

Practical Work of Crack Growth and Environmental Stress Cracking Resistance of Semicrystalline Polymers

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ABSTRACT: The area fraction of tie molecules at the crystal–amorphous interface, amorphous phase dynamics, average crystal strength against stem sliding, and crack growth tortuosity concepts have been used simultaneously, for the first time, to develop a model for predicting the environmental stress cracking resistance of semicrystalline polymers. The model is based on the analogy of crack growth through the amorphous phase of semicrystalline polymers in a harsh environment at adhesive polymer–substrate interfaces. The model variable consists of the practical work of crack growth (G_c) times the crack growth path tortuosity (Γ) and correlates very well with the time to failure in the full notch creep test (FNCT) through a sigmoidal-type equation: $\text{FNCT} = a\{1 + \exp[(b - G_c\Gamma)/c]\}^{-1}$, where a (3386), b (0.16), and c (0.006) are constants ($r^2 = 0.999$). G_c is calculated by multiplication of the area fraction of tie molecules at the crystal–amorphous interface,

the amorphous phase loss factor value at -25°C , and the sample storage shear modulus at the test temperature, whereas Γ is estimated as the product of the sample molecular weight and its distribution. The application of the Kendall rank correlation coefficient test as a primitive gross criterion of comparison among the proposed correlations also shows reasonable values of the rank correlation coefficient (0.891) and probability (0.000) for the new model. In other words, a point-to-point increasing or descending trend among the experimentally found data is ignored in comparison with the sound physical basis of the correlation toward the development of a comprehensive model. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2756–2762, 2008

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INTRODUCTION

Environmental stress cracking (ESC) is a slow crack growth process originating from continuous load applications on materials simultaneously exposed to aggressive environments. This mode of failure is characterized by the presence of macroscopic cracks preceded by crazed fibrillar structures.¹ ESC accounts for over 30% of all premature in-service failures of plastic parts.² In the peculiar case of polyethylene (PE), especially in such applications as blow-molded parts, geomembranes, transoceanic fiber-optic cables, and highly demanding water and gas pipes, the elucidation and specifically predictability of ESC could be of crucial importance.^{3,4}

The environmental stress cracking resistance (ESCR) of crystalline polymers is commonly believed to be governed by the population of tie molecules.^{4–9} They are polymer chains that link two or more crystalline lamellae through the amorphous phases.⁴ The existence of tie molecules was demonstrated by

Keith et al.¹⁰ in their microscopic studies. In addition, the central role of tie molecules in determining the fracture strength of crystalline polymers has been quantified by various experimental methods.^{11–17} For example, Backman and DeVries¹² measured the number of tie molecules by cutting PE with a razor blade and counting the number of resultant free radicals by an electron spin resonance technique. Also, Brown and Ward¹⁴ showed the effect of tie molecules on the low-temperature fracture stress in high- and low-molecular-weight and slowly and quickly cooled materials. Accordingly, they presented an equation for calculating the number of tie molecules in terms of the low-temperature fracture stress. Vibrational spectroscopy and Raman spectroscopy were also proved to be efficient techniques for probing the mechanically active chains that bear the main part of the load in oriented PEs by Lustiger and Ishikawa¹⁷ and Lagaron et al.,¹ respectively.

Besides experimental approaches, tie molecules are well established and have been included in various theoretical treatments through the use of statistical mechanics.^{18–21} Assuming random walk approximation for a completely isotropic amorphous phase on a cubical lattice, Guttman et al.¹⁸ computed

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the fractions of chain loops and bridges or tie chains in a semicrystalline polymer. On the other hand, Lacher and Byrant²¹ studied the influence of molecular architecture on the probability of tie molecule formation in ethylene copolymers. The effect of counts on the polymer characteristic ratio (C_∞) was the main focus of their model. Moreover, Huang and Brown²² proposed a different statistical approach aimed at the assessment of tie molecule probability for an isolated chain whose topology did not change by crystallization.

