

Influence of Microstructure and Morphology on Stress–Strain Behavior of Commercial High Density Polyethylene

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Received 26 December 2007; accepted 7 May 2008

DOI 10.1002/app.28677

Published online 9 July 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In the previous paper (Zahedi et al.,¹ *J Appl Polym Sci*, to appear) the optimal conditions of a new modeling procedure for correlating a scalar response to an input spectrum were established. In this article the developed model is applied to correlate the stress–strain behavior of several commercial high density polyethylene samples to the spectrums of microstructure and morphology. Molecular weight and lamellar thickness distributions were considered as the input spectrums and Young modulus, stress and strain at the yield and break points were considered as the objective responses. The shape of the kernel functions over molecular weight and lamellar thickness distribution spectrums for each mechanical property gives an explanation of how different regions of the spec-

trums contribute to create the considered property. The simplicity of the procedure facilitates the interpretation of the complex influences and interactions of different structures and morphologies in various aspects of the mechanical performance of the samples. The proposed model can be used in designed experiments with samples of controlled microstructure and morphology to provide detailed information about the structure–property relationships. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 624–631, 2008

Key words: structure–property relations; mechanical properties; molecular weight distribution; lamellar thickness distribution

INTRODUCTION

In the last few decades, as various complex statistical methods have been developed, chemical engineers have become accustomed to explore nonlinear multivariable correlations between input and output variables more and more in detail. With the increasing accuracy and precision of analytical measuring methods, the necessity of advanced methods for prediction of the desired responses and interpretation of the mechanisms and correlations has become clearer.

When one is encountered with uncontrolled set of input and output experimental values, it is common to find the statistical correlations between each pair of variables as the first step. Different criteria like *P*-value or Pearson product moment (PPM) are being used to find the strength of correlations. The regression models using forward and backward elimination procedures can provide a nonlinear multivariable function for each of responses.² If one can control the input variables, experimental design methods are pre-

ferred. Different experimental design methods can provide different kinds of prediction of the responses according to their experimental runs template and statistical analysis.³

These methods can provide good predictions; nonetheless they can not be used for extrapolation beyond the operational window, because the mechanism behind the numbers has been ignored. If one can translate the mechanism to the governing equations, it becomes possible to solve the equations, analytically or using different advanced numerical methods. The procedure is not like a black box anymore but predictions are not always improved, because these methods obligatorily need some constants associated with the process or the materials that are not always available or even measurable. It is common to find the constants with optimization procedures to achieve the best fitness between experimental values and predictions.

In more complex systems where numbers of unknown constants are high or even the physics behind the process is a not clearly interpretable, advanced simulation methods like artificial neural networks which have recently found intensive use among chemical engineers in different areas are preferred.⁴

The mentioned methods are useful for correlating scalar inputs to scalar responses. But because of

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TABLE I
Input Averages from GPC and DSC Measurements and Calculated Average Lamellar Thickness

Sample	M_n	M_w	PDI	$X_c\%$	\bar{L} (nm)
HDPE A	13,700	57,100	4.2	32.1	12.2
HDPE B	19,700	58,200	3.0	46.7	13.1
HDPE C	13,000	59,400	4.6	64.7	16.9
HDPE D	9500	40,100	4.2	58.5	20.9
HDPE E	16,400	107,000	6.5	44.2	15.5
HDPE F	6500	143,000	22.0	53.6	14.1
HDPE G	13,900	136,000	9.8	48.7	14.6
HDPE H	5900	157,000	26.6	51.7	16.1
HDPE I	7900	52,100	6.6	62.5	19.1

statistical nature of chain growth during polymerization it is more common to deal with distribution or spectrum of input and output variables in polymer engineering problems. May be some standard distribution functions can be adjusted to the input and output spectrum and the question reduces to dealing with parameters of the selected functions, but it is more practical to correlate the exact spectrums to each other. Some authors have tried to correlate their responses to the discrete spectrum of input variables and have determined the most important portions of the input spectrums.^{5,6} However determination of the number and length of each slice affects the final results and even can make the solution to diverge.

