



An Extended Halpin–Tsai Model for Predicting the Tensile Modulus of Semi-Crystalline Polymer Nanocomposites: The Effect of Induced/Intrinsic Crystallinity

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ABSTRACT

In this study, a novel strategy was devised to evaluate the mechanical properties of semi-crystalline polymer nanocomposites. To this end, the Halpin-Tsai model was comprehensively improved to also include the impact of dispersion quality, nanoparticle aggregation/agglomeration, the formation of the polymer/particle interphase region and induced/self-crystallinity. Besides enhancing the tensile modulus of the system, a particular fraction of either dispersed or clustered nanoparticle domains was considered to participate in the induced crystallization process (active domains). The content of active domains was estimated using the Gutzow-Dobrev theory or a specifically designed method based on the requirements of the system. On the contrary, the so-called inactive domains were assumed to remain distributed within the polymer matrix and contribute to the system response mechanism. The mechanical features of the interphase region were defined using the De Gennes's self-similar carpet theory considering the molecular characteristics of the polymer phase. Moreover, the porosity index and bonding nature between aggregated or agglomerated nanoparticles were used to estimate the tensile modulus of the clustered domains. The model validation process was conducted via benchmarking its predictions against the obtained data from the literature, which showed acceptable agreement and proved the model to be a quite accurate interpretation tool.

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1. Introduction

In polymer nanocomposites, the interaction between the polymer matrix and nanoparticles is commonly pointed out as the main factor to define the final physical/mechanical features of the nanocomposite system [1, 2]. Defining the dispersion quality of the nanoparticles in the polymer medium is the primary stage to evaluate the contribution of nanoparticles to responses against environmental driving forces [3, 4]. The dispersed or clustered nanoparticle domains are proved to have quite different effects on the system since they can offer a versatile set of capabilities, depending on their structure [5, 6]. Nanoparticle clusters are formed by aggregated and agglomerated nanoparticles of which considerable differences originate from the type of interparticle bonding [7, 8]. The aggregated nanoparticles leverage the formation of a sinter bridge between each pair of nanoparticles in the cluster. The sinter bridge is a particular connection bond between two nanoparticles, holding them firmly and resulting in the formation of a strong network of interlocked nanoparticles [2, 9, 10]. On the other hand, it is the relatively weak Van der Waals force between agglomerated nanoparticles that gathers them together in a cluster [11-13]. This type of interparticle bonding usually leads to the formation of a very loose structure that can barely resist even very small force fields. Different studies report that the nanoparticle clusters formed in a nanocomposite system are a product of either the synthesis or mixing stages, and they consist of both aggregated and agglomerated nanoparticles [14-16]. The structure of the cluster directly affects its ability to withstand the force transferred from the matrix. These structures, regardless of the arrangement of the nanoparticles, are intrinsically porous due to the presence of vacant spaces and consequently, affected by their porosity index. However, the role of

porosity in changing the actual volumetric content of nanoparticle domains, interphase, polymer matrix, etc. is mostly neglected.

The formation of crystals in semi-crystalline polymer matrices can be categorized into induced and inherent classes [17-19]. The inherent crystallization chiefly depends on the molecular characteristics of the polymer matrix, whereas the induced crystallization occurs due to the presence of nucleation agents such as impurities, nanoparticles, etc. [20-22]. The dispersed and clustered nanoparticle domains are prone to becoming the nuclei of newborn crystals and to enhancing the degree of crystallinity. Generally, crystals act as reinforcing sub-structures in a semi-crystalline polymer matrix, however, the magnitude of the resultant reinforcement strictly depends on the amount and size of crystals [10, 23, 24]. This also applies to semi-crystalline polymer nanocomposites, in which, besides the nanoparticle domains, crystals also act as reinforcing constituents. Notably, while assessing the performance of the constituents of the system, it is imperative to distinguish between the active nanoparticle domains contributing to the induced crystallization process and those simply distributed in the amorphous phase. Obtaining such specific information enhances the understanding of the complex behavior of the nanocomposite systems; however, it is also accompanied by particular challenges, such as those in experimental processes.

The formation of the polymer/particle interphase region is introduced as a key phenomenon in polymer nanocomposites, which affects almost all components of the system [11, 25, 26]. Combining this with the high surface area of nanoparticles clarifies the better performance of polymer nanocomposites compared to micro/macromposites [27, 28]. Polymer chains tend to sediment on the surface of

adsorbing nanoparticles based on the molar weight. The high molar mass physisorption theory states that the relatively large adjacent polymer chains are more likely to be adsorbed onto the surface of nanoparticles [2, 29, 30]. This, combined with the scaling theories, leads to the conclusion that the physical/mechanical features within the interphase are distance-dependent and vary with the molecular characteristics of the polymer [31-33].

