave is also dependent predominantly on

Table 2 Necessary constants in Eq. (1) for the estimation of modulus [34, 37]

Samples	T_m^0 (K)	ΔH_m^0 (J/g)	E_a (GPa)	E_c (GPa)	α	β	γ
H1, R1, R2	481	148	0.01	6.6	0.32	0.51	2.43

the supermolecular structure of the core. By considering the dependence of group velocity of longitudinal sound waves on crystallinity, the generated experimental data can be linearly extrapolated to 100% crystalline polymer. Calculations are carried out by using the Eq. (4):

$$E_c = u_l^2 \rho_{cr} \,. \tag{4}$$

Where u_1 is the group velocity of the longitudinal sound wave, ρ_{cr} is the density of crystalline phase is 936 kg/m^3.

The linear extrapolation was done based on two materials, homopolymer (H1) and random copolymer (R1) samples. We have selected a homopolymer and a random copolymer grade because the ethylene content in the random copolymer may have an influence on the propagation rate, but theoretically the two materials should provide the same value for the perfect crystal since it is a perfect iPP crystal. Linear lines fitted and the propagation rate to $X = 1$ for both materials were extrapolated. The estimated values were 2608 and 2560 m/s for R1 and H1 respectively, which values are very close to the original literature value, that was 2650 m/s [38], meaning that the way of estimation of E_c and the results are reliable (see Fig. 2). Since the original work contained much more data than our verification experiment, we used the literature value of 2650 m/s for our calculation, which was taken from the book of van Krevelen and te Nijenhuis [38]. Accordingly, the obtained E_c is found to be 6.6 GPa. The experimental results were in very good agreement with our expectation that propagation rate decreases steeper in R1 due to its less regular chain structure and reduced crystallinity.

Before interpreting the location dependency results, it is important to understand skin-core structure of polymers. Skin-core is a typical crystal morphology in injection molded products. For these specimens, based on PLM evaluations (illustrated in Fig. 3) core constitutes around 85% of the whole optimized injection molded specimens. Even the lowest core composition is predominantly accountable for small deformations. Therefore, as stated before, the samples were taken from only core of the specimens.

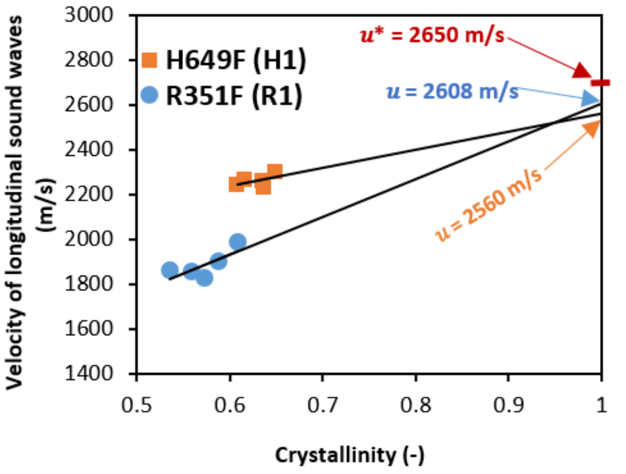


Fig. 2 Propagation velocity of sound waves as a function of crystallinity ($R_{R1}^2 = 0.86$; $R_{H1}^2 = 0.73$). * Propagation velocity of longitudinal sound waves (u) for perfectly crystalline polymer ($X = 1$) according to van Krevelen and te Nijenhuis [38]