In the previous paper a new method for correlating input spectrums to the final responses using cubic splines which was first introduced by Nele et al.⁷ was explained and used for correlating some rheological properties to the molecular weight distribution (MWD).⁸ Although it was found that a kernel function including five spline nodes with boundary nodes limited to zero and also zero boundary slopes where the input spectrum have zero slope and contains no amount, gives the optimal modeling conditions. However application of this method led to a relatively same precision as a simple regression but the main breakthrough of this method is that it provides a graphical explanation of the mechanism beyond the correlations. Manifestation of the effects of different regions of the spectrum is very useful in understanding the way they contribute and interact or even make opposite influences.

In this article, the optimal modeling is applied for correlating some mechanical properties of HDPE samples to the spectrums of microstructural and morphological properties. The considered mechanical properties are stress-strain characteristics including yield stress and strain, break stress and strain and Young modulus and distribution of molecular weight and lamellar thickness were considered as the input spectrums.

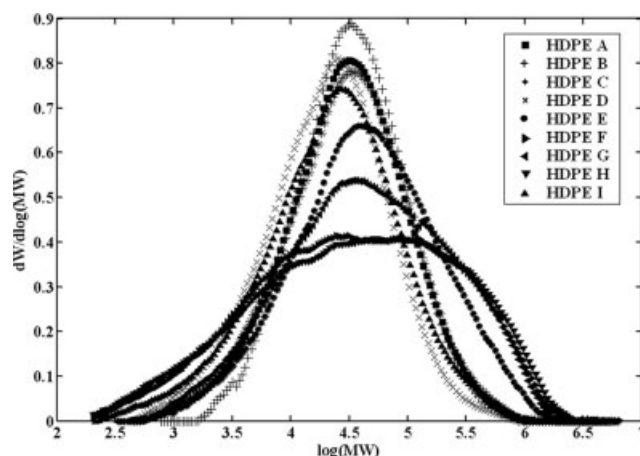


Figure 1 Molecular weight distribution of HDPE samples.

EXPERIMENTAL

Nine commercial HDPE samples with various distributions of molecular weight were selected from different producers. MWDs were determined using gel permeation chromatography (GPC) (PL-210) at 140°C using 1,2,4-trichlorobenzene as solvent. The differential scanning calorimetry (DSC) measurements were carried out in a temperature range of 30–250°C at a heating and cooling rate of 10°K/min with a Mettler-Toledo DSC model 822e. Molecular weight averages from GPC measurements and degree of crystallizations ($X_c\%$) from DSC measurements are listed in Table I. The corresponding curves of MWD and melting peaks are illustrated in Figures 1 and 2.

Polyethylene sheets were prepared using a hot press model Dr. Collin P200P, at 185°C and under pressure of 40 bars for 5 min. After 40 h, conditioning at 32°C, the dumbbell specimens were punched from sheets. The uniaxial stress-strain tests were

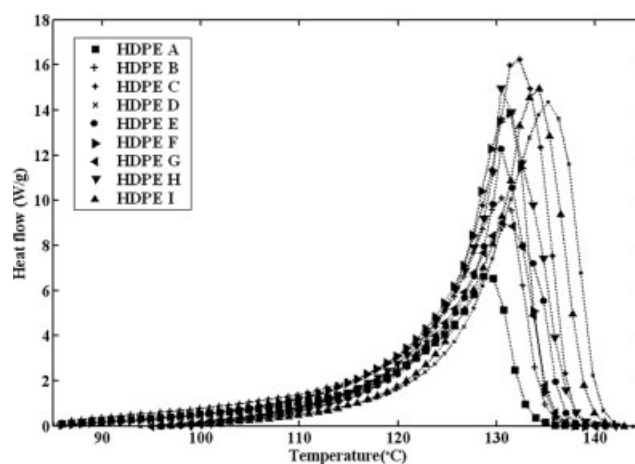


Figure 2 DSC scans of HDPE samples.