The analytical modeling techniques to predict the tensile modulus of semi-crystalline polymer nanocomposites are known as sophisticated approaches to define the interaction between the constituents of the system. They can facilitate the comprehension of the system performance based on the behavior of the internal components. Semi-crystalline polymer nanocomposites, besides being affected by the presence of nanoparticle domains, are also involved with the induced/inherent crystallization phenomenon which, can defy all common understandings of such systems. Accordingly, the analytical modeling approach can be regarded as a very practical tool to delve into the system behavior on considerably small scales. To this end, in this study, the Halpin-Tsai (HT) model was improved to predict the tensile modulus of semi-crystalline polymer nanocomposites. A deep parametric correlation between the HT related system factors and actual controlling phenomena in the nanocomposite system was formed. The volumetric content of dispersed and clustered nanoparticle domains was defined based on the dispersion quality and porosity index. The percentage of induced crystallinity was calculated using a developed form of the Gutzow–Dobrev theory based on the thermal behavior of nanocomposite samples at different cooling rates. This helped to define the amount of the residual nanoparticle domains within the amorphous phase as well as indicating their direct role in

enhancing the mechanical features of the polymer matrix. The average mechanical characteristics of the interphase region were approximated using a specially developed distance-dependent scaling function around both dispersed and clustered nanoparticle domains. The proposed model, besides preserving the structure of the original equation of the HT model, provides a considerably sophisticated framework to predict the tensile modulus of semi-crystalline polymer nanocomposites. The validation process was performed using the comparison of the model data with the experimental results obtained from the literature. The results showed that the model could perfectly estimate the induced crystallization and characterize the particular interaction between active components against the exerted force. The analysis of parameters (e. g. sensitivity, correlation, etc.) revealed the independent and direct influence of main model parameters on the final results. Moreover, the almost negligible values of the error obtained in the validation stages proved the capabilities of the model to be used as an interpreting tool for assessing the distinguished behavior of each constituent of the system. The results also showed that at the low volumetric content of nanoparticles up to 35% of the crystallinity degree can be achieved due to the induced crystallization phenomenon, attributed to the high dispersion quality. The expanded model explicitly suggests that the participation of the nanoparticles in the crystallization process affects the mechanical properties of the nanocomposite systems. This key point, as a novel approach to defining the detailed collaboration of the polymer/particle interphase, was found to be the main advantage of the present model compared to similar ones.

2. Analytical modeling

The Halpin-Tsai mechanical model has been widely used due to its simplicity and efficiency. However, this model is based on ideal assumptions, including perfect interface adhesion, uniform distribution of nanoparticles, and neglect of nanoscale effects. These assumptions lead to considerable discrepancies between the predicted results and experimental data. Factors such as the physical/mechanical features of the interphase, the formation of nanoparticle networks, the orientation of the filler, and phenomena such as the aggregation and agglomeration of nanoparticles are determinative parameters in polymer nanocomposites that are not considered in the classical Halpin-Tsai model. Consequently, a related model was designed and developed considering the following terms:

- Dispersion quality for nanoparticles
- Difference between aggregation and agglomeration phenomena
- Nanoparticle clusters include both aggregated and agglomerated nanoparticles
- Formation of polymer/particle interphase
- Impact of Cluster size
- No polymer penetration within the cluster structure
- Impact of crystals on the mechanical properties of the system
- Participation of nanoparticles in the induced crystallization process

The classical Halpin-Tsai model is as follows [34]:

$$E_c = E_m \frac{1 + \xi \eta \nu_f}{1 - \eta \nu_f} \quad (1)$$

$$\eta = \frac{\left(\frac{E_f}{E_m}\right) - 1}{\left(\frac{E_f}{E_m}\right) + \xi} \quad (2)$$

where, E_m is the modulus of the pure matrix, ξ is the shape parameter dependent on the reinforcement geometry, E_f and ν_f are the modulus and volume fraction of nanoparticle respectively. In this article, the shape factor is considered as $\xi = 2$ for spherical nanoparticles [34]. The extended model including all mentioned fundamental terms can be stated as follows:

$$E_{nc} = E'_m \frac{1 + \xi \eta_r \nu_{rX}}{1 - \eta_r \nu_{rX}} \quad (3)$$

$$\eta_r = \frac{\left(\frac{E_{rX}}{E'_m}\right) - 1}{\left(\frac{E_{rX}}{E'_m}\right) + \xi} \quad (4)$$

According to Equations (3) and (4), three phases are included in the model: (i) the matrix phase, including amorphous and crystalline regions, with an effective tensile modulus of E'_m (ii) the interphase region, and (iii) dispersed/clustered nanoparticle domains. Notably, E'_m represents the improved tensile modulus of the matrix, due to induced crystallinity, ν_{rX} and E_{rX} are the crystallinity-dependent effective volume fraction and effective modulus of the total nanoparticle domains respectively. Generally, ignoring the influence of crystallinity degree, the effective volume of nanoparticles can be stated as follows:

$$\nu_r = \frac{V_p^d}{V_t} \left(1 + \frac{V_i^{d^{total}}}{V_p^d}\right) + \frac{V_p^c}{(1 - \chi)V_t} \left(1 + \frac{V_i^{c^{total}}}{V_p^c}\right) \quad (5)$$

Where, χ denotes the porosity index, which is reported to be in the range of 36-37% for fully packed random clusters [35]. V_t is the total volume of the system, V_i^d and V_i^c are the volumes of the interphase region around a single dispersed and clustered nanoparticle domain respectively, V_p^d and V_p^c are the volumes of the fully dispersed nanoparticles and the total volume of the nanoparticles

clusters respectively. Besides, the overall volumes of the interphase region around all dispersed and clustered nanoparticle domains are denoted by $V_i^{d^{total}}$ and $V_i^{c^{total}}$ respectively:

$$V_i^d = \frac{4}{3}\pi((R_n + \tau)^3 - R_n^3) \quad (6)$$

$$V_i^c = \frac{4}{3}\pi((R_c + \tau)^3 - R_c^3) \quad (7)$$

$$V_i^{d^{total}} = \frac{V_p^d V_i^d}{V_n} \quad (8)$$

$$V_i^{c^{total}} = \frac{V_p^c V_i^c}{V_c} \quad (9)$$

$$V_p^d = V_t D \phi_{np} \quad (10)$$

$$V_p^c = V_t (1 - D) \phi_{np} \quad (11)$$

where, ϕ_{np} is the total volume fraction of nanoparticles, R_n and R_c are the radii of the nanoparticle and cluster respectively. D represents the dispersion quality of nanoparticles in the matrix ($0 \leq D \leq 1$). Notably, nanoparticle clusters are considered as spherical structures in the present study which besides simplifying the modeling procedure also bring about some limitations. Chiefly, nanoparticle aggregates/agglomerates have random shapes which directly affect the volume of the formed polymer/particle interphase in the system. Moreover, the stress distribution in a randomly shaped cluster of random form can considerably differ from its distribution in a perfectly spherical structure, due to the significant difference in the average number of contact points per nanoparticle. Similarly, ignoring the effect of crystallinity on the effective modulus of the system, E_r can be stated as follows:

$$E_r = \gamma^d \frac{(E_n V_p^d + \bar{E}_i V_i^{d^{total}})}{V_r^d} + \gamma^c \frac{(E_c V_p^c + \bar{E}_i V_i^{c^{total}})}{V_r^c} \quad (12)$$

where, $V_r^d = V_p^d + V_i^d$, $V_r^c = V_p^c + V_i^c$, E_c is the effective tensile modulus of a nanoparticle cluster, $V_r = \nu_r V_t$, E_r is the effective tensile modulus of nanoparticle domains, including dispersed and clustered domains, $\bar{E}_i$ and E_n are the tensile modulus of the interphase and dispersed nanoparticles respectively. γ^d and γ^c are the fractions of dispersed and clustered nanoparticle domains and can be defined as follows:

$$\gamma^d = \frac{V_p^d}{V_p^d + \frac{V_p^c}{(1-\chi)} \left(\frac{D_n}{D_c}\right)^3} \quad (13)$$

$$\gamma^c = \frac{V_p^c}{V_p^c + V_p^d (1-\chi) \left(\frac{D_c}{D_n}\right)^3} \quad (14)$$

Given the presence of sinter bridges and weak Van der Waals forces between aggregated and agglomerated nanoparticles, respectively, E_c can be stated as follows:

$$E_c = \alpha E_n + (1-\alpha) E_{vdw} \quad (15)$$

where, α is the fraction of aggregated particles and $(1-\alpha)$ is the fraction of agglomerated nanoparticles, E_n represents the tensile modulus of nanoparticles and E_{vdw} is the van der Waals modulus between two nanoparticles for the aggregated state, also defined using the Hamaker model as follows:

$$E_{vdw} = \frac{A_H}{3R_n H^2} \quad (16)$$

where, A_H is the Hamaker constant, H is the separation distance between agglomerated nanoparticles [9].

Now, to obtain $\bar{E}_i$ the average interphase modulus, a circular element was considered for a nanoparticle and its interphase region, and using the gradient model and two boundary conditions of $R_1 = R_n \rightarrow E(r) = E_n$ and

$R_2 = (R_n + \tau) \rightarrow E(r) = E_m$, the average interphase Young's modulus was calculated as follows [36]:

$$\bar{E}_i = \frac{1}{V_i} \int_{R_n}^{R_n+\tau} E(r) 2\pi r^2 dr = \frac{3E_n}{(R_n + \tau)^3 - R_n^3} \cdot \frac{\tau}{\ln\left(\frac{E_n}{E_m}\right)} \left[(R_n + \tau)^2 - R_n^2 \right] \quad (17)$$

where, V_i and τ are the volume and thickness of the interphase region. Notably, no particular difference between the interphase formed around the dispersed or clustered nanoparticle domains is assumed in Equation (17). It is common to assume τ equal to the gyration radius (R_g) of the polymer chains around the nanoparticle domains ($R_g^2 \approx nl^2 C_\infty / 6$, n denotes the average number of mers per chain, l is the length of the C-C bond and C_∞ represents Flory's characteristic ratio).

Given that nanoparticle domains contribute to crystallization, it is crucial to distinguish between induced and intrinsic crystallinity. Accordingly, the overall crystallization degree in a polymer nanocomposite (X_{cr}) can be stated based on the induced and intrinsic crystallization degrees (X_{cr}^{ind} and X_{cr}^{int} , respectively) as follows:

$$X_{cr} = X_{cr}^{int} + X_{cr}^{ind} \quad (18)$$

$$X_{cr}^{ind} = \left(\frac{B^* - B}{B} \right) \times 100 \quad (19)$$

$$E_m' = \Gamma \left(E_a (1 - X_{cr}) + E_{cr} X_{cr} \right) \quad (20)$$

where, Γ is a component correlation factor, adjusting the interaction between amorphous and crystalline sections of the system, E_a is the amorphous modulus, E_{cr} denotes the crystal modulus and the ratio $((B^* - B)/B)$ is the relative intensity of the nucleation by nanoparticles, which can be obtained using the Gutzow-Dobrev theory [18]. Parameters B

and B^* should be measured based on the thermodynamic characteristics of the nanocomposite system at different cooling rates (for more information, please refer to reference No. [18]). We have previously proposed a practical strategy to define E_{cr} based on the combination of the intrinsic crystallinity degree of the polymer matrix (X_{cr0}) with a particularly designed equivalent box model according to which $E_{cr} = E_m - E_a (1 - X_{cr0}) / X_{cr0}$ [18].