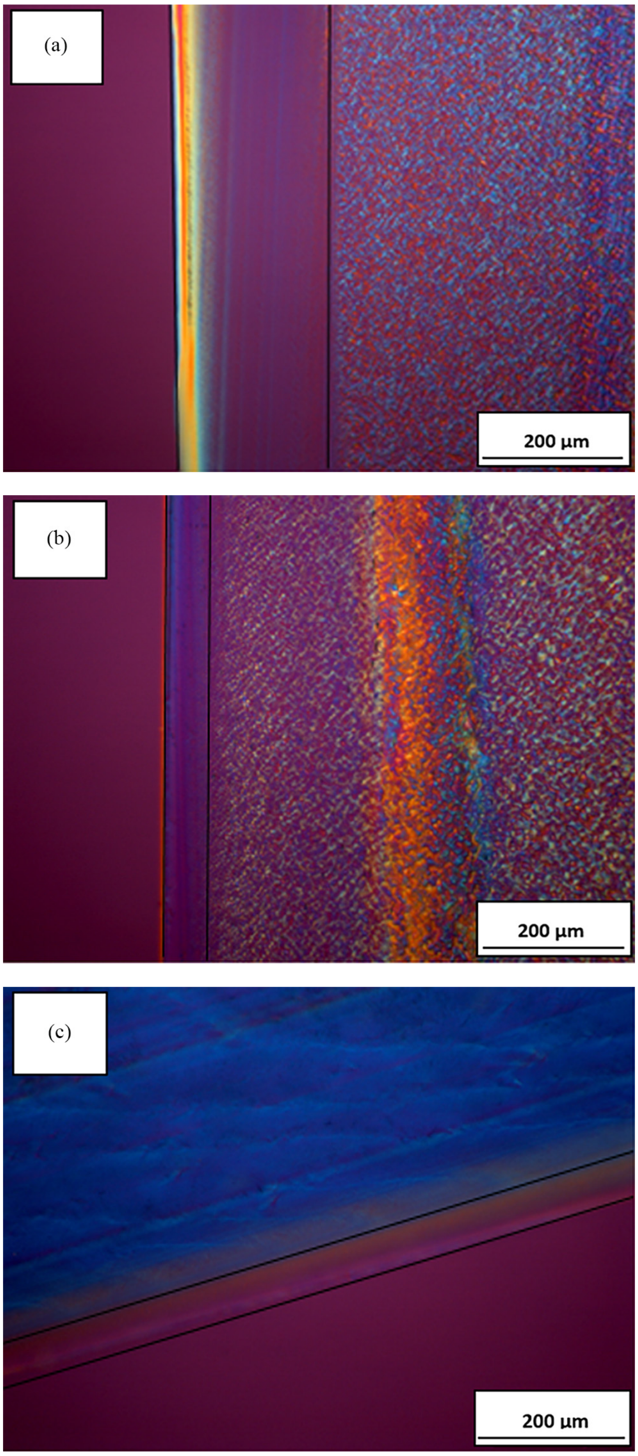


Fig. 3 PLM images of samples – (a) H1, (b) R1, (c) R2

First, location dependency of the calculated modulus values was evaluated to see if taking samples from different arbitrary points of the specimen has any considerable effect on the results. Thus, samples were cut out from different points of the dumbbell shape specimen as illustrated in Fig. 4 and calorimetric measurements were performed, subsequently, by employing DSC 7. Based on the generated melting curves, crystallinity and average melting temperature were estimated via Eqs. (2) and (3), respectively.

Interpreting the obtained results, and it can be clearly seen that no significant effect of localization was observed. The average and the standard deviation of the results are given in Table 3. The standard deviation for the crystallinity, and average melting temperature was small and they were originated from the standard experimental inaccuracies of a calorimetric measurements. This fact implies that injection molding was carried out well and if so, it should not matter from which location the samples were cut.

In the next step, tensile modulus of the materials was evaluated with tensile testing machine. Load-deformation data was extracted from apparatus, and modulus values were calculated manually by using Eq. (5) based on the raw specimen data for each sample:

$$E = \frac{l_0}{A} \times \text{slope} \, . \tag{5}$$

Where l_0 is the length of the specimen, A is the cross-section area, that is the multiplication of width and thickness of the specimen.

As it is demonstrated in Fig. 5, the equation of the fitted line is evaluated in the initial stage of elongation, precisely, in the 0.1–0.3 percentage deformation range and the slope was determined. Length, width, and thickness values were constant, being 115, 10, and 4 mm respectively.

