THE EFFECT OF MFI OF HIGH-DENSITY POLYETHYLENE ON THE MATHEMATICAL MODELING OF TENSILE CHARACTERSTICS

Ibtisam M. Kamal
Chemical Engineering Department – College of Engineering – University of Basrah – Iraq

ABSTRACT

Several high density polyethylene grades produced in the State Company of Petrochemical Industries (SCPI) were fabricated to sheets and tested for tensile strength. The stress-strain curves were analyzed and the tensile data were estimated. Mathematical models were designed and correlations were developed to express the effect of melt flow index (MFI) as an additional independent variable of the models. The exponential form of the model for the grades with MFI values >1 seemed to represent the real tensile behaviour of the grades. Less positive effect on the developed models was observed for grades of MFI <1. The developed models are candidated to be used to determine tensile characteristics of all polyethylene grades produced in SCPI specially those of MFI>1 without the need carrying out destructive tensile tests.

INTRODUCTION

Polyethylene is a thermoplastic, chemically rather inert and electrically, a first –class insulator. It combines flexibility and toughness with insensitivity to moisture, low volume cost and ease of fabrication[1].

Commercially available polyethylenes have densities in the range 0.91-0.97 g/cm^3 and are divided into two categories low density (density range: 0.91-0.94 g/cm^3) and high density(density range 0.94-0.97 g/cm^3)[2]

In the State Company of Petrochemical Industries (SCPI), two main types of polyethylenes are produced; homopolyethlenes and 1-hexene/ethylene copolymers in which the ethylene is the major constituent; the latter may contain various amount of 1-hexene.

Both homopolymers and copolymers are obtained in various grades [3]. The grades of the indivitual types have virtually approximate density, but they differ in melt viscosity. Some physical properties of polyethylenes produced in SCPI are given in table (1).

The properties of particular grade depend primarily on molecular weight and degree of crystallinity. Both factors are controlled during the polymerization process [4].

Because density is related to crystallinity, and is easier as well as more convenient to be measured, it is usual to quantify the density of a polyethylene rather than its crystallinity. However, density is not a complete index of the structural state of polyethylene.

In practice, the molecular weight is not determined, but melt viscosity is determined and expressed as the melt flow index (MFI) at 190°C and 2.16 kg[5]. Thus, polyethylenes are classified in terms of density and MIF. One of the most important characteristics of polyethylene is its mechanical properties from which the end uses become apparent and limitations recognized [6]. Among these characteristics are the tensile stress – strain properties, the test of which represents as plots of the force required to produce a given elongation for sample specimens of standard sizes.

Because of the fundamental viscoelastic nature of polymers, the stress-strain properties and other aspects of mechanical behavior often very strongly influenced by rate of application of stress and temperature [7, 8, 9].

In the present work, the tensile stress-strain characteristics for eight different grades of high density polyethylenes produced by SCPI were investigated experimentally, and the acquired tensile parameters were determined. The tested grade were divided into two categories; the first is of 0< MFI <1 and the second MFI >1 . An optimization technique using Least-Square method was adopted to the mathematical analysis of the mechanical data. Two mathematical models (linear and exponential), describing the true stress-strain behaviour of high density polyethylenes, were estimated. The independent variables of the models were the elastic models and melt flow index. The coefficient of the models and the well-known adjacent factors[10, 11] were determined. The designed models were efficient to describe and represent the true mechanical behaviour of the polyethylenes. The models are recommended to use for prediction the stress-strain behaviour for any polyethylene grades produced in SCPI without the need of destructive tests.

EXPERIMENTAL

Different high-density polyethylene grades produced by SCPI were fabricated to the desired sample sheet using injection-molding technique. Dumpbell shape specimens were cut by a specimen cutting press then tested for tensile strength in controlled condition i.e temperature $=23\pm1^{\circ}C$, humidity $= 50 \pm 1$ % using tensile testing machine (Instron 1193). The specimens were stretched at a crosshead speed 50mm/min. The load-elongation curves were recorded and several mechanical parameters were estimated including: ultimate stress σ_u, yield stress σ_y, break stress σ_B, elastic modulus E, % elongation at ultimate stress % ε_u and % elongation at break %ε_B . Typical stress-stress curve of one of the eight polyethylene grades showing the mentioned mechanical parameters is shown in figure (1).