Besides the method represented for calculating X_{cr}^{ind} based on Gutzow-Dobrev theory, it is also possible to estimate the induced crystallinity degree using the difference between the melting enthalpy of the nanocomposite sample (ΔH_{nc}^m) and neat polymer (ΔH_{nc}^p), ignoring the effect of nanoparticle domains on the intrinsic crystallinity

$$X_{cr}^{ind} = (\Delta H_{nc}^m - \Delta H_P^m) / ((1 - w_n) \Delta H_{P_0}^m),$$

$\Delta H_{P_0}^m$ is the melting enthalpy of a 100% crystalline system and w_n denotes the weight fraction of nanoparticles). However, the impact of nanoparticle domains on the chain relaxation and cooling rate of the system is neglected in this strategy, but it still can be regarded as a simple approach in cases where DCS results at different cooling rates are not available.

Notably, Equation (20) represents a new scale to define the tensile modulus of the polymer matrix affected by the induced crystallinity. However, not all dispersed or clustered nanoparticles contribute to the formation of polymer crystals. The volume of active and inactive nanoparticle domains (V_{ap}^j and V_{iap}^j , respectively) in the crystallization process can be stated using the crystallization participation coefficient (f_{cr}) as follows:

$$f_{cr}^j = \frac{X_{cr}^{ind}}{X_{cr}^{ind}|_{\max}} \left(\frac{R_n}{R_j} \right)^\beta ; j = d, c \quad (21)$$

$$V_{ap}^j = f_{cr}^j V_p^j ; j = d, c \quad (22)$$

$$V_{iap}^j = (1 - f_{cr}^j) V_p^j ; j = d, c \quad (23)$$

where, $X_{cr}^{ind}|_{\max}$ is the maximum percentage of the induced crystallization in a nanocomposite system. ($X_{cr}^{ind}|_{\max} = AX_{cr}^{ind}$, A is a model parameter ($A > 1$)) and β represents the size correlation factor. The ratio $(R_n/R_j)^\beta$ equals 1 for dispersed nanoparticle domains while its value decreases by increasing the size of clustered domains, suggesting the lower capability of big clusters to participate in the induced crystallization process. In line with this, the total volume of the interphase region around the inactive dispersed or clustered nanoparticle domains can be stated as ($V_{iai}^j = (1 - f_{cr}^j) V_i^{j^{total}}$; $j = d, c$).

Therefore, using Equation (23), it is possible to incorporate the effect of the induced crystallization into Equation (5) and define v_{rX} as follows:

$$v_{rX} = \frac{V_{iap}^d}{V_t} \left(1 + \frac{V_{iai}^d}{V_{iap}^d} \right) + \frac{V_{iap}^c}{(1 - \chi)V_t} \left(1 + \frac{V_{iai}^c}{V_{iap}^c} \right) \quad (24)$$

Similarly, the same correction should be applied in the case of Equation (12) to define E_{rX} :

$$E_{rX} = \gamma^d \frac{(E_n V_{iap}^d + \bar{E}_i V_{iai}^d)}{V_{inr}^d} + \gamma^c \frac{(E_c V_{iap}^c + \bar{E}_i V_{iai}^c)}{V_{inr}^c} \quad (25)$$

where, $V_{inr}^d = V_{iap}^d + V_{ini}^d$ and

$$V_{inr}^c = V_{iap}^c + V_{ini}^c.$$

3. Results and Discussion

As discussed in Section 2, the complexity of the interactions between system components made it imperative to involve almost all impactful factors in the modeling procedures. This, however, improves the reliability and accuracy of the model but also increases the number of the included parameters, especially those to be obtained via fitting approaches. Accordingly, a sensitivity analysis was performed to assess the impact of the main parameters on the final analytical results. Table 1 shows that the sensitivity of the model to some parameters, such as A , E_n , D , Γ , E_m , R_n , ϕ_{np} , X_{cr} , etc., is significantly high, while to other parameters it is categorized in the moderate class. This suggests that the material characteristic factors as well as the correlative features between system components are decisive in analyzing the mechanical properties of the system.

On the other hand, the correlation analysis between the main impactful parameters (Figure 1) shows the least dependence of the fitting parameters and their direct impact on the accuracy of the model.

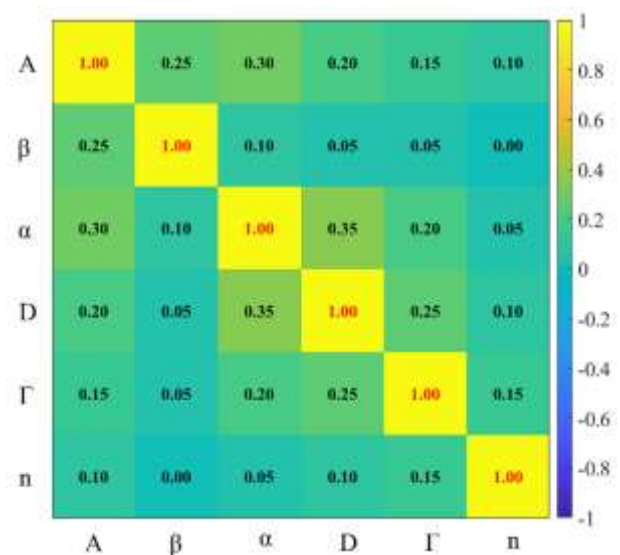


Figure 1. Correlation analysis between the main parameters of the model.

