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EFFECTS OF THERMAL HISTORY ON THE PROPERTIES OF SEMICRISTALLINE THERMOPLASTICS: POLYPROPYLENE

Carmen Albano*, Rosalba Sciamanna, David Kaiser D,. and Gerardo Delgado.
*Universidad Central de Venezuela, Facultad de Ingeniería, Escuela de Ingeniería Química. Los Chaguaramos, *P O Box: 48146, Caracas 1041 A, Venezuela. E-mail: albanoc@camelot.rect.ucv.ve, albanoc@cantv.net*
Fax: +58-2-6053178, phone: +58-2-6053175

SUMMARY: Several variables affect the solidification process of plastics, being the thermal history given to the polymer and its molecular weight the more important. Therefore, this paper is aimed at : 1) analyzing the effect of the crystallinity degree reached at different cooling rates and at different molecular weights on the mechanical properties of a crystalline polymer, polypropylene (PP); and 2) developing a model of a relation between thermal history, mechanical properties, and molecular weight of PP, of the mechanical property =*f* (molecular weight, crystallinity) type. The results obtained lead us to infer that the crystallinity degree tends to increase with a decrease in the cooling rate, and, in turn, decreases when PP molecular weight increases. The models obtained were found to be reasonably adjusted to the results of the mechanical properties and crystallinity. Therefore, they represent an important tool to estimate the mechanical behavior of these polymers with regard to the degree of crystallinity and the molecular weight, particularly for an industry that is always demanding products which meet its specific requirements.

KEYWORDS: Thermal history, mechanical properties, mathematical model, polypropylene.

INTRODUCTION

Once a thermoplastic polymer has been synthesized, it must be submitted to a transformation process to obtain the finished product. This process includes different variables, which influence final characteristics of the product; the most important of them are the thermal history given to the polymer during the solidification process and the molecular weight (Velisaris and Seferis) [1]. Therefore, the effect of thermal history on polymers should be studied in detail, since the degree of crystallinity reached by these polymers depends on this history; this crystallinity degree, in turn, governs the behavior of mechanical properties such as tenacity, rigidity, resistance, etc. (Kamal and Chu) [2], (Cebe and Hong) [3], (Nielsen) [4]; (Albano et al.) [5].

When semi-crystalline polymers are used in manufacturing process of finished products, heat transfer taking place during solidification influences crystallinity degree of the finished product and therefore its final properties. Consequently, non-uniform crystallinity profiles can be produced in the material or more than one physical crystalline structure can be developed on the walls of the plastic product manufactured (DePorter et al.) [6].

Therefore, the development of a suitable method to characterize and analyze the influence of thermal history given to a plastic product, consisting of semi-crystalline polymers, at the time of its manufacture, will help to optimize processing cycles and design a proper control of the thermal parameters involved.

Therefore, this paper is aimed at: 1) analyzing the effect of the crystallinity degree reached at different cooling rates and at different molecular weights on the mechanical properties of a crystalline polymer, polypropylene (PP); and 2) developing a model of a relation between thermal history, mechanical properties and molecular weight of PP, of the mechanical property =*f* (molecular weight, crystallinity) type.

EXPERIMENTAL

Five samples of different molecular weight were used for the experiments carried out in this research. The commercial names of these PP samples are: Profax, J-300, J-600, J-700 and B325.

Plaques were prepared for the experimental tests in an automated molding press by dynamically cooling the melt polymer at different cooling rates (20, 15, 10, 5, and 2,5ºC/min). Samples were first melted over their fusion temperature that is at 200°C, and maintained at this temperature for 10 minutes to erase previous thermal history of the polymer. Then, samples were cooled at different constant velocities from 200 to 40 °C. Therefore, samples with different degrees of crystallinity were obtained.

Once prepared, the plaques were cut and latched to produce specimens according to the ASTM standards, which were submitted to traction and impact tests (ASTM D638-77a and D256-78e), respectively. Between 14 and 16 probes per sample were submitted to assay (per each molecular weight and per each solidification rate). Traction assays were carried out in an Instron Universal testing machine, and impact assays in a Zwick impact assays machine; in this case a 2-Joule pendulum was used.

Also, a small sample of the plaques obtained was used for X-rays diffraction, with the purpose of determining the degree of crystallinity reached by the polymer after its thermal treatment in the molding press.

The average weight molecular of the different samples used was determined by means of a viscometric method, using o-Dicholine-benzene as a solvent.

With these data about mechanical properties, degree of crystallinity, and molecular weight, three-dimensional matrices were obtained, which were used to apply a multivariable non-lineal regression method. The aim was to adjust data matrices by means of mathematical expressions that represent the behavior of different mechanical properties as a function of crystallinity and molecular weight.

Finally, three-dimensional views of the surfaces generated by the mathematical expressions were obtained to have a better view of the results and models developed.

RESULTS AND DISCUSSION

The results of the crystallinity (X) and molecular weight (Mv) are presented in Table 1. The degree of crystallinity obtained for the different rates (V) and the different molecular weight used, tends to increase slightly as the velocity of the solidification process decreases. Similar results were obtained by Curtis et al. [7].

Table 1 shows the results obtained from the mechanical tests (IR: Impact strength; ε_Y: yield elongation; σ_Y : yield strength; σ_B: breaking strength; ε_B: elongation at break; E: Young's modulus) to which the studied polypropylenes were submitted.

Three-dimensional matrices were obtained from the experimental data; in those matrixes, each axis represents the molecular weight, the degree of crystallinity and each mechanical property studied.