Recently, Men et al.²³ studied the effect of amorphous phase dynamics in terms of the loss factor ($\tan \delta$) at -25°C on ESCR of various PE samples with different weight-average molecular weights (M_w 's) and molecular weight distributions. They found longer failure times in samples with a higher amorphous phase $\tan \delta$ value at -25°C . They attributed their findings to longer crazed fibril capability for sustaining lower stresses leading to less deformation and fracture. The enhanced degree of mobility, as quantified by $\tan \delta$ at -25°C , was considered a factor increasing the amount of material that could be sucked in by crazed fibrils and used as the representative parameter in the ESC rate prediction.

Despite the quite long investigation history of the subject, it appears that each time just one of the effective mechanisms has been considered for rationalizing the observed material behavior. Besides the necessity of simultaneous consideration of the tie molecule density and amorphous phase dynamics, the strength of the crystals anchoring tie molecules and the real crack growth path need to be included as important parameters in new models as well. Huang and Brown²² combined the effective parameters involved in the slow crack growth of semicrystalline polymers and proposed the following predictive model:

$$\delta_0 = A\beta/(Bl_c t)\sigma^n \exp(-Q/RT) \quad (1)$$

where δ_0 , A , β , B , l_c , t , σ , n , Q , R , and T are the rate of crack opening displacement, a constant, the fraction of mobile tie molecules, a constant related to the anchoring strength of tie molecules to the crystals, the crystal thickness, the number of taut tie molecules per unit of cross-section area of the fibril, the applied stress, a material parameter, the activation energy for the micromolecular motion, the gas constant, and the test temperature, respectively. In this study, the tie molecule population, amorphous phase mobility, average crystal strength, and crack growth tortuosity have been combined to develop a new model, based on a practical work of crack growth concept, to elucidate and predict the ESCR of semicrystalline polymers.

CALCULATION OF TIE MOLECULE PROBABILITY

For predicting the ESCR of some PE samples, Men et al.²³ recently used the amorphous phase dynamics criterion and ignored completely the effect of the tie molecule population. Accordingly, they found some discrepancies in the correlation made among their measured properties, that is, ESCR versus $\tan \delta$. To overcome the shortcomings and approach a more reliable and predictive model, the tie molecule probability of Men et al.'s diverse and well-characterized samples was calculated according to Huang and Brown's equation.²² The samples were 11 PEs consisting of 8 linear homopolymers (labeled H), 1 unimodal broad molar mass distribution copolymer with two C_4H_9 branches per 1000 backbone carbon atoms (UMB), 1 bimodal molar mass distribution copolymer with 3.7 C_2H_5 branches per 1000 backbone carbon atoms (BM1), and 1 bimodal molar mass distribution copolymer with 3.1 C_4H_9 branches per 1000 backbone carbon atoms (BM2).

In Huang and Brown's equation,²² the probability of intercrystalline tie molecule formation in a chain during its crystallization from the melt (P) is quantified through the counting of chain segments long enough to span an amorphous layer plus two adjacent crystalline lamellae:

$$P = \frac{\int_L^\infty r^2 \exp(-b^2 r^2) dr}{3 \int_0^\infty \exp(-b^2 r^2) dr} \quad (2)$$

where b^2 is equal to $3/2\langle h^2 \rangle$. $\langle h^2 \rangle$ is the mean-square end-to-end distance of the entire chain in a random coil conformation:

$$\langle h^2 \rangle = C_\infty n l^2 \quad (3)$$

In other words, chain segments longer than $L = 2l_c + l_a$ form tie molecules, where l_c and l_a are the thicknesses of the crystal lamella and amorphous layer, respectively. For PE, $C_\infty = 6.8$, $l = 0.153$ nm, and n are the characteristic ratio, C—C bond length, and number of bonds, respectively. The value of L in the lower limit of the integration in eq. (2) holds for the computation of the number of chain segments having an end-to-end distance greater than L . The factor 3 in the denominator of eq. (2) denotes the effect of the lamellar geometry because each tie molecule forms along one of its dimensions.