Table 1.

Parameter sensitivity analysis.

Parameter	Description	Category	Sensitivity
A	Model constant (>1)	Fitting	High
β	Size correlation factor	Fitting	Low
α	Cluster aggregation fraction	Fitting	Moderate
D	Dispersion quality	Fitting	High
Γ	Matrix model coefficient	Fitting	High
E_m	Matrix Modulus	Measurable	High
ξ	Shape factor	Constant	Moderate
R_n	Nanoparticle radius	Measurable	High
ϕ_{np}	Volume fraction	Measurable	High
χ	Porosity index	Constant	Low
A_H	Hamaker constant	Physical	Low
H	Inter-particle distance	Physical	Moderate
E_n	Nanoparticle Modulus	Physical	High
M_n	MW (Mn)	Measurable	Moderate
C_∞	Flory ratio	Physical	Moderate
M_u	Unit MW	Physical	Low
l	Bond length	Physical	Low
V_t	Total volume	Setup	Low
B^*	Pure GD parameter	Measurable	Moderate
B	NC GD parameter	Measurable	High
X_{cr}	Crystallinity	Measurable	High
E_a	Amorphous Modulus	Physical	Moderate
X_{cr0}	Ref Crystallinity	Measurable	Moderate

To better comprehend the parametric interactions, some comparative analyses were also performed. The impact of the interphase region on the physical/mechanical features of a polymer nanocomposite system was previously discussed. This region, in addition to enhancing the interaction between the polymer and nanoparticle regions, elevates the overall tensile modulus of the polymer matrix. According to Equation (17), the tensile modulus of the interphase directly depends on the physical/mechanical features of the nanoparticle domain (e. g. size and tensile modulus) and the related thickness of the region. As shown in Figure 2, increasing R_n , at any value of τ decreases E_i , which can be ascribed to the corresponding adverse effect on

the mechanism of the formation of the interphase. According to the high-molar mass physisorption theory, the formation of the polymer/particle interphase begins with the adsorption of larger polymer chains followed by smaller ones [29, 37]. Given the constant thickness of the interphase, the increase in the polymer/particle interface area necessarily causes more small chains to be entrapped within the region which naturally alleviates the tensile modulus. This, evidently, can be compensated by increasing the thickness of the interphase region, which theoretically can be interpreted as higher adsorption energy from the nanoparticle domain, resulting in more resistant against the external forces [11].

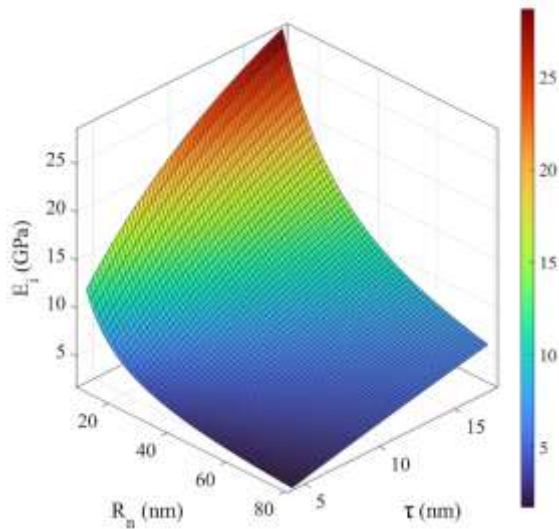


Figure 2. Variation of the tensile modulus of the interphase (E_i) with the size of the nanoparticle domain (R_n) and thickness of the interphase region (τ)

According to Equation (3), the contribution of nanoparticle domains to the crystallization phenomenon affects both their effective tensile modulus and volume fraction. Figure 3(a) demonstrates the impact of the porosity index and crystallization participation coefficient of clustered nanoparticle domains on ν_{rx} . Clearly, the increase in f_{cr}^c at any value of χ

decreases the overall available volumetric content of nanoparticle domains in the amorphous phase, attributed to the increasing participation of clustered domains in the induced crystallization process. Besides, the augmentation of the porosity index, at any value of f_{cr}^c , causes ν_{rx} to increase, since a higher porosity index can be theoretically referred to as bigger clusters. This simplifying assumption, which considers the clustered domains as a spherical object consisting of gathered nanoparticles and vacant spaces, was employed to mitigate the modeling complexities. Notably, this increasing trend is more significant at lower values of f_{cr}^c where the clustered nanoparticles are less likely to be wrapped by crystals. Based on the results illustrated in Figure 3(b), increasing f_{cr}^d also decreases ν_{rx} due to the similar adverse impact of the induced crystallinity. These variations are clearly independent of the porosity index since χ only affects the clustered nanoparticle domains.