THEORETICAL ANALYSIS

In order to put in advance a reliable tool for analyzing the mechanical behaviour of the eight high density polyethylene grades, the trend is devoted to establish a mathematical model to represent this behviour as best as possible as well as to activatate it for adequate predication of the related parameters without conducting any experiment for further grades under consideration.

The investigated eight grades were divided into two categories dependent on MFI values, the first category have $0 < MFI < 1$, while the other have $MFI > 1$. A mathematical model was designed using Least-Square method[10,11]. The model was designed in two formatic types: linear algebraic type and exponential type. The dependent variables were the mechanical parameters (σ_y, σ_u, σ_B, ε_y, ε_u and ε_B) while the independent variable was the elastic modulus E. This sort of modeling would lead a singled-value function of each mechanical property, say y (where y is any one of the dependent variables listed before, as related with the independent one E, i.e $y = f(E)$. Now if this function is proposed to be first-order in E, then:

$$y = k_o + k_1 (E) \quad (1)$$

which refers simply to linear algebric type whereas the non-linear (exponential) type would be suggested as:

$$y = k_o (E)^{k1} \quad \text{or} \quad \ln y = \ln k_o + k_1 (\ln E) \quad (2)$$

In both types of these functions, the terms k_o and k_1 are the model coefficients ought to be determined. Noting that these coefficients are expected to be different in magnitudes in spite of their similar appearance in either one of equations (1,2). However they would be corresponded specifically to the group of the same range of MFI.

A second sort of modeling has been introduced in this work to corporate the effect of MFI directly on the mechanical behaviour of all grades together. In this case, the mathematical type of the linear and exponential functions of y should be in the forms:

$$y = k_o + k_1(E) + k_2(MFI) \quad (3)$$

$$y = k_o \, (E)^{k1} \, (MFI)^{k2}$$

Or

$$\ln y = \ln k_o + k_1 (\ln E) + K_2(\ln MFI) \quad (4)$$

respectively. The addition coefficient k_2, in above two types of functions is responsible to account the new effect of (MFI).

The numerical procedure , to evaluate the required coefficient in the linear models of equations (1,3) , is the well – known Least – Square technique (□). Which insure the existence of best values for these constants to minimize the total error squares between the true values of y, say y_{true} and the estimated ones from the previous functions. In short, if:

$$e. = y_{true} - y \quad (5)$$

denotes this difference at any record number n of the data (n= 1,2,3 …, N as maximum) then the total error squares, say E_T becomes:

$$E_T = \sum_{n=1}^{N} (y_{true} - y)^2 \quad (6)$$

obviously ,E would be function of k_0, k_1 and k_2 .

The principle of minimum E_T existence, yields:

$$\frac{\partial E_T}{\partial Ko} = \frac{\partial E_T}{\partial k_1} = \frac{\partial E_T}{\partial k_2} = 0 \qquad (7)$$

Which leads to a system of linear-simultaneously equations in these coefficients. An applied software program, for solving of these equations, is sufficed to carry out the job.

The same numerical approach, can be utilized to determine the necessary coefficients in the exponential type of functions in equations (2, 4) through replacing simply the term y by (lny) and k_o by ($\ln k_o$) any where in the later relations (5-7).

To distinguish between the ability level of each mathematical model in representing the true behaviour of the grades, the adjacent factor (R) is inforced to take the role of this aim. It is a fractional indicator $0<R<1$ whose value interpratetes the closeness of the imposed model to represent the actual true functions (or values). As close as R approaches unity, the mathematical model would be more acceptable .Its value can be computed from:

$$R^2 = \frac{\sum_{n=1}^{N} (y - \bar{y})^2}{\sum_{n=1}^{N} (y_{true} - \bar{y})^2} \qquad (8)$$

where denotes the means of all y- readings, i.e:

$$\bar{y} = \frac{\sum_{n=1}^{N} y}{N}$$

RESULTS AND DISCUSSION

The acquired experimental data estimated from the recorded stress-stress curves of the eight high density polyethylene grades are tabulated with their MFI as shown in table (2).