The L value can be calculated as follows:²⁴

$$l_c = d_{ac} \alpha_c \quad (4)$$

$$l_a = d_{ac} - l_c \quad (5)$$

$$L = 2l_c + l_a \quad (6)$$

where d_{ac} is the long spacing of lamellar stacks (deduced from small-angle X-ray scattering results)

TABLE I
Computed Values of l_c , l_a , and L for Samples 1–11

L (nm)	l_a (nm)	l_c (nm)	Sample
48.11	6.69	20.72	1
50.30	7.70	21.30	2
49.30	7.90	20.70	3
52.95	9.65	21.65	4
52	9.80	21	5
57.50	13.50	22	6
50.97	11.63	19.67	7
36.41	8.59	13.89	8
39.23	9.57	14.83	9
40	8.81	15.59	10
45.27	10.33	17.47	11

and α_c is the crystal volume fraction.²³ Our computed values of l_c , l_a , and L for Men et al.'s²³ samples are presented in Table I. The degree of chain coiling and tie molecule probability depend on the polymer molecular weight. Accordingly, P/ρ (where ρ is the polymer density) was also used as a molecular-weight-independent measure of the tie molecule probability.²⁵ In addition, Seguela²⁵ recently proposed a modified version of Huang and Brown's model for calculating the overall area fraction of tie molecules at the crystal–amorphous interface (F_s):

$$F_s = P\rho N_A l_0 s_0 / M_0 (1 - \alpha_c) \quad (7)$$

where P , N_A , l_0 , s_0 , and M_0 are the probability of forming a tie molecule per chain, Avogadro's number, the length of a polymer monomer unit (0.25 nm for PE), the cross-sectional area of a single stem emerging from the crystal surface (0.18 nm² for PE), and the molecular weight of a polymer monomer unit (28 g/mol for PE), respectively.

Table II presents the M_w values, molecular weight distributions, polydispersity indices (PDIs), polymer type, time to failure in the full notch creep test (FNCT) at 80°C, and measured $\tan \delta$ values at –25°C for Men et al.'s²³ samples, which were used in the new framework for calculations, data analysis, and new model development in this study.

DISCUSSION

Although Men et al.²³ believed in the exponential enhancement of their samples' time to failure in FNCT with their corresponding degree of amorphous phase mobility, there were definitely some deviations in the expected trend (Table II). For example, samples 2 and 3 as well as samples 8 and 9 showed similar amorphous phase mobilities but different ESCRs. More remarkably, however, sample 6 provided higher ESCR than sample 5 but had a lower $\tan \delta$ value at –25°C. To evaluate quantitatively the primitive extent of the correlation between

these sets of data points, the Kendall rank correlation coefficient (τ) test was used.^{26,27} The outputs of this test are τ and probability P (please note that it is not related to the tie molecule probability, although the same letter P is used) of the null hypothesis, that is, the absence of a trend, being correct. Every data point is compared to every other data point. If the rising or descending tendency of the curve is respected when two data points are compared, a value of 1 is assigned; otherwise, a value of –1 is assigned. The higher τ is and the closer P is to 0, the less chance there is for data set randomness and their better correlation. The application of the Kendall test to the FNCT– $\tan \delta$ data set (Table II) resulted in $\tau = 0.945$ and $P = 0.000$. The obtained values of τ and P for Men et al.'s correlation showed a significant positive one among the data, the value of $\tau < 1$ emanating from the aforementioned discrepancies.