TABLE II
Mechanical Properties from Stress–Strain Test

Sample	Yield stress (MPa)		Yield strain (%)		Break stress (MPa)		Break strain (%)		Modulus (MPa)	
	Quantity	Std ^a	Quantity	Std	Quantity	Std	Quantity	Std	Quantity	Std
HDPE A	13.78	0.44	30.88	1.71	10.27	2.70	1079	198.82	114.4	30.73
HDPE B	18.57	0.50	25.91	0.63	11.34	5.31	1352	206.56	145.3	21.46
HDPE C	27.10	1.02	22.70	1.88	13.16	6.29	2031	195.61	211.4	46.52
HDPE D	29.20	0.99	21.60	0.61	13.85	13.13	157	53.09	226.5	38.99
HDPE E	21.81	0.53	28.24	1.23	32.78	8.94	1919	165.51	164.0	34.27
HDPE F	23.16	0.45	24.08	0.33	26.04	1.12	1353	45.23	178.2	29.43
HDPE G	23.19	0.34	25.14	0.36	33.61	1.09	1622	36.26	188.7	32.52
HDPE H	28.08	0.60	25.47	0.22	37.11	0.32	1613	12.26	189.3	16.02
HDPE I	28.02	1.24	21.50	0.68	7.97	0.82	980	299.52	210.4	18.26

^a Standard deviation.

performed with an Instron 4465 tensile tester. Measurements were performed at 25°C with a strain rate of 50 mm/min. The final obtained curve was the average of at least five replicates. Five points including stress and strain at yield and break points and Young modulus were selected as the representatives of stress–strain behavior of each sample. The corresponding experimental measurements are listed in Table II.

RESULTS AND DISCUSSION

It is known that it took the polymer melt rheology community some half a century to arrive at constitutive equations that are not only valid in simple shear flows but also can deal with extensional flows.^{8–13} The pom-pom model developed by Larson and McLeish, based on molecular characteristics, quantitatively describes the melt rheology of linear and even branched polymers, in complex flows.^{14–17} The constitutive equations are not so developed for the solid state mechanical properties in comparison with the melt state, because unlike the melt state, polymers are compressible inhomogeneous materials at the solid state. The dominant behavior at the solid state depends on number of known and unknown parameters from the material or the process. Aftermath of the interactions and interrelations exist between different structural parameters and process conditions, the effect of each parameter can not be interpreted independently and the overall analysis should consider the effects of all parameters and their interactions at the same time.¹⁸

The stress–strain test is the most widely used of all mechanical tests in polymer industry that polymer engineers should have a feeling for. However the relationship between stress–strain results and the end use properties in the application is not so clear but at least it provides qualitative information about mechanical properties of the polymer that can be

used in quality control and comparisons. This test can be more difficult to interpret than many other mechanical tests because the stress can become heterogeneous while several different processes can come into play. Morphology of the crystalline phase, spherulite, and lamella break up in semicrystalline polymers like HDPE in addition to amorphous chain segments reorientation, chain microstructure like MWD, existence of voids, cracks, and crazes; affect the mechanical properties of these materials strongly.^{18,19}

Distribution of the lamellar thickness can be considered as a representative of the crystalline phase morphology. The lamellar thickness of a polymer is related to the melting temperature of a single crystal by Gibbs-Thomson equation^{20–22}:

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{l\Delta H_f} \right) \quad (1)$$

where l is the longitudinal dimension of the crystal or the lamellar thickness, T_m is the melting temperature, T_m^0 is the equilibrium melting temperature (418.7°K), ΔH_f is the melting enthalpy (285 J/cm³), and σ_e is the free surface energy of the faces at which chains fold (9×10^{-6} J/cm²). The thickness distribution of the crystalline lamella can be defined by the following equation:

$$f(l) = \frac{1}{M} \frac{dM}{dl} \quad (2)$$

where M is the mass of lamellae and dM is defined as

$$dM = \frac{dE}{dT} \frac{dT}{\Delta H_f} \rho_c \quad (3)$$

where ρ_c is density of the crystalline phase (0.997 g/cm³) and dE is the energy necessary for melting of

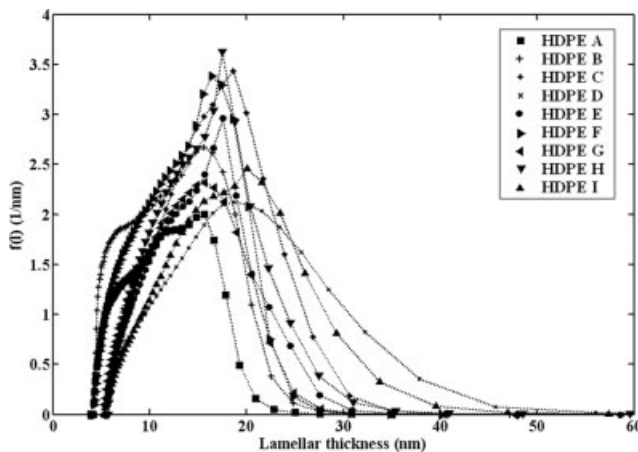


Figure 3 Calculated lamellar thickness distribution of HDPE samples.