The model coefficients (K_o & K_1) and the corresponding R-values for each one of the six best fitted linear relationships are evaluated and listed in table (3) for two groups of MFI data collection. Table (4) summerize the overall results taking into account the new effect of MFI as an additional dependent variable.

Correlation's of various parameters involved in the developed models are represented in figures (2-13).

The mathematical analysis of the tensile data and the developed models confirmed that, mechanical characteristics are strongly distinguished for polyethylenes of MFI>1 and the exponential formatic type of the developed model gives more accurate results compared with the linear-algebric form. The adjustment factor values revealed this truth since the computed R values ranged from 0.93 to 0.99.

The less positive resulted effect of MFI<1 on the developed models specially for the linear algebric form, gives an evidence that the mathematical models developed in this work are capable to be modified by incorporating other independent variables concerning the physical properties of the produced grades, such as percent crystallinity. The latter suggestion deserves paying attention and focusing in a further study.

CONCLUSIONS

The mathematical analysis optimization method developed in this study may be considered very useful to predict the tensile characteristics of polyethylene grades produced in the State Company for Petrochemical Industries (SCPI), specially those grades of MFI>1, without the need of carrying out destructive mechanical tensile tests. The developed mathematical models are capable to be expanded and modified to cover and incorporate other physical properties.

REFERENCES

1. R. M. Ogirorkiewiz "Engineering Properties of Thermoplastics", Wiley Interscience, London pp. 38 (1970) .
2. M. P. Stevens "Polymer Chemistry- An Introduction" 3rd ed., Oxford Univ. USA (1999)
3. Provisional data sheets, SCPI- State Company for Petrochemical Industries, Barah-Iraq. (2000) .
4. M. Sittig " Polyolefin Prouction Processes" Noyes, USA. (1975).
5. N. G. McCrum, C. P. Buckley and C. B. Buchnall "Principle of polymer engineering" 2nd ed. N. Y. pp. 312 (1997).

6. L. E. Nielson "Mechanical Properties of Polymers and Composites" vol. 1, Marcel Dekker, N. Y. (1974).
7. E. M. Arruda, M. C. Boyce and R. Jayachandram "Effect of Strain Rate, Temp. and Thermomechanical Coupling on the Finite Strain Deformation of Glassy Polymers". Mechanics of Mats. pp. 193-212 (1995).
8. R. G. Raj, B. V. Kokta and C. Daneanlt "A Comparative Study on the Effect of Ageing on Mechanical Properties of LDPE Composites", J of App. Polym. Sci, 40, 645-655 (1990).
9. R. W. Hertzberg "Deformation and Fracture Mechanics of Engineering Material", Chapter 6, John Wiley and sons, USA (1996).
10. J. Johnson "Economic Methods" 2nd ed., McGraw Hill press (1972).
11. B. Finlayson "The Method of Weighted Residuals Variational Properties" Academic press (1972).

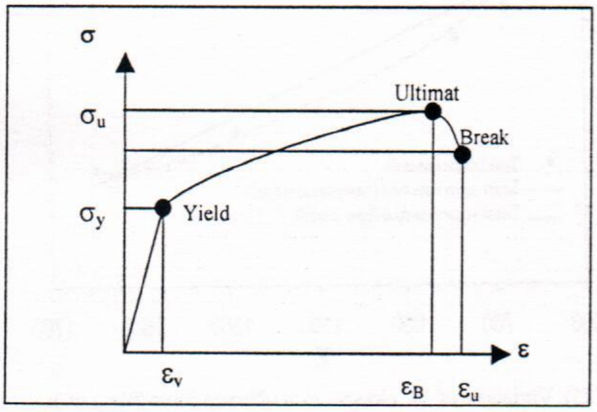

Fig. (1) Typical stress-strain curve for one of the high density polyethyene grades