The manual calculation was preferred in order to evade possible inaccuracies and errors of automated results in the favor of more precise results. The experimental modulus values evaluated based on the tensile test specimen raw data are shown in Table 4. The manually deduced data is taken as reference for further comparison to predicted values with model Eq. (1).

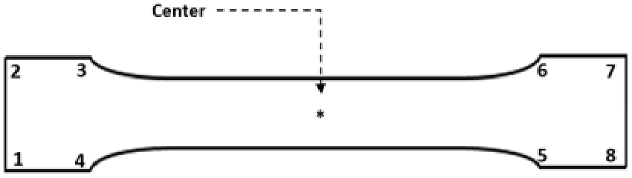


Fig. 4 Location of measurement points

Table 3 Obtained results for different location points of the specimens

	ΔH_m (J/g)	X (%)	T_{ave} (°C)
H1	85.50 ± 3	0.60 ± 0.02	156.20 ± 1
R1	78.60 ± 3	0.52 ± 0.02	130.10 ± 1
R2	82.38 ± 5	0.56 ± 0.04	131.30 ± 2

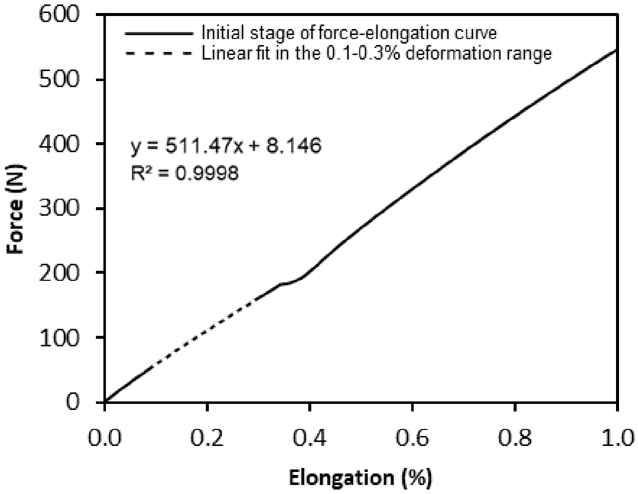


Fig. 5 Evaluation of slope of the force-elongation curve

Also, to be confident about the consistency of tensile test evaluations, the correlation between yield stress values and moduli was checked. Based on Fig. 6, the results can be counted as reliable.

3.2 Calculation of modulus based on calorimetric data

We have to note that Eq. (1) predicts tensile moduli with reasonable accuracy [33–35], however the shape of the

Table 4 Manually evaluated modulus values for each material

iPP grade name	Modulus values (manual) (GPa)	Standard deviation
H1	1.48	0.02
R1	0.80	0.01
R2	1.01	0.01

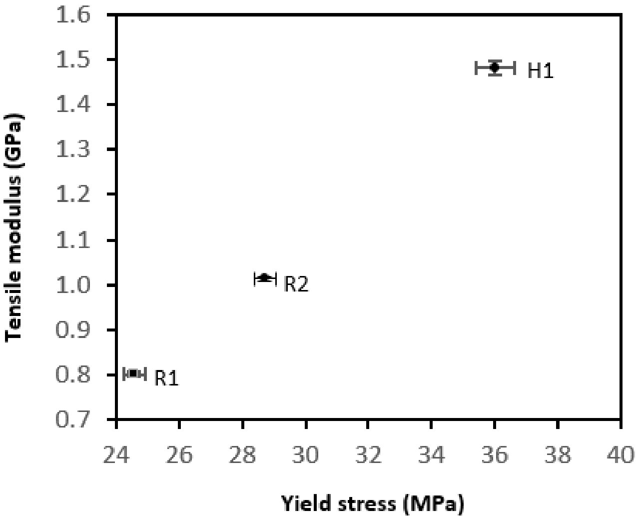


Fig. 6 Modulus as a function of yield stress for used materials

correlation is an exponential function instead of an S-type curve. Accordingly, in higher crystallinity ranges, around $X = 99\%$, the decrease in crystallinity is accompanied by steep decrease of modulus. However, we may speculate on this question, since a very small decrease in crystallinity should not result in large drop of modulus, similarly that small increase in crystallinity does not enhance modulus in the amorphous region. Accordingly, we have two fixed points at E_c and E_a, moreover, a lot of experimental points in a relatively wide crystallinity range between E_c and E_a. This function should give an S-type curve, thus the previous form of the equation was transformed into a new one (Eq. (6)). This new mathematical form represents an S-type logistic function curve and allows the prediction of moduli in higher crystallinity values mathematically possible.