the crystalline mass of dM in the temperature range between T and $T + dT$. Combining eqs. (1) to (3) it is possible to express the lamellar thickness distribution (LTD) as follows:

$$\frac{1}{M} \frac{dM}{dT} = \frac{dE/dT(T_m^0 - T_m)^2 \rho_c}{2\sigma_e T_m^0 M} \quad (4)$$

where the consumed energy for melting can be determined from DSC measurements by the following equation:

$$\frac{dE}{dT} \frac{1}{M} = \text{Heat Flow} \left[\frac{J}{\text{kg min}} \right] / \text{Cooling or Heating Rate} \left[\frac{^\circ\text{C}}{\text{min}} \right] \quad (5)$$

Figure 3 shows the calculated LTD of HDPE samples. The average lamellar thicknesses of the samples

listed in Table I are calculated according to the following equation:

$$\bar{L} = \int_0^{\infty} l f(l) dl \quad (6)$$

It is obvious that, $f(l)$ (thickness distribution) should be normalized before calculating each of the average lamellar thicknesses. Statistical correlation analysis was carried out to find the most relevant input and output parameters. The PPM which is near to 1 or -1 and the P -value which is near to zero for the most correlated parameters were calculated as criteria for determination of the strength of correlations. Results of the statistical correlation analysis are depicted in Table III. It is clear that the parameters which are related to the secondary bonds are more related to the crystallinity and lamellar thickness while the parameters that are related to the primary bonds are more dependent to molecular weight and its distribution. At the first stages of the deformation, the applied force has to overcome the weak secondary bonds between chains such as van der Waals forces to deform the sample but at higher deformation ratios the applied force directly faces the strong primary bonds like covalent forces between monomer units to deform the sample.^{9,10} Crystallinity increases the secondary bonds and therefore Young modulus, stress and strain at the yield point are strongly dependent to the degree of crystallinity and the lamellar thickness. On the other hand stress at the break point is more dependent to the molecular weight and poly dispersity index (PDI) while break strain is independent of all considered parameters. Forward elimination regression was implemented and the resulted equations are illustrated in Table IV with the corresponding

TABLE III
Statistical Correlation Analysis of the Average Parameters

	Criterion	M_n	M_w	PDI	$X_c\%$	\bar{L} (nm)
$X_c\%$	PPM	-0.4491	-0.1382	0.0743	-	0.7599
	P -value	0.2252	0.7229	0.8494	-	0.0175
\bar{L} (nm)	PPM	-0.4569	-0.3315	-0.1093	0.7599	-
	P -value	0.2163	0.3835	0.7796	0.0175	-
Modulus	PPM	-0.5178	-0.04	0.1114	0.916	0.8854
	P -value	0.1533	0.9187	0.7754	0.0005	0.0015
Yield stress	PPM	-0.6128	0.084	0.2894	0.8836	0.8651
	P -value	0.0793	0.8299	0.4501	0.0016	0.0026
Yield strain	PPM	0.4692	0.1728	-0.0515	-0.9551	-0.7882
	P -value	0.2026	0.6565	0.8953	0.0001	0.0116
Break stress	PPM	-0.1835	0.9173	0.6815	-0.1611	-0.1759
	P -value	0.6364	0.0005	0.0432	0.6788	0.6507
Break strain	PPM	0.2881	0.4913	0.2163	-0.0668	-0.4732
	P -value	0.4522	0.1793	0.5761	0.8643	0.1982

TABLE IV
Forward Elimination Regression Results Including Equations,
P-Values and R-Squared

		Constant	M_w	$X_c\%$	\bar{L} (nm)	R-squared
Yield stress	P-value	–	0.003	0.006	0.001	98.1
	Coefficient	–10.197	4×10^{-5}	0.222	1.187	
Yield strain	P-value	–	–	0	–	91.2
	Coefficient	40.112	–	–0.293	–	
Break stress	P-value	–	0.001	–	–	84.1
	Coefficient	–0.265	2.3×10^{-4}	–	–	
Modulus	P-value	–	0.060	0.011	0.009	96.5
	Coefficient	–40.559	1.7×10^{-4}	1.815	7.129	

P-value and R-squared values. No meaningful statistical equation was found for break strain while equation of the yield stress includes two parameters of average lamellar thickness and weight average molecular weight.