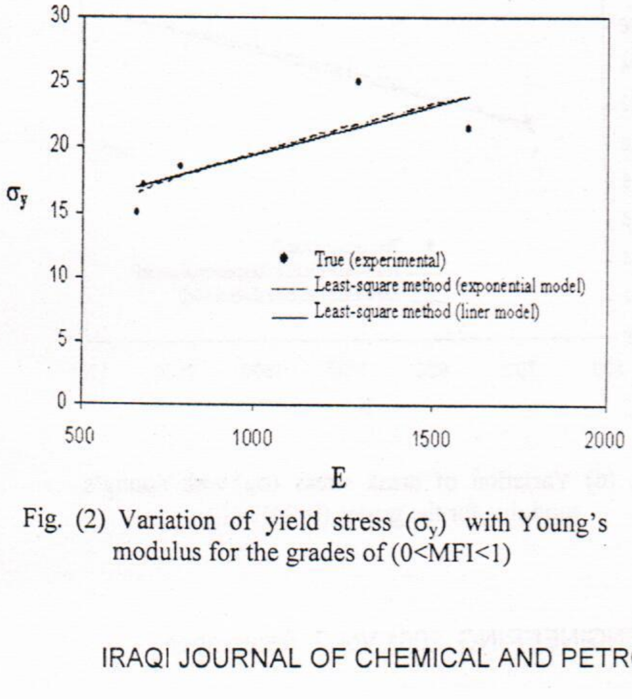

Fig. (2) Variation of yield stress (σ_y) with Young's modulus for the grades of (0<MFI<1)

Table (1) Some types, grades, and physical properties of polyethylenes produced by SCPI

Density g/cc^3	MFI g/10 min	Grade	Type
0.958	0.25–0.4	EHM 6003	High Density
0.953–0.957	0.25–0.45	HHM 5502	
0.942–0.945	0.08–0.14	TR 401	
0.961	5–7	M 624	
0.954–0.957	0.85–1.2	HHM 5710	
0.960	2.5–4	EMN 6030	
0.994–0.947	0.23–0.33	TR 140	
0.964	0.50–0.75	6006	
0.955	0.3	TR 416	
0.962	6.5	HMN 6060	
0.950	10	HXM 50110	
0.964	0.7	TR 160	
0.921–0.924	0.28–0.38	463	Low Density
0.9205–0.923	1.8–2.2	461	
0.922–0.924	21–23	203	

Table (2) The required experimental tensile data and MFI values for the poluethylene grades

Grade	$\%\varepsilon_y\times10^2$	σ_y	$\%\varepsilon_u\times10^2$	σ_u	$\%\varepsilon_B\times10^2$	σ_B	E	MFI
6030	1.667	27.500	3.333	31.964	4.083	30.000	1757.41	3.0
6060	1.833	25.000	4.417	31.428	5.250	29.639	1489.01	6.5
6006	2.000	25.000	4.083	29.639	4.417	28.568	1285.93	0.7
6003	2.583	18.568	6.542	23.570	7.208	21.785	788.45	0.3
5710	2.000	20.536	5.667	26.783	5.583	25.355	1114.07	1.0
TR 140	1.500	21.428	3.083	25.712	3.417	24.284	1600.00	0.3
TR 401	2.583	17.140	7.417	23.035	8.000	21.250	678.50	0.1
TR 416	2.583	14.998	9.417	21.250	9.250	19.369	660.65	0.3

Table (3) Model coefficients of the all poluethylene taking MFI as an additional variable