$$E = E_a + \frac{E_c - E_a}{1 + \left(\left(\frac{1-X}{X} \right)^{\alpha} + \left(\frac{T_m^0 - T_{av}}{T_m^0} \right)^{\beta} \right)^{\gamma}} \tag{6}$$

The next open question is how to obtain modulus values in the high crystallinity range, which can assist the fitting of Eqs. (1) and (6). The problem with this crystallinity range is that experimentally recorded modulus cannot be obtained here. We have assumed that the modulus value can be calculated using Eq. (4) and the slope of the linear correlation represented in Fig. 2 for H1 (H649F). We have used the slope of homopolymers, since this can be closer to the ideal crystal structure than the data of random copolymers. The iterative constants of Eq. (6) are presented in Table 5 and the results of the fitting procedure is given in Fig. 7. Both of the equations, Eqs. (1) and (6) are fitted and compared in the Fig. 7. An insertion about the high crystallinity range demonstrates the major difference between the two equations. It should be noted that all material constants, like E_a, E_c, T_m^0 remained the same as in Table 2.

The fitting of Eqs. (1) and (6) were done on data points published earlier [33–35], and the R-square of the fitting was always larger than 0.995. Both equations give almost similar trends in the range of crystallinity between 0.4 and 0.8, which covers mostly the practical range of most frequent PP samples in the practice. It can be seen clearly that Eq. (6) fits much better to the simulated results at high crystallinity range. Although, we have to note that the simulated points cannot be handled as an evidence, but the trend presented by Eq. (6) seems to be more realistic according to our assumption described above.

Table 5 New iterative constants of Eq. (6)

Samples	α	β	γ
H1, R1, R2	0.33	0.35	4.80

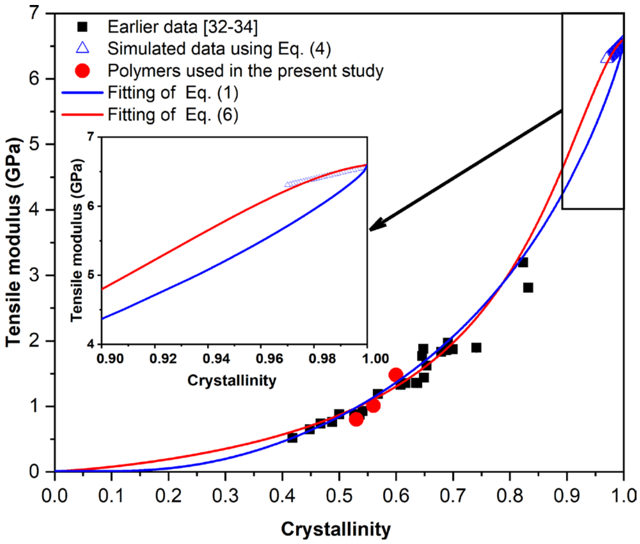


Fig. 7 Fitting results of Eqs. (1) and (6)

Modulus prediction was done for all materials included in Table 1 using both Eqs. (1) and (6). The characteristic data of crystallization was determined using five different calorimetric instruments, that mentioned in the experimental part in detail. The goal was to verify the robustness of the prediction model by checking it with various calorimetric devices that have different working principles.

Based on the results, that are summarized in Table 6 and visually demonstrated in Fig. 8, it can be claimed that generally, a reasonably good agreement was found between the estimated results and experimentally measured ones, which was valid in the case of each instrument and each material. However, some instruments showed more accuracy than others. Unsurprisingly, DSC 7 and DSC Diamond performed the best among all, since these particular instruments with power compensation working principles are known to be comparably accurate in general.