The optimal modeling conditions were then applied to the current problem. Each mechanical property was calculated according to the following equation:

$$P = \int_a^b f(M)w(M)dM \quad (7)$$

where P is the considered response, M is the considered input with the spectrum from a to b and weight of $w(M)$ for values between M and $M + dM$ and $f(M)$ is the adjusted kernel function. Five spline nodes were used and adjusted by Nelder-Mead simplex method^{23,24} to construct the best kernel functions. The values of two boundary nodes and the corresponding slopes were fixed to be zero where the input spectrum gradually decreases to zero. The considered input spectrums were MWD and the calculated LTD. It should be mentioned that the slope at lower thicknesses was considered to be adjustable because the spectrum of LTD does not show a gradual decrease in this region (Fig. 3).

Figure 4 shows the obtained kernel functions over MWD and LTD for yield stress. Stern et al. have previously shown that a linear relation exist between the yield stress and the maximum lamellar thickness.^{21,25–27} Figure 4(b) shows that the yield stress is more dependent to the fraction of the thicker lamellas. Nevertheless the contribution of thinner lamellas reminds that the yield stress is also dependent to the degree of crystallinity. Figure 4(a) shows the effect of MWD on yield stress. It is obvious that the yield stress is more dependent to low molecular weight region rather than high molecular weight region which is attributed to the dependence of crystallinity on MWD.

Figure 5 shows the effect of MWD on degree of crystallinity and average lamellar thickness. As it

was expected, crystallinity increases with the fraction of low molecular weight chains. However from the thermodynamic point of view, chain ends that increase with decrease of molecular weight play the role of defect in crystallization, but from the synthetic point of view, these chains have more ability of crystallization due to their more mobility. As a

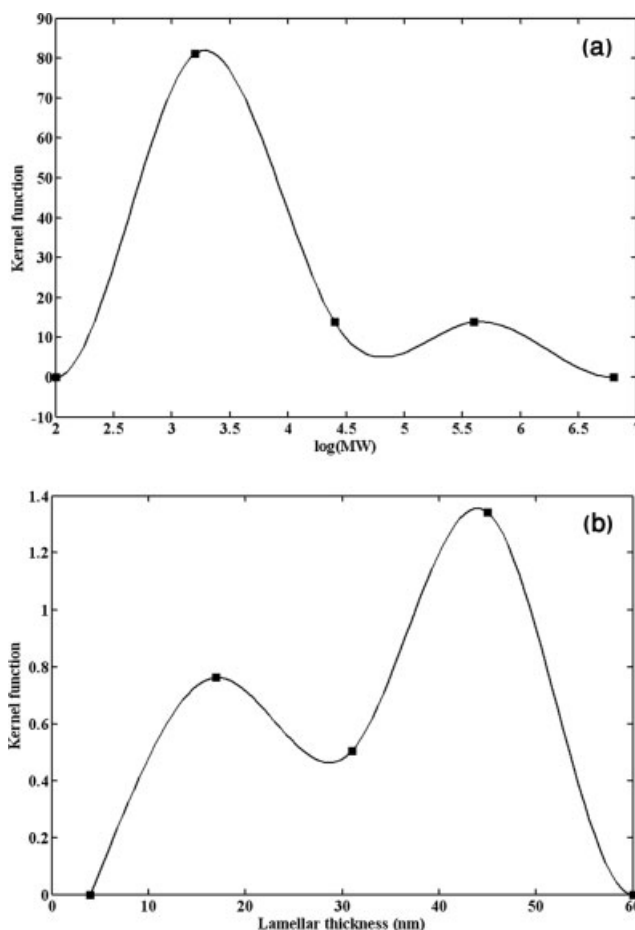


Figure 4 Obtained kernel functions for yield stress over a) MWD (R -squared = 46) and b) LTD (R -squared = 80.7).