Dependent Variable	(All Samples)				
	Model	K_o	K_1	K_2	R
ε_y	Linear	11.3852	7.9563×10^{-3}	0.3688	0.9084
	Exponential	1.3386	0.3944	3.702×10^{-2}	0.9304
ε_y	Linear	3.2893	-1.0537×10^{-3}	2.5529×10^{-2}	0.9717
	Exponential	157.4296	-0.6174	4.0966×10^{-2}	0.9756
ε_u	Linear	18.5989	5.9838×10^{-3}	0.6955	0.9104
	Exponential	6.2683	0.2084	5.2750×10^{-2}	0.9386
ε_B	Linear	11.3725	-5.2347×10^{-3}	0.1677	0.9421
	Exponential	27786.6329	-1.2218	0.1051	0.9905
σ_B	Linear	16.8445	6.2045×10^{-3}	0.6222	0.8989
	Exponential	4.7861	0.2378	5.1853×10^{-2}	0.9349
ε_B	Linear	11.5309	-5.1287×10^{-3}	0.2484	0.9541
	Exponential	14904.2831	-1.1198	0.1161	0.9944

Table (4) Model coefficients for two different categories of high density polyethylene differ in MFI

Dependent variables	Grades: (6003, 6006, TR 401, TR 140, TR 416) 0< MIF <1				Grades: (5710, 6030, 6060) MIF >1			
	Model	K_o	K_1	R	Model	K_o	K_1	R
σ_y	Linear	12.0109	0.0074	0.7974	Linear	8.5060	1.0898×10^{-2}	0.9978
	Exponential	1.0661	0.4218	0.8543	Exponential	0.2230	0.6450	0.9991
ε_y	Linear	3.4046	-1.1518×10^{-3}	0.9882	Linear	2.5792	-5.1319×10^{-4}	0.9956
	Exponential	114.1093	-0.5769	0.9579	Exponential	30.7319	-0.3885	0.9837
σ_u	Linear	19.0014	5.6246×10^{-3}	0.7344	Linear	17.9461	8.3337×10^{-3}	0.9448
	Exponential	4.3401	0.2528	0.8001	Exponential	1.5630	0.4056	0.9610
ε_u	Linear	11.8300	-5.7158×10^{-3}	0.9393	Linear	9.7199	-3.6105×10^{-3}	0.9985
	Exponential	11906.6836	-1.1183	0.9846	Exponential	16067.6040	-1.1302	0.9817
σ_B	Linear	16.9591	6.1295×10^{-3}	0.7395	Linear	17.4425	7.4920×10^{-3}	0.9366
	Exponential	3.0984	0.2923	0.8083	Exponential	1.6827	0.3883	0.9546
ε_B	Linear	12.1619	-5.6881×10^{-3}	0.9719	Linear	8.2278	-2.2401×10^{-3}	0.9186
	Exponential	7922.4270	-1.0489	0.9949	Exponential	489.2700	-0.6330	0.8807

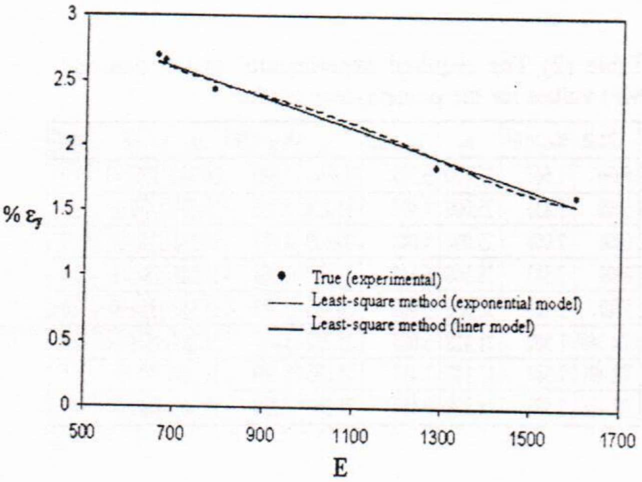

Fig. (3) Variation of % elongation at yield (%ε_y) with Young's modulus for the grades of (0<MFI<1)