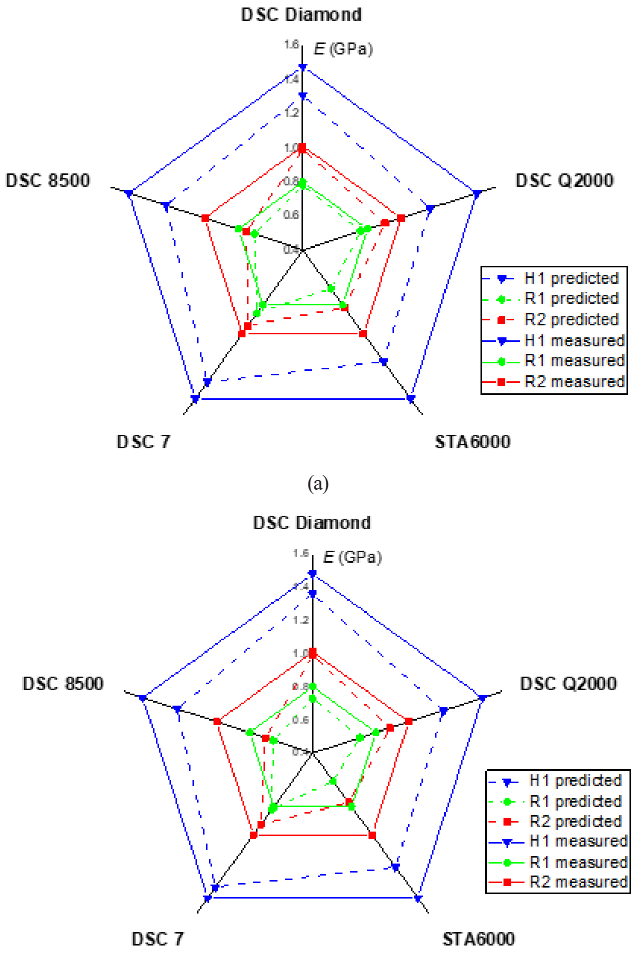
The visual depiction of the results (Fig. 8) evidently shows that the exponential and the logistic model equations presented similar outcomes, except the latter one being relatively more accurate in case of copolymers.

In fact, there are other factors that have an influence on the outcomes, such as the calibration of the instruments, the internal architecture of the devices, the precision of proper baseline setting meanwhile evaluating the melting curves et cetera. Moreover, the aforementioned two calorimeters were comparably more accurate due to the fact that the introduced model with its constants was adjusted to these instruments, meaning that there is a direct link between the calibration of these instruments and the model.

Table 6 Comparison of predicted moduli with 5 calorimetric instruments to experimentally measured values

Name of the instrument	H1		R1		R2	
	Exponential[a] (GPa)	Logistic[b] (GPa)	Exponential[a] (GPa)	Logistic[b] (GPa)	Exponential[a] (GPa)	Logistic[b] (GPa)
DSC 7	1.40 ± 0.10	1.36 ± 0.09	0.82 ± 0.08	0.86 ± 0.06	0.93 ± 0.13	0.95 ± 0.11
DSC Diamond	1.36 ± 0.06	1.31 ± 0.06	0.73 ± 0.07	0.78 ± 0.06	0.99 ± 0.11	0.99 ± 0.10
DSC Q2000	1.23 ± 0.07	1.19 ± 0.07	0.70 ± 0.13	0.76 ± 0.11	0.89 ± 0.12	0.91 ± 0.11
DSC 8500	1.26 ± 0.07	1.25 ± 0.05	0.65 ± 0.07	0.70 ± 0.06	0.70 ± 0.07	0.75 ± 0.06
STA6000	1.25 ± 0.11	1.21 ± 0.08	0.61 ± 0.06	0.68 ± 0.05	0.77 ± 0.10	0.82 ± 0.05
Experimental values	1.48 ± 0.02		0.80 ± 0.01		1.01 ± 0.01	