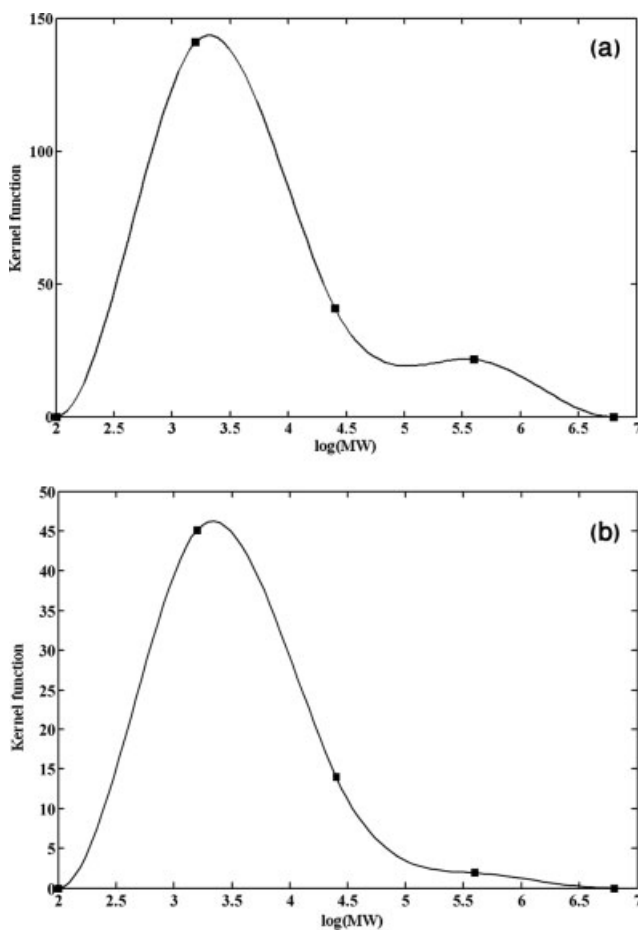


Figure 5 Obtained kernel functions over MWD for a) $X_c\%$ (R -squared = 32) and b) L (nm) (R -squared = 57).

result, crystallinity decreases with molecular weight as Figure 5(a) indicates.^{21,28} Figure 5(b) reveals that the average lamellar thickness shows a relatively same trend. First it should be reminded that this curve has been obtained for the average of lamellar thickness that linearly increases with crystallinity (as Tables I and III indicate). As a result, average thickness also has a synthetic nature and a second peak may appear at terminal zone after thermal treatment.

Figure 6 shows the dependence of yield strain to the MWD which implies that the extensibility of the sample increases as the percent of crystallinity decreases and the entanglement increases by increase of longer chains. Figure 7 shows the kernel functions obtained for dependence of break stress on MWD and LTD. Figure 7(a) indicates that the break stress strongly depends on the fraction of longer chains. When a semicrystalline polymer is deformed, plastic yielding occurs after the yield point. At this condition, the lamellas start to orientate themselves parallel to the deformation direction and therefore, interlamellar slipping occurs, coupled with the unfolding of the lamellas until the ultimate break.^{29,30}

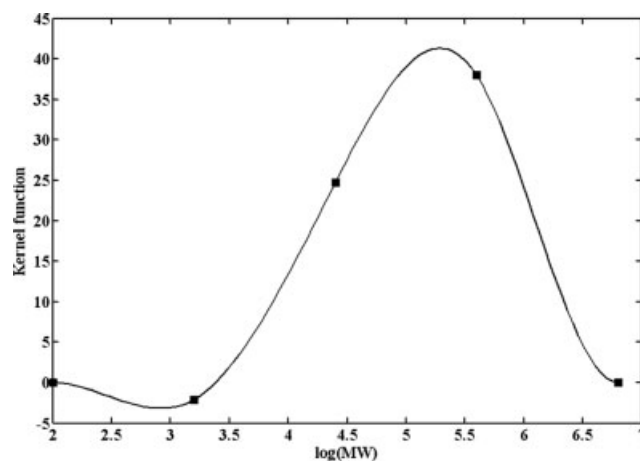


Figure 6 Obtained kernel function for yield strain over MWD (R -squared = 42.7).