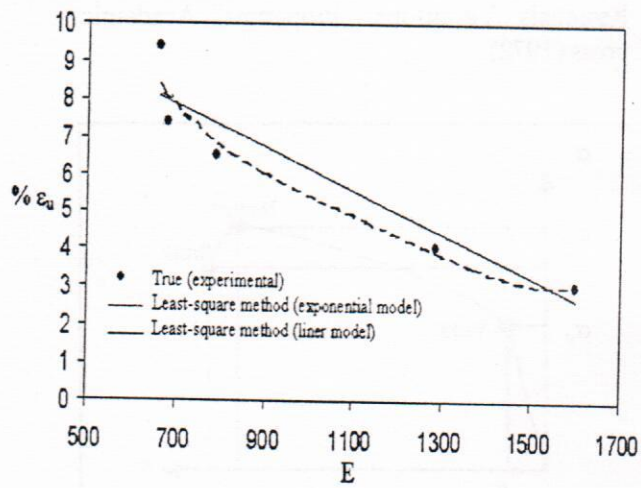

Fig. (5) Variation of % elongation at ultimate stress (%ε_u) with Young's modulus for the grades of (0<MFI<1)

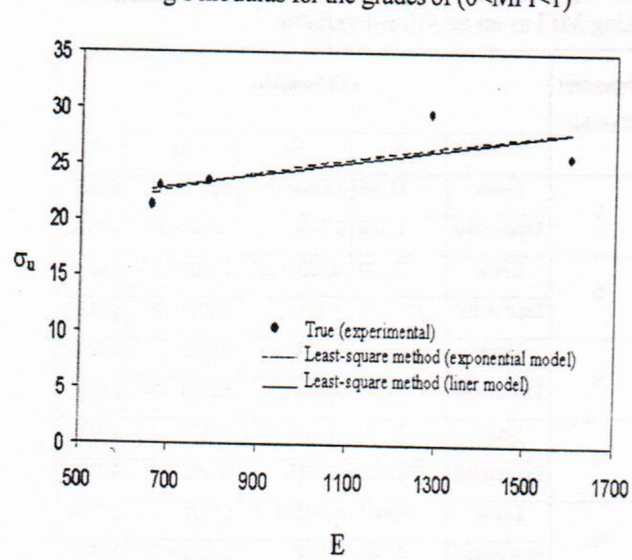

Fig. (4) Variation of ultimate stress (σ_u) with Young's modulus for the grades of (0<MFI<1)

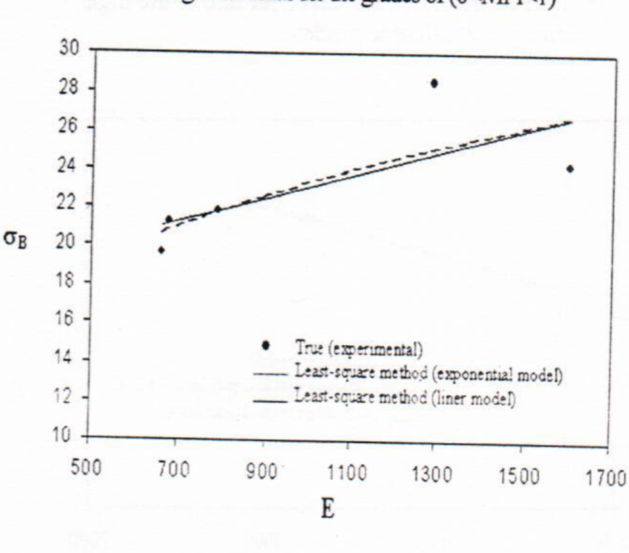

Fig. (6) Variation of break stress (σ_B) with Young's modulus for the grades (0<MFI<1)