To overcome anomalies detected in Men et al.'s²³ results, the time to failure in FNCT of their samples was plotted versus another important governing parameter, that is, P , in Figure 1. Although FNCT increased exponentially with P for samples 1–8, it deviated for the rest of the samples. The values of τ and P were calculated for this data set to be 0.709 and 0.002, respectively. The substitution of P by P/ρ or F_s resulted in Figures 2 and 3. Applying the Kendall test to the data of Figures 2 and 3 led to $\tau = 0.709$ and $P = 0.002$ for the FNCT– P/ρ data set and $\tau = 0.587$ and $P = 0.012$ for the FNCT– F_s data set. The increased discrepancies can be attributed to other neglected important parameters that affect ESCR simultaneously. The dynamics of crack growth media (the amorphous phase in this case) during ESC need to be considered in one way or another. In addition, the tie molecule average anchoring strength to the lamellae and the possible crack growth path tortuosity have to be taken into account.

TABLE II
Selected Characteristics and Properties of Men et al.'s²³ Samples

Sample	$M_w \times 10^{-5}$ (g/mol)	PDI	Type	Time to failure in FNCT (h) at 80°C	$\tan \delta$ at –25°C
1	1.2	7.7	H	0.23	0.0130
2	2.1	8.9	H	0.6	0.0150
3	2.6	10.9	H	0.8	0.0150
4	3.2	11.5	H	1.4	0.0170
5	4.1	8.3	H	2.6	0.0194
6	6.8	8.2	H	7.9	0.0190
7	6.2	7.2	H	10.6	0.0198
8	8.1	8.5	H	22.5	0.0218
9	3.9	22	UMB	23	0.0218
10	3.3	38	BM1	1930	0.0260
11	4.4	44	BM2	3386	0.0317

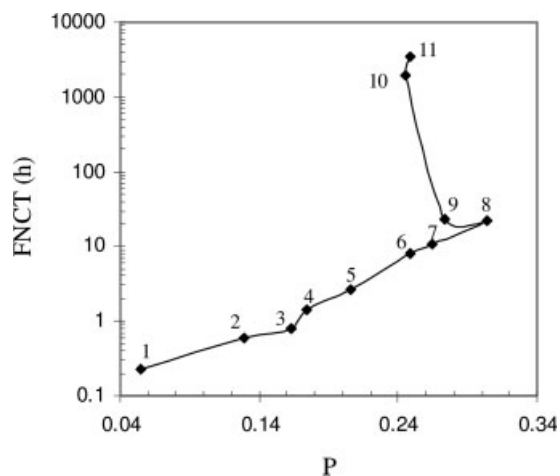


Figure 1 Time to failure in FNCT versus the calculated P parameter of the samples (the number of each sample is shown; the solid line is a guide to eye).

If this is the case, one needs to select a physically based model for combining the key governing parameters in a formula leading to a designing and predictive criterion in this respect. Sharif et al.²⁸ studied the role of the interfacial interactions and loss function of model adhesives in their adhesion to glass through the well-known Gent-Schultz equation:²⁹

$$G = WF(v) \quad (8)$$

where G is the practical work of adhesion. In addition, W is the thermodynamic work of adhesion, which depends on the density and strength of the interactions between the adhesive and substrate.

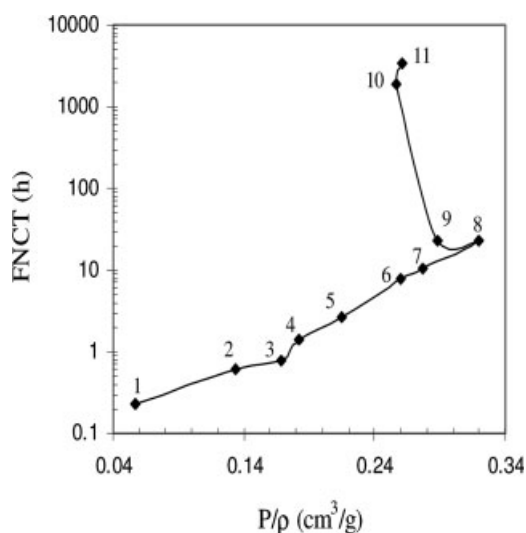


Figure 2 Time to failure in FNCT versus the calculated P/ρ parameter of the samples (the number of each sample is shown; the solid line is a guide to eye).