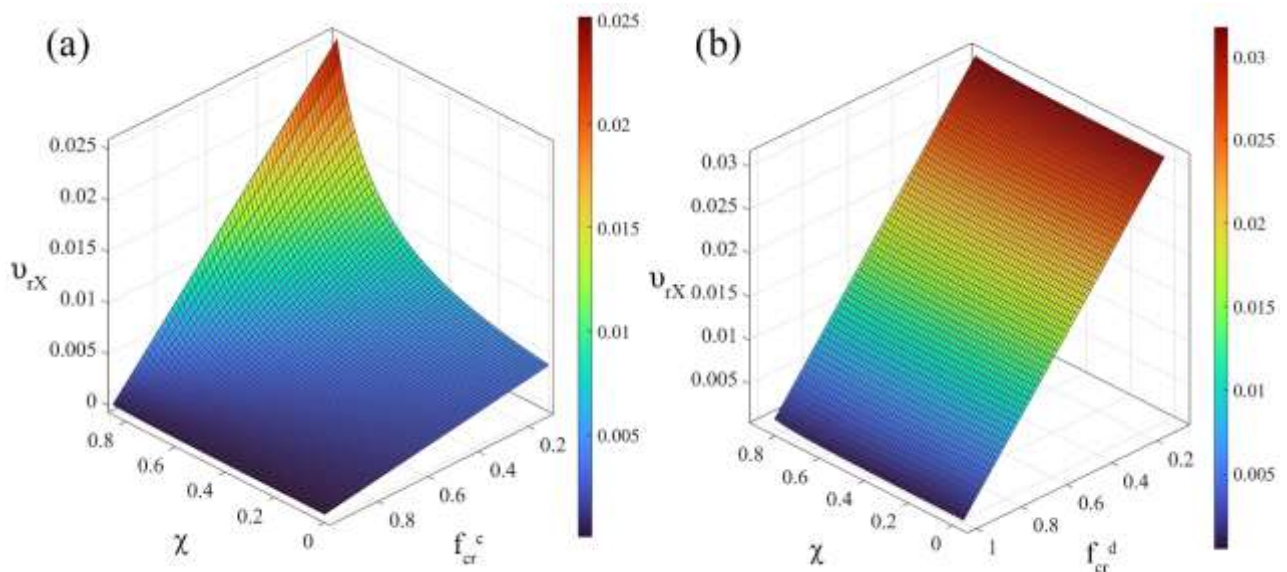


Figure 3. Variation of the crystallinity-dependent effective volume fraction of nanoparticle domains (ν_{rx}) with the porosity index (χ) and crystallization participation coefficient of (a) clustered and (b) dispersed nanoparticle domains.

The variation of E_{rX} with τ and X_{cr} is demonstrated in Figure 4. It is clear that regardless of the value of the crystallinity degree, the increase in τ decreases the effective tensile modulus of the nanoparticle domains. This may seem contradictory at first glance since, based on the results exhibited in Figure 2, the increase in τ increases E_i . It should be mentioned that Equation (25) defines the effective tensile modulus as a combination of the tensile modulus of the nanoparticle domains and the interphase around them. Subsequently, the increase in the interphase thickness increases its volumetric contribution and decreases E_{rX} , since this particular region has a considerably lower tensile modulus than the core nanoparticle domain. On the other hand, as is clear, the variation of X_{cr} has no impact on E_{rX} since the variation of the crystallinity degree has no particular impact on the polymer/particle interactions. This indicates the independent performance of parameters related to interphase and crystallinity.

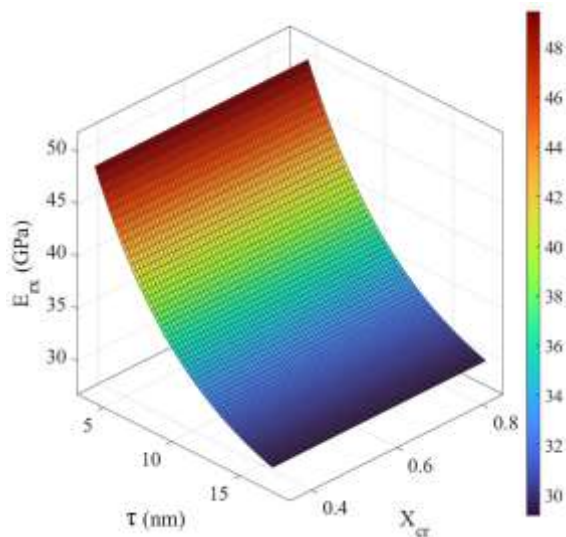


Figure 4. Variation of the effective tensile modulus of nanoparticle domains (E_{rX}) with the interphase thickness (τ) and crystallinity degree (X_{cr}).

As stated by Equation (20), the intrinsic tensile modulus of the semi-crystalline polymer

matrix can be affected by the presence of the nanoparticle. This can also be attributed to the contribution of nanoparticle domains to the induced crystallization phenomenon, which also significantly alters the performance of the crystalline phase. Based on the results reflected in Figure 5, at any value of Γ , the increase in the degree of crystallinity increases E'_m , however, this increasing trend is more significant as Γ shifts toward higher values. From a physical perspective, the interaction between amorphous and crystalline phases can be quite complicated in semi-crystalline polymer nanocomposites and can not be defined using a simple rule of mixtures. However, the introduced component correlation factor theoretically reflects the effect of amorphous/crystalline interface, the presence of nanoparticle nuclei in crystals and the dispersion quality of crystals on the overall tensile modulus of the matrix and compensates for the undesired discrepancies. The present model, as mentioned before (Table 1), is highly sensitive to Γ , which makes this particular parameter quite impactful in improving the accuracy.