[a] Predicted Modulus with exponential function and [b] Predicted Modulus with logistic function



(a)

(b)

Fig. 8 Visual representation of instrument dependency of the modulus estimations based on logistic function (a), and exponential function (b)

4 Conclusions

This study aims to verify the reliability of a modulus prediction model for semicrystalline polymers. The reliability analysis was carried out by inspecting the dependency of the results on the implemented instruments and test location of the specimen. The details regarding the model are described in the paper step by step to make it reproducible for other materials. Moreover, the modified model equation that is applicable to estimate tensile modulus in case of high crystallinity values ($X \approx 99\%$) is introduced. It is also significant to note that estimation of completely crystalline iPP based on the propagation velocity of sound waves was performed and turned out be well-matched with the value in the literature. In general, reasonably good agreement was found between predicted and measured modulus values in case of both versions of the model equation. It was revealed that some instruments, namely, power compensated type calorimeters. are more reliable for this study than the others and also if injection molding is done properly, then it doesn't matter where the samples are taken from the specimen.

Data availability statement

The processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The research reported in this paper is part of project no. BME-NVA-02, implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021 funding scheme.

References

[1] Krigbaum, W. R., Roe, R.-J., Smith, K. J. "A theoretical treatment of the modulus of semi-crystalline polymers", Polymer, 5, pp. 533–542, 1964. https://doi.org/10.1016/0032-3861(64)90202-2

[2] Schrauwen, B. A. G., Janssen, R. P. M., Govaert, L. E., Meijer, H. E. H. "Intrinsic deformation behavior of semicrystalline polymers", Macromolecules, 37(16), pp. 6069–6078, 2004. https://doi.org/10.1021/ma035279t

[3] Boyd, R. H. "The Mechanical Moduli of Lamellar Semicrystalline Polymers", Journal of Polymer Science: Polymer Physics Edition, 21(4), pp. 493–504, 1983. https://doi.org/10.1002/pol.1983.180210401

[4] Bigg, D. M. "Mechanical property enhancement of semicrystalline polymers—A review", Polymer Engineering and Science, 28(13), pp. 830–841, 1988. https://doi.org/10.1002/pen.760281303

[5] Kennedy, M. A., Peacock, A. J., Mandelkern, L. "Tensile Properties of Crystalline Polymers: Linear Polyethylene", Macromolecules, 27(19), pp. 5297–5310, 1994. https://doi.org/10.1021/ma00097a009

[6] Kalay, G., Sousa, R. A., Reis, R. L., Cunha, A. M., Bevis, M. J. "The enhancement of the mechanical properties of a high-density polyethylene", Journal of Applied Polymer Science, 73(12), pp. 2473–2483, 1999. https://doi.org/10.1002/(SICI)1097-4628(19990919)73:12<2473::AID-APP16>3.0.CO;2-O

[7] Schrauwen, B. A. G., Breemen, L. C. A. V., Spoelstra, A. B., Govaert, L. E., Peters, G. W. M., Meijer, H. E. H. "Structure, deformation, and failure of flow-oriented semicrystalline polymers", Macromolecules, 37(23), pp. 8618–8633, 2004. https://doi.org/10.1021/ma048884k

[8] Galeski, A. "Strength and toughness of crystalline polymer systems", Progress in Polymer Science, 28(12), pp. 1643–1699, 2003. https://doi.org/10.1016/j.progpolymsci.2003.09.003

[9] Horváth, F., Bihari, L., Menyhárd, A. "Effect of *N*,*N*′-Dicyclohexyl Terephthalic Dihydrazide on the Crystallization and Properties of Isotactic Polypropylene", Periodica Polytechnica Chemical Engineering, 66(2), pp. 182–191, 2022. https://doi.org/10.3311/PPch.19074

[10] Popli, R., Mandelkern, L. "Influence of structural and morphological factors on the mechanical properties of the polyethylenes", Journal of Polymer Science Part B: Polymer Physics, 25(3), pp. 441–483, 1987. https://doi.org/10.1002/polb.1987.090250301