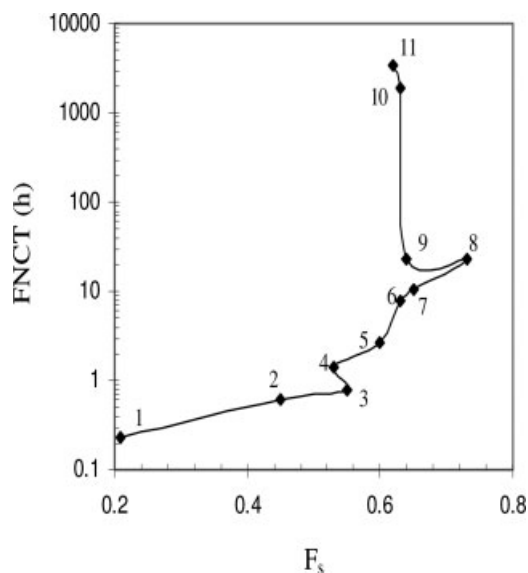


Figure 3 Time to failure in FNCT versus the calculated F_s parameter of the samples (the number of each sample is shown; the solid line is a guide to eye).

Furthermore, $F(v)$ is the joint energy dissipation term,³⁰ which depends on the crack growth rate (v). They estimated W and $F(v)$ through the surface analysis of the adhesive and substrate and the $\tan \delta$ characterization of the adhesive at the adhesion measurement temperature, respectively.²⁸ Accordingly, they could predict the interfacial adhesion of their system reasonably.

In analogy with the practical work of adhesion, crack growth under environmental stresses may be estimated by a measure of the interfacial interaction density and its strength at the crystal-amorphous interface along with the amorphous phase mobility. In other words, tie molecules can be viewed as a glue that holds the crystalline regions together and thus resists crack growth.¹⁷ Accordingly, their resistance can be estimated on the basis of their population and the lamellar stem sliding strength against pullout. In a review of the relaxation processes in crystalline polymers, Boyd³¹ interpreted the micro-molecular motion of the α relaxation as the sliding of molecular chains within the crystals. In other words, sample elasticity at the test temperature for a semicrystalline polymer depends mainly on the tie molecule anchoring strength to lamellae or the disentanglement rate [Huang and Brown's model,²² eq. (1)]. Therefore, the storage shear modulus (G') of each sample at the test temperature²³ was used as an estimation of the lamellar stem sliding strength. On the other hand, the amorphous phase $\tan \delta$ value at -25°C (for PE) can be imagined as a crack growth media energy dissipation term. Consequently, the product of P , P/ρ , or F_s by G' at the test temperature and the amorphous phase $\tan \delta$ value at -25°C can

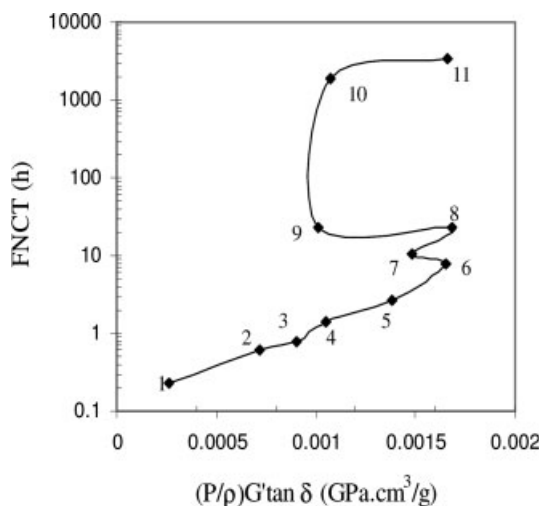


Figure 4 Time to failure in FNCT versus the calculated $(P/\rho)G'\tan\delta$ parameter of the samples (the number of each sample is shown; the solid line is a guide to eye).

be considered as the new criterion, the practical work of crack growth (G_c), that governs ESCR:

$$G_c \approx F_s G' \tan \delta \quad (9)$$

The $F_s G'$ and $\tan \delta$ terms of eq. (9) correspond to the W and $F(v)$ terms of the practical work adhesion [eq. (8)], respectively.