At the break point the tie chains which hold separated lamellar blocks together are responsible for tolerating against the applied load. Thus break stress is proportional to the fraction of the tie chains. Figure 7(b) also implies that however thicker lamellas have more effect on break stress but the thinner lamellas

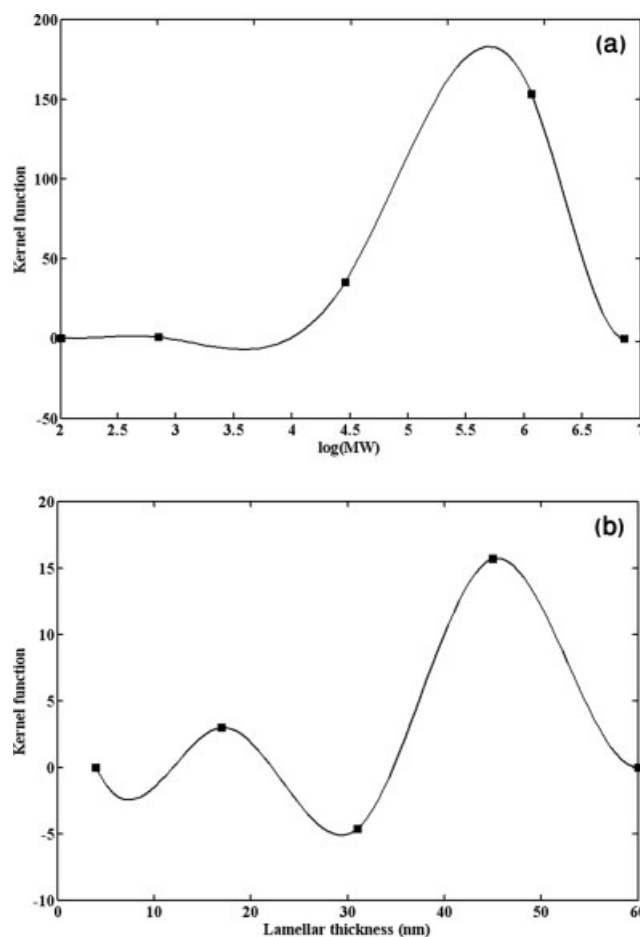


Figure 7 Obtained kernel functions for break stress over a) MWD (R -squared = 85.6) and b) LTD (R -squared = 48.5).

also contribute by facilitating the cold drawing process.

Figure 8 shows the effect of MWD and LTD on Break strain. It appears that every phenomenon that may help the extensibility can increase the break strain. Consequently as it was expected, the break strain decreases with the lamellar thickness, as Figure 8(b) shows clearly. Figure 8(a) indicates that break strain increases directly with the fraction of longer chains which create more entanglement and inversely with the fraction of short chains which mainly contribute to the crystallization.

Figure 9 shows that the kernel functions representing the dependence of Young modulus on the MWD and LTD are very similar to the functions obtained for the yield stress. Therefore the modulus is strongly dependent to the low molecular weight regions and therefore to the degree of crystallinity and the lamellar thickness, as well.

The *R*-squared values of different applied methods, including the regression using average inputs and spline-based method using spectrums as inputs shows that in most cases regression provides better predictions and in some cases especially when