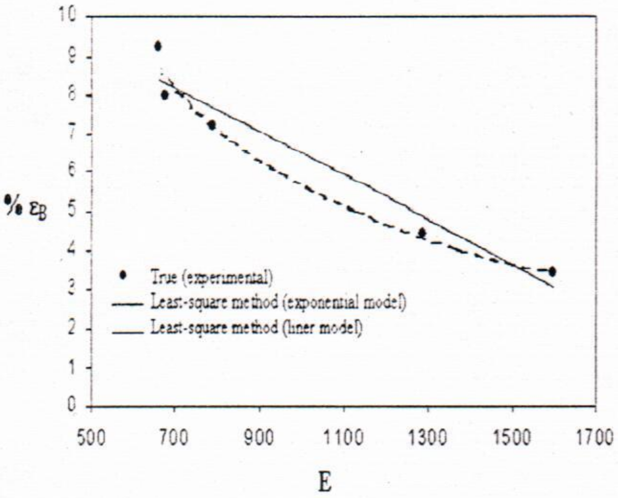

Fig. (7) Variation of % elongation at break (%ε_B) with Young's modulus for the grades (0<MFI<1)

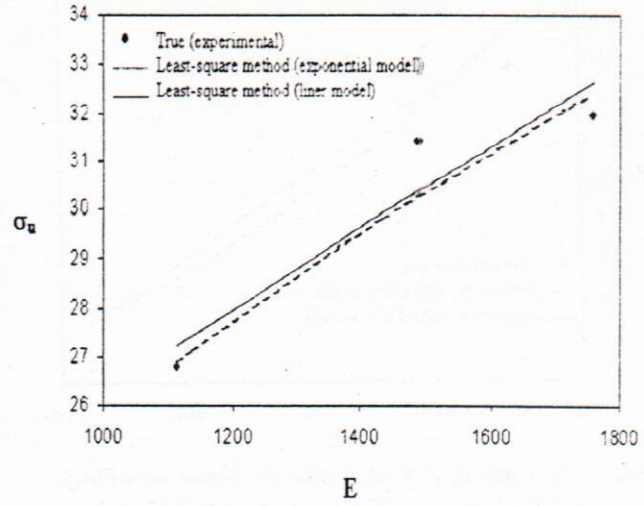

Fig. (10) Variation of ultimate stress (σ_u) with Young's modulus for the grades of (MFI ≥ 1)

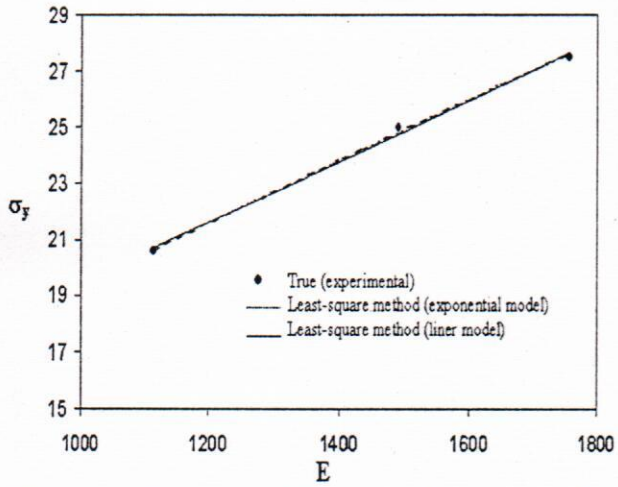

Fig. (8) Variation of yield stress (σ_y) with Young's modulus for the grades (0<MFI<1)

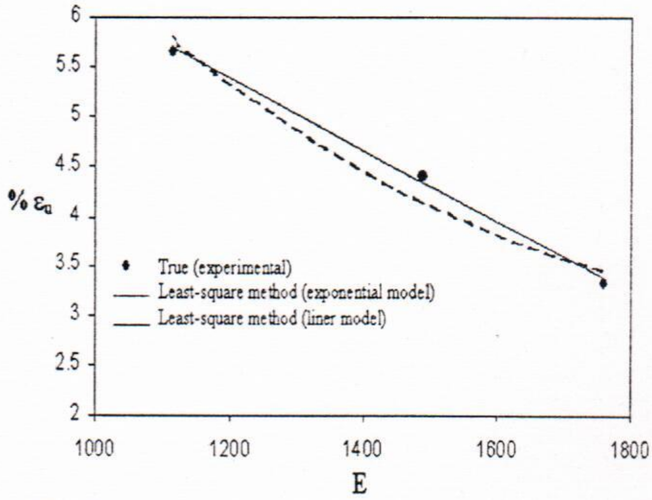

Fig. (11) Variation of % elongation (ε_u) with Young's modulus for the grades of (MFI ≥ 1)