For validation of the proposed new criterion, the FNCT of Men et al.'s²³ samples was plotted versus G_c . For the sake of rigor, however, only P/ρ and F_s were used as measures of tie molecule probability (Figs. 4 and 5). The values of $\tau = 0.6$ and $P = 0.01$ and of $\tau = 0.345$ and $P = 0.13$ were found for the

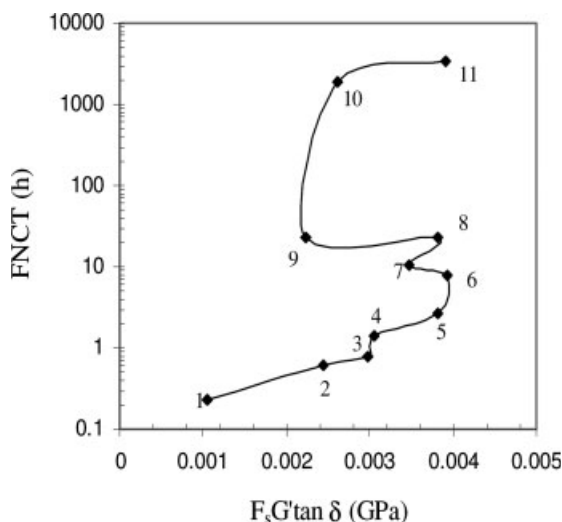


Figure 5 Time to failure in FNCT versus the calculated $F_s G'\tan\delta$ parameter of the samples (the number of each sample is shown; the solid line is a guide to eye).

FNCT- $(P/\rho)G'\tan\delta$ and FNCT- $F_s G'\tan\delta$ data sets, respectively. Worsening of τ can be attributed to other important effective parameters ignored so far.

In other words, the observed jump in FNCT of samples 10 and 11 can be mainly ascribed to the existence of high-molecular-weight fractions along with localization of short-chain branches on them.^{1,7} Long- and short-chain PEs may also take part in the formation of long and short fibrils, respectively.³²

Sharif et al.³³ used the concept of heterogeneous bond strength to justify the observed synergism in promoting polyurethane/styrene-butadiene rubber interfacial adhesion strength. The principle behind the concept was the tortuous path establishment of crack growth at the interface due to the formation of interfacial bonds with different strengths. Accordingly, the concept was used here to consider the high ESCR of bimodal PEs (samples 10 and 11 in the model). Recalling the determining role of the fibril length on craze stabilization,²³ one can conclude that crazes containing fibrils with different lengths possess different rupture resistances. Heterogeneity in rupture resistance will force a crack to grow in a tortuous path among fibrils with different lengths (Fig. 6) and consequently lead to crack growth retardation, which in turn prolongs the time to failure markedly. Considering PE chains of higher molecular weights as the basis of longer crazed fibril formation,³² one could imagine molecular weight distribution enhancement as the partitioning motive among chains with different sizes during crystallization nucleation.³⁴ Therefore, the sample's M_w multiplied by its PDI was used as the parameter implying the crack growth path tortuosity (Γ). To include the Γ term in the new model for predicting the sample FNCT, however, it seems logical to bring all the effective parameters in the same magnitude. Thus, M_w PDI values of the samples were divided by the

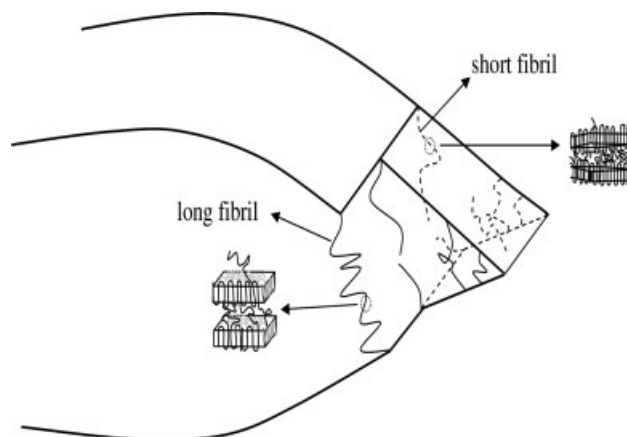


Figure 6 Schematic illustration of the preferred crack growth path through short fibrils.