[11] Katti, S. S., Schultz, M. "The microstructure of injection-molded semicrystalline polymers: A review", Polymer Engineering and Science, 22(16), pp. 1001–1017, 1982. https://doi.org/10.1002/pen.760221602

[12] Doyle, M. J. "On the effect of crystallinity on the elastic properties of semicrystalline polyethylene", Polymer Engineering and Science, 40(2), pp. 330–335, 2000. https://doi.org/10.1002/pen.11166

[13] Humbert, S., Lame, O., Séguéla, R., Vigier, G. "A re-examination of the elastic modulus dependence on crystallinity in semi-crystalline polymers", Polymer, 52(21), pp. 4899–4909, 2011. https://doi.org/10.1016/j.polymer.2011.07.060

[14] Seferis, J. C., McCullough, R. L., Samuels, R. J. "Influence of Structure on the Dynamic Mechanical Properties of Crystalline Polymers", Journal of Macromolecular Science, Part B, 13(3), pp. 357–380, 1977. https://doi.org/10.1080/00222347708208764

[15] Andrews, E. H. "Morphology and Mechanical Properties in Semicrystalline Polymers", Pure and Applied Chemistry, 39(1–2), pp. 179–194, 1974. https://doi.org/10.1351/pac197439010179

[16] Janzen, J. "Elastic moduli of semicrystalline polyethylenes compared with theoretical micromechanical models for composites", Polymer Engineering and Science, 32(17), pp. 1242–1254, 1992. https://doi.org/10.1002/pen.760321710

[17] McCullough, R. L., Wu, C. T., Seferis, J. C., Lindenmeyer, P. H. "Predictions of limiting mechanical performance for anisotropic crystalline polymers", Polymer Engineering and Science, 16(5), pp. 371–387, 1976. https://doi.org/10.1002/pen.760160517

[18] Crist, B., Fisher, C. J., Howard, P. R. "Mechanical Properties of Model Polyethylenes: Tensile Elastic Modulus and Yield Stress", Macromolecules, 22(4), pp. 1709–1718, 1989. https://doi.org/10.1021/ma00194a035

[19] Lee, B. J., Parks, D. M., Ahzi, S. "Micromechanical modeling of large plastic deformation and texture evolution in semi-crystalline polymers", Journal of the Mechanics and Physics of Solids, 41(10), pp. 1651–1687, 1993. https://doi.org/10.1016/0022-5096(93)90018-B

[20] Kardos, J. L., Raisoni, J. "The potential mechanical response of macromolecular systems—A composite analogy", Polymer Engineering and Science, 15(3), pp. 183–190, 1975. https://doi.org/10.1002/pen.760150310

[21] Horn, T. D., Heidrich, D., Wulf, H., Gehde, M., Ihlemann, J. "Multiscale simulation of semi-crystalline polymers to predict mechanical properties", Polymers, 13(19), 3233, 2021. https://doi.org/10.3390/polym13193233

[22] Nikolov, S., Doghri, I., Pierard, O., Zealouk, L., Goldberg, A. "Multi-scale constitutive modeling of the small deformations of semi-crystalline polymers", Journal of the Mechanics and Physics of Solids, 50(11), pp. 2275–2302, 2002. https://doi.org/10.1016/S0022-5096(02)00036-4

[23] Laschet, G., Spekowius, M., Spina, R., Hopmann, C. "Multiscale simulation to predict microstructure dependent effective elastic properties of an injection molded polypropylene component", Mechanics of Materials, 105, pp. 123–137, 2017. https://doi.org/10.1016/j.mechmat.2016.10.009

[24] Sedighiamiri, A., Van Erp, T. B., Peters, G. W. M., Govaert, L. E., van Dommelen, J. A. W. "Micromechanical Modeling of the Elastic Properties of Semicrystalline Polymers: A Three-Phase Approach", Journal of Polymer Science Part B: Polymer Physics, 48(20), pp. 2173–2184, 2010. https://doi.org/10.1002/polb.22099