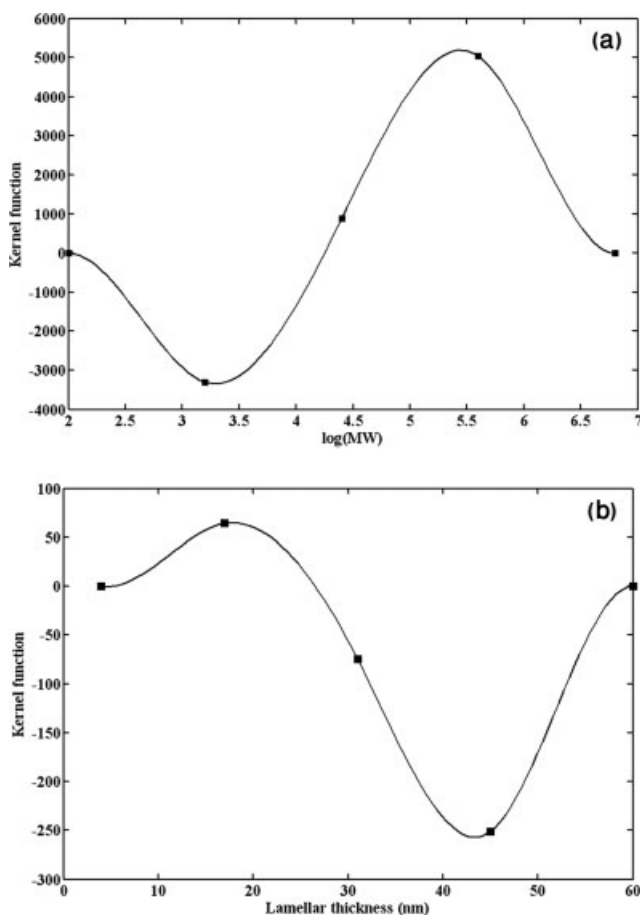


Figure 8 Obtained kernel functions for break strain over a) MWD (*R*-squared = 65.1) and b) LTD (*R*-squared = 77.3).

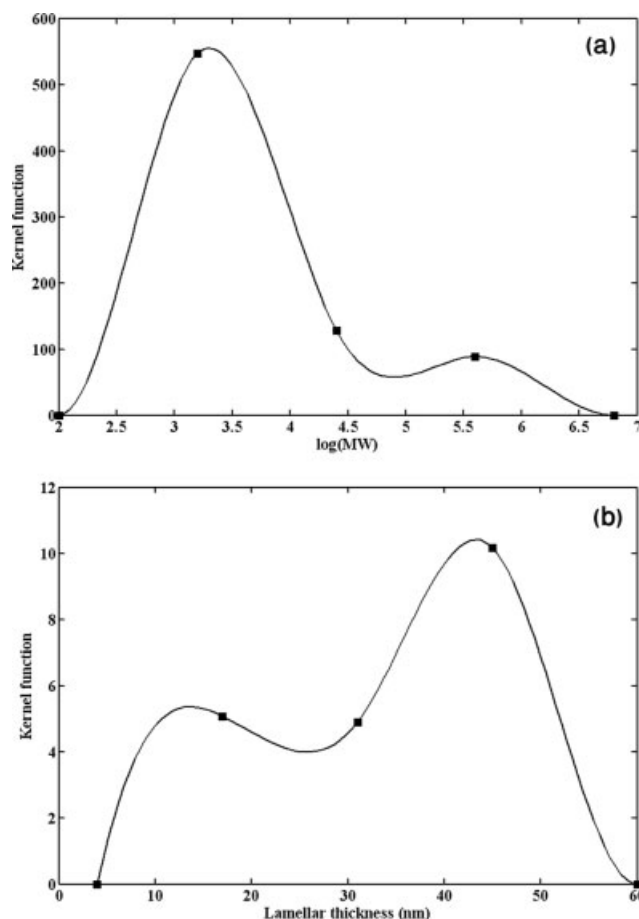


Figure 9 Obtained kernel functions for Young modulus over a) MWD (*R*-squared = 40.7) and b) LTD (*R*-squared = 70.4).

regression is unable to predict, the spline-based method is superior. But the main advantage of using the second method is to find a better understanding about the mechanism involved in each property.

CONCLUSIONS

In this article a new method was used to correlate a scalar mechanical property to the spectrum of MWD as a representative of the microstructure and LTD as a representative of crystalline phase morphology. This method is useful in polymer engineering problems, because of the statistical nature of chain growth during polymerization which translates to the spectrum of properties. The main advantage of this method is that it clarifies the physical mechanism of each property and therefore the structure-property relationship. It was shown that the properties which are related to the weak secondary bonds between polymer chains are mainly influenced by the crystallization and the morphology of crystalline phase. As a result stress at the yield point and Young modulus are dependent to the short chains which mainly contribute in crystallization rather

than the long chains. On the other hand the properties that are related to the strong primary bonds between the monomer units are influenced by the molecular weight and its distribution. Therefore break stress is strongly dependent to the long chains which act as the tie chains holding lamella blocks together during extension. Extensibility properties like strain at the yield and break points increase with molecular weight and decrease with crystallinity, as well.

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