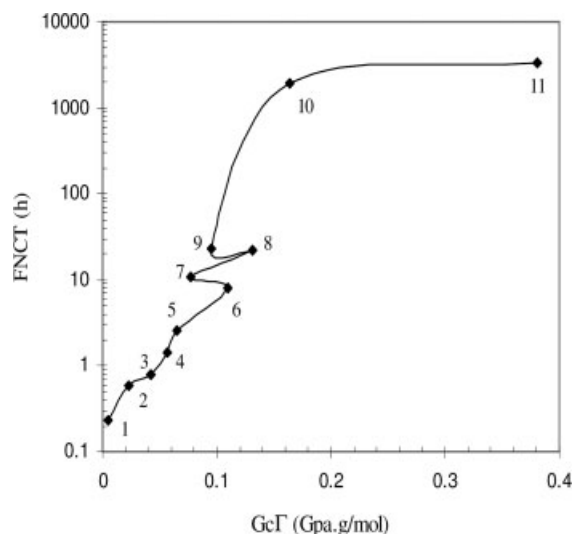


Figure 7 Time to failure in FNCT versus the calculated $G_c\Gamma$ parameter of the samples (the number of each sample is shown; the solid line is a guide to eye).

arbitrary number of 200,000. Consequently, FNCT scales the pivotal properties of G_c and Γ as follows:

$$\text{FNCT} \approx G_c\Gamma \quad (10)$$

A plot of Men et al.'s²³ samples' FNCT versus $G_c\Gamma$ yielded $\tau = 0.891$ and $P = 0.000$ (Fig. 7). Even though the FNCT- $G_c\Gamma$ correlation of Men et al.'s samples carries less merit regarding τ than the FNCT- $\tan \delta$ one, the proposed new model contains all the important key effective parameters governing ESCR. On the other hand, τ compares data sets point by point in an X and Y increasing or descending format. In addition, the measured quantities used for model verification suffer a lack of any standard deviation and accordingly accept the full penalty of -1 due to any minor change. Therefore, the Kendal test appears to be just a gross comparison technique. Accordingly, fine tuning of the current physically based model with Men et al.'s data points was performed, and a reasonable fitting ($r^2 = 0.999$) with the following sigmoidal-type equation was found:

$$\text{FNCT} = a\{1 + \exp[(b - G_c\Gamma)/c]\}^{-1} \quad (11)$$

where $a = 3386$, $b = 0.16$, and $c = 0.006$ are equation constants.

It is worth mentioning that the proposed model needs to be tested by the relevant data sets for other PE and semicrystalline polymers. Besides ESCR data points for other PE and semicrystalline polymers, however, samples' $\tan \delta$ values, molecular weights, molecular weight distributions, and exact crystalline

structure must be known. Data sets with the aforementioned characteristics are scarce in the literature as far as we know.

CONCLUSIONS

A new model, based on $G_c\Gamma$, was proposed from the analogy of crack growth under environmental stresses in semicrystalline polymers with debonding at adhesive polymer-substrate interfaces. G_c was derived from multiplication of the calculated F_s value, the measured amorphous phase $\tan \delta$ value at -25°C , and the sample G' value at the test temperature. Furthermore, Γ was estimated on the basis of the sample M_w PDI value divided by the arbitrary number of 200,000. Finally, a sigmoidal-type equation with three constants was fitted to the recently reported data according to the model.

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