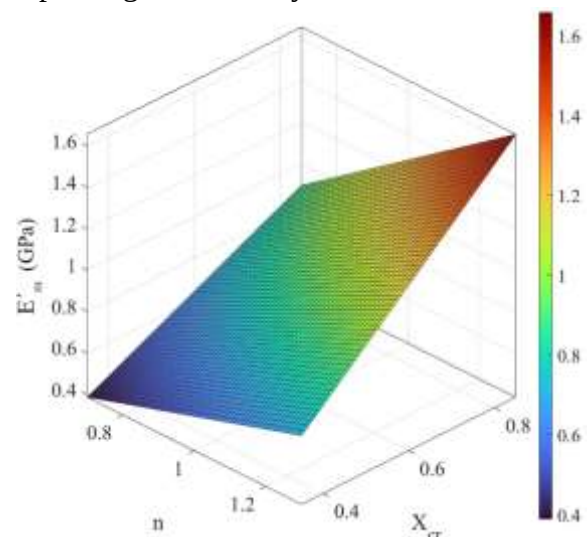


Figure 5. Variation of the effective tensile modulus of the polymer matrix (E'_m) with the component correlation factor (Γ) and crystallinity degree (X_{cr}).

To validate the model, a different set of data was obtained from the literature regarding the tensile modulus and crystallinity features of various polymer nanocomposite systems. It should be noted that to employ the present model, it is essential to acquire particular experimental information such as the result of

tensile/DMTA and DSC tests. Also, all nanocomposite samples chosen for benchmarking the accuracy of the model contain spherical nanoparticles with specific dispersion quality. The information regarding the evaluated nanocomposite samples is summarized in Table 2.

Table 2.

Characteristic parameters of the nanocomposite systems used to validate the model (PE: Polyethylene+silica nanoparticles, PEM: Polyethylene + surface-modified silica nanoparticles and PA: Polyamide + silica nanoparticles).

Sample	ϕ_p (Vol.%)	E_m (Mpa)	R_n (nm)	D_c^* (nm)	R_g (nm)
PE5 [18]	0.5	960	30	689	8.69
PE5 [18]	0.75			816	
PE2 [18]	2			1122	
PEM5 [18]	0.5			720	
PEM75 [18]	0.75			876	
PEM2 [18]	2			1792	
PA1 [38]	0.42	1780	20	403	2.89
PA3 [38]				612	

E_n (Mpa) = 72e3 [18]; A_H = 6.2e-2 [9]; H = 0.2e-9 [9]; χ = 36% [39]

*Fitting parameter

Also, Table 2 presents the fitted and experimental values for each sample. As it can be seen, parameter A , which defines the $X_{cr}^{ind} \big|_{\max} / X_{cr}^{ind}$ ratio, is almost the same for all PE and PEM samples, denoting the maximum participation of the dispersed nanoparticles in the induced crystallization process. However, for PA samples, the corresponding A values indicate the absence of a significant fraction of nanoparticle domains serving as nucleation agents. This can be attributed to the lower tendency of polymer chains compressed around nanoparticle domains to form crystals due to effects such as polarity. The size correlation factor is also the same for all PE and PEM samples, while it takes higher values in the case of PA samples. This can be also ascribed to the effect of the segmental chain behavior around nanoparticle domains. In

other words, when the polymer chains are prone to form induced crystals, the amount of active nanoparticle domains increases, which corresponds to the decrement of parameter β . On the contrary, the alleviation in the ability of the polymer chain to relax around an arbitrary nucleus increases β and, given that R_n/R_c is a decimal number, decreases f_{cr}^j . According to the sensitivity analysis table, parameter α has a moderate impact on the accuracy of the model; however, the analytical assessments showed that it still can adversely affect the analytical outcomes if not optimize them. As shown in Table 2, the fraction of aggregated nanoparticles in silica clusters can be considered similar in the PE and PEM samples, regardless of the size of clustered domains. Based on the correlation analyses (Figure 1), α , besides parameter A that is constant, is

positively correlated to D , meaning that the variation of D somewhat compensates for the ignored changes in α . The value of Γ for each sample decreases by increasing the content of nanoparticles. This can be ascribed to the reliance of the polymer matrix on the nanoparticle domains, rather than the crystals, to resist the exerted force. This also suggests that the presence of nanoparticle domains, which are covered with the interphase region, can negatively affect Γ . The degree of crystallinity is another factor that increases by increasing the nanoparticle content, indicating

the active role of certain domains in the induced crystallization process. Low error values reveal the accuracy of the developed Halpin-Tsai model and prove the practicality of the applied fundamental assumptions. It should be noted that the present model, as mentioned before, includes some fitting parameters that, in addition to providing profound insight into the performance of semi-crystalline polymer nanocomposites, demonstrate that the model can be quite reliable as an interpretive tool.

Table 3.

Model parameters and analytical results for the evaluated samples.