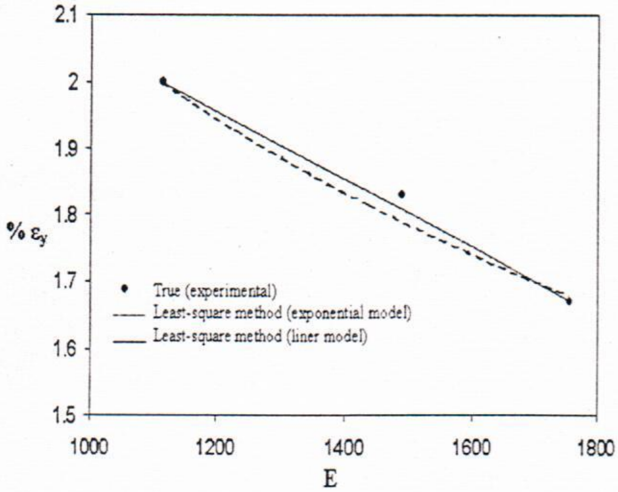

Fig. (9) Variation of % elongation at yield (%ε_y) with Young's modulus for the grades (0<MFI<1)

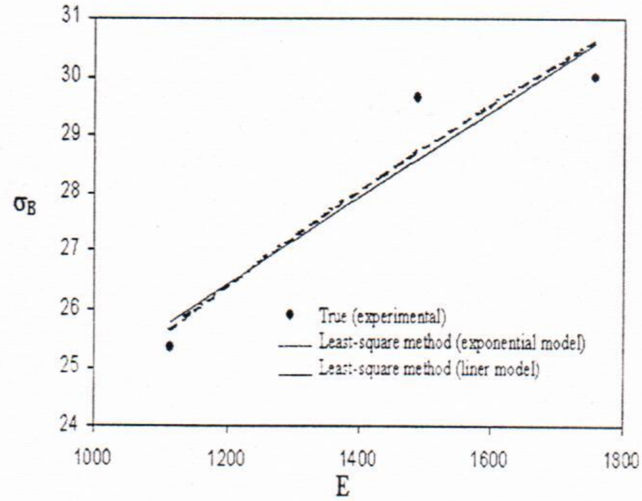

Fig. (12) Variation of break stress (σ_B) with Young's modulus for the grades (MFI ≥ 1)

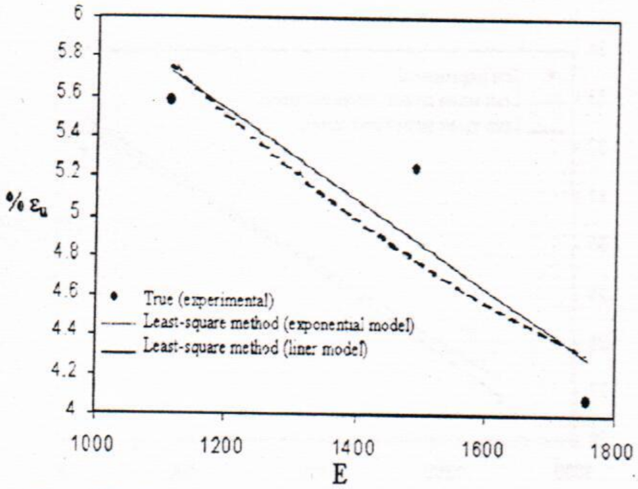

Fig. (13) Variation of % elongation at ultimate stress (%ε_u) with Young's modulus for the grades of (MFI $\geq$ 1)