[25] Mori, T., Tanaka, K. "Average stress in matrix and average elastic energy of materials with misfitting inclusions", Acta Metallurgica, 21(5), pp. 571–574, 1973. https://doi.org/10.1016/0001-6160(73)90064-3

[26] Benveniste, Y. "A new approach to the application of Mori-Tanaka's theory in composite materials", Mechanics of Materials, 6(2), pp. 147–157, 1987.
https://doi.org/10.1016/0167-6636(87)90005-6

[27] Hill, R. "Theory of mechanical properties of fibre-strengthened materials–III. self-consistent model", Journal of the Mechanics and Physics of Solids, 13(4), pp. 189–198, 1965.
https://doi.org/10.1016/0022-5096(65)90008-6

[28] Hori, M., Nemat-Nasser, S. "Double-inclusion model and overall moduli of multi-phase composites", Journal of Engineering Materials and Technology, 116(3), pp. 305–309, 1994.
https://doi.org/10.1115/1.2904292

[29] Gueguen, O., Ahzi, S., Belouettar, S., Makradi, A. "Comparison of micromechanical models for the prediction of the effective elastic properties of semicrystalline polymers: Application to polyethylene", Polymer Science Series A, 50(5), pp. 523–532, 2008.
https://doi.org/10.1134/S0965545X08050064

[30] Tucker, C. L., Pham, T. N. "Microstructural Development of Polymer Blends in Chaotic Flows", AIP Conference Proceedings, 712, pp. 22–27, 2004.
https://doi.org/10.1063/1.1766495

[31] Horváth, Z., Menyhárd, A., Doshev, P., Gahleitner, M., Tranninger, C., Kheirandish, S., Varga, J., Pukánszky, B. "Effect of molecular architecture on the crystalline structure and stiffness of iPP homopolymers: Modeling based on annealing experiments", Journal of Applied Polymer Science, 130(5), pp. 3365–3373, 2013.
https://doi.org/10.1002/app.39585

[32] Pukánszky, B., Mudra, I., Staniek, P. "Relation of Crystalline Structure and Mechanical Properties of Nucleated Polypropylene", Journal of Vinyl & Additive Technology, 3(1), pp. 53–57, 1997.
https://doi.org/10.1002/vnl.10165

[33] Menyhárd, A., Suba, P., László, Z., Fekete, H. M., Mester, Á. O., Horváth, Z., Vörös, G., Varga, J., Móczó, J. "Direct correlation between modulus and the crystalline structure in isotactic polypropylene", Express Polymer Letters, 9(3), pp. 308–320, 2015.
https://doi.org/10.3144/expresspolymlett.2015.28

[34] Molnár, J., Jelinek, A., Maloveczky, A., Móczó, J., Menyhárd, A. "Prediction of tensile modulus of semicrystalline polymers from a single melting curve recorded by calorimetry", Journal of Thermal Analysis and Calorimetry, 134(1), pp. 401–408, 2018.
https://doi.org/10.1007/s10973-018-7487-1

[35] Molnár, J., Hertner-Horváth, A., Menyhárd, A. "Prediction of tensile modulus from calorimetric melting curves of polylactic acid with pronounced cold crystallization ability", Polymer Testing, 95, 107112, 2021.
https://doi.org/10.1016/j.polymertesting.2021.107112

[36] ISO "ISO 527-1:2019 Plastics – Determination of tensile properties – Part 1: General principels", International Organization for Standardization, Geneva, Switzerland, 2019.

[37] Monasse, B., Haudin, J. M. "Growth transition and morphology change in polypropylene", Colloid and Polymer Science, 263(10), pp. 822–831, 1985.
https://doi.org/10.1007/BF01412960

[38] van Krevelen, D. W., te Nijenhuis, K. "Properties of polymers: Their correlation with chemical structure; their numerical estimation and prediction from additive group contributions", 4th ed., Elsevier, 2009. ISBN 9780080548197