Sample	A^*	β^*	α^*	D^* (%)	Γ^*	X_{cr} (%)	X_{cr}^{int} (%)	X_{cr}^{ind} (%)	E_{exp} (Mpa)	E_{nc} (Mpa)	err (%)
PE5	1.001	0.01	0.79	92	0.997	64.72	44.71	20.01	980	980.62	6e-6
PE75				90	0.991	65.39	61.43	3.96	984	984.01	8e-8
PE2				80	0.987	67.55	64.39	3.16	1011	1011.3	2e-6
PEM5				90	0.997	62.23	61.31	0.92	945	944.4	5e-6
PEM75	1.003			82	1.146	63.21	61.81	1.4	1102	1102.1	5e-7
PEM2	1.001			71	1.125	66.21	62.91	3.3	1131	1131.2	2e-4
PA1	1.6	0.8	0.87	96	2.44	32.1	29.53	2.57	2383	2383	-
PA3	1.49	0.61	0.81	84	2.3	33.7	29.41	4.29	2385	2385.4	2e-6

*Fitting Parameter

4. Conclusion

In this study, we addressed a critical gap in the analytical modeling of polymer nanocomposites: the frequent omission of complex microstructural features that dictate macroscopic performance. By integrating fundamental physical phenomena specifically dispersion quality, the distinction between aggregates and agglomerates, the formation of the polymer/particle interphase, and the impact of induced crystallization into a modified Halpin–Tsai framework, we have developed a more robust and detail-aware predictive model. Our findings demonstrate that treating nanoparticle domains, as a combination of dispersed and clustered phases, provides a significantly more realistic representation of

nanocomposite morphology than traditional homogeneous assumptions. The developed approach for distinguishing the mechanical contributions of clustered domains (comprising both aggregated and agglomerated nanoparticles) proves to be a practical tool for understanding the heterogeneous nature of these materials. Furthermore, our analysis confirms that the interphase modulus is a function of the constituent moduli, interphase thickness, and domain size, while the Gutzow–Dobrev theory provided reliable insights into the role of induced crystallization. The sensitivity analysis further highlighted that while fitting parameters operated independently, and their relative influence on the mechanical outcome

varied significantly, underscoring the complexity of the underlying physics. Despite the improved accuracy of the proposed framework, certain limitations must be considered to ensure a balanced perspective. The predictive power is inherently tied to the precise optimization of empirical fitting parameters; as such, its application requires accurate input data that may be difficult to obtain without extensive characterization. Additionally, while the model accounts for clustering, it utilizes simplified geometric representations that may not fully capture the nature, high degree of polydispersity, or the complex three-dimensional connectivity of real-world nanoparticle networks. Finally, the current framework focuses on the tensile modulus and does not yet account for time-dependent viscoelasticity or nonlinear failure mechanisms. These limitations define the most promising directions for future research. Moving forward, it is essential to validate this framework against experimental datasets where dispersion states, interphase thickness, and crystallinity are independently controlled and characterized via advanced microscopy (TEM/SEM) and scattering techniques. Such work will allow for the transition from empirical parameter fitting toward a more deterministic approach. Future iterations of the model should also aim to incorporate nanoparticle surface functionalization and non-uniform interphase properties, eventually extending the framework to predict time-dependent and damage-related behaviors. Such advancements will be vital for the widespread application of this model in the design of high-performance, functional polymer nanocomposites.

Declarations

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There are no conflicts of interest between the authors to declare.

Authors' contributions:

Atiyeh Haji Mohammadi: Investigation, Validation, Formula Analysis, Writing (Review & Editing), Conceptualization, Methodology, Formula Analysis.

Esmail Sharifzadeh: Supervision, Project administration, Writing (Review & Editing), Visualization, Investigation, Validation, Conceptualization, Methodology, Resources, Formula Analysis, Software.

Nomenclature Table

Parameter	Definition
E_m	Modulus of the pure matrix
ξ	Shape parameter
E_f	Modulus of nanoparticle
V_f	Volume fraction of nanoparticle
E'_m	Effective tensile modulus
V_{rX}	Crystallinity-dependent effective volume fraction
E_{rX}	Effective modulus of the total nanoparticle domains
χ	Porosity index
V_t	Total volume of the system
V_i^d	Volume of the interphase region around a single dispersed nanoparticle domain
V_i^c	Volume of the interphase region around a clustered nanoparticle domain
V_p^d	Volume of the fully dispersed nanoparticles
V_p^c	Total volume of the nanoparticles clusters
$V_i^{d^{total}}$	Overall volume of the interphase region around all dispersed nanoparticle domains

$V_i^{c\ total}$	Overall volumes of the interphase region around all clustered nanoparticle domains
ϕ_{np}	Total volume fraction of nan
R_n	Radius of the nanoparticles
R_c	Average radius of cluster domains
D	Dispersion quality
$\overline{E_i}$	Tensile modulus of the interphase
E_n	Tensile modulus of dispersed nanoparticles
γ^d	Fractions of dispersed nanoparticle domains
γ^c	Fractions of clustered nanoparticle domains
α	Fraction of aggregated particles
A_H	Hamaker constant
H	Separation distance between agglomerated nanoparticles
V_i	Volume of the interphase region
τ	Thickness of the interphase region
R_g	Gyration radius
n	Average number of mers per chain
l	C-C bond length
C_∞	Flory's characteristic ratio
X_{cr}	Overall crystallization degree in a polymer nanocomposite
X_{cr}^{ind}	Induced crystallization degrees
X_{cr}^{int}	Intrinsic crystallization degrees
Γ	Component correlation factor
E_a	Amorphous modulus
E_{cr}	Crystal modulus
X_{cr0}	Intrinsic crystallinity degree of the polymer matrix
ΔH_{nc}^m	Melting enthalpy of the nanocomposite sample
ΔH_{nc}^p	Melting enthalpy of the neat polymer
V_{ap}^j	Volume of active nanoparticle domains
V_{iap}^j	Volume of inactive nanoparticle domains
f_{cr}	Crystallization participation coefficient
$X_{cr}^{ind} \big _{\max}$	Maximum percentage of induced crystallization in a nanocomposite system

A	Model parameter
β	Size correlation factor

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