Mv g/gmol)	V (C/min)	X (adm)	IR (J/cm^2)	σ_Y (MPa)	ε_Y (%)	σ_B (MPa)	ε_B (%)	E (MPa)
210000	20	0.658	0.427	47.031	17.59	31.29	90.16	602.69
	15	0.673	0.436	47.588	16.07	29.69	39.57	613.92
	10	0.668	0.450	47.718	17.28	29.78	39.51	635.51
	5	0.673	0.447	49.735	17.03	31.34	31.69	671.54
	2.5	0.697	0.466	50.188	16.54	33.97	30.73	719.77
305000	20	0.647	0.279	49.302	15.45	43.41	18.70	712.95
	15	0.684	0.271	49.430	14.27	43.57	17.78	716.26
	10	0.688	0.291	49.442	13.88	44.42	17.42	732.35
	5	0.699	0.266	48.329	13.68	45.05	15.85	746.46
	2.5	0.703	0.266	49.575	13.58	45.95	14.22	765.04
390000	20	0.611	0.250	49.232	15.63	44.43	18.70	697.33
	15	0.667	0.237	47.922	15.31	44.33	18.81	816.01
	10	0.669	0.240	50.132	15.13	44.48	18.70	740.02
	5	0.665	0.249	47.414	14.47	44.39	15.85	719.54
	2.5	0.679	0.241	47.570	13.58	44.56	14.06	775.51
575000	20	0.605	0.609	39.683	21.28	39.22	928.74	442.21
	15	0.602	0.654	39.210	20.53	40.62	901.25	491.17
	10	0.608	0.653	40.197	20.11	41.35	895.27	520.13
	5	0.607	0.668	40.288	21.16	42.86	869.29	507.11
	2.5	0.629	0.657	40.798	20.67	44.26	859.06	537.72
800000	20	0.605	0.265	32.795	13.73	28.51	18.68	535.15
	15	0.602	0.274	33.206	13.57	30.10	16.21	494.93
	10	0.625	0.281	33.739	12.84	32.75	14.03	484.83
	5	0.619	0.269	34.485	12.73	33.04	13.77	524.95
	2.5	0.629	0.264	34.503	12.01	33.44	13.45	558.26

Table 1. Mechanical behavior of the various PP, at different solidification rates (V).

To achieve one of the main goals of this work, that is, to obtain several models with the form, mechanical property = *f* (molecular weight, crystallinity), that can be adjusted to the experimental information obtained, it was necessary to use a method of non-linear multivariable regression. The purpose of the regression analysis is to determine which are the constant values of a function that allow it to be adjusted to a series of data.

A commercial software, NLREG, was used to develop this model; this is a very versatile tool for regression analysis, which allows us to carry out multivariable analysis, linear, polynomial, exponential, logistic functions, etc. The algorithm used by this program is a combination of Gauss-Newton and Levenberg-Marquardt methods.

Various approaches or criteria were used to assess the effectiveness of the models, based on how each one could be adjusted to the experimental data from which it was developed. The first criterion is the average deviation, which is the average difference between the predicted values of the mechanical property for each pair of values (crystallinity and molecular weight), and the real values experimentally obtained. The second criterion is the maximum deviation, the largest deviation for each model. Finally, the average relative deviations, that is, the deviation (percentage) obtained by dividing each deviation by the experimental value.

Three-dimensional views of the surfaces, generated by the mathematical expressions, were obtained to have a better view of the results obtained and the models developed. To this end, MathCad®, a software for mathematical functions, was used.

Five models were developed: impact strength, yield strength, yield elongation, elongation to break and breaking strength. No model was developed for the Young's modulus, since this property showed abnormal behavior with regard to the molecular weight. Therefore, no proper models can be developed based on this experimental information, because these would not represent the true behavior of the mentioned property.

The equations of the obtained models are as follows:

Impact strength (J/cm^2):

$$IR = -5.27E\text{-}7*MW - 4.2076*X_c + 3.3438 \quad (3)$$

Yield strength (MPa):

$$\sigma_Y = -2.506E\text{-}5*MW + 23.658*X_c + 40.069 \quad (4)$$

Yield elongation (%):

$$\varepsilon_Y = -1.347E\text{-}5*MW - 93.29*X_c + 82.57 \quad (5)$$

Breaking strength (MPa):

$$\sigma_B = -3.543E\text{-}4*MW + 26.03*X_c + 23.41 \quad (6)$$

Elongation at break (%):

$$\varepsilon_B = 2.457E\text{-}10*MW^2 - 2.936E\text{-}4*MW - 71.95*X_c + 139.5 \quad (7)$$

Where:
MW: viscometric molecular weight (g/gmol).
Xc: degree of crystallinity.

The deviations obtained from the different models regarding experimental results (Table 1) are shown in Table 2.

Table 2. Deviation among the models developed, and experimental data for PP.

Mechanical property	Average deviation	Maximum deviation	Average relative deviation
Impact strength	0.096 J/cm^2	0.317 J/cm^2	20.84 %
Yield strength	1.395 MPa	4.546 MPa	3.06 %
Yield elongation	1.413 %	4.678 %	8.52 %
Breaking strength	5.614 MPa	10.486 MPa	15.01 %
Elongation to break	6.795 %	48.885 %	21.96 %

Models of impact strength and breaking elongation (Figures 1 and 2) showed the highest relative deviations, 20.84% and 21.96 %, respectively, which means that there are non quantified factors influencing this mechanical properties, such as size of the spherulites or other changes in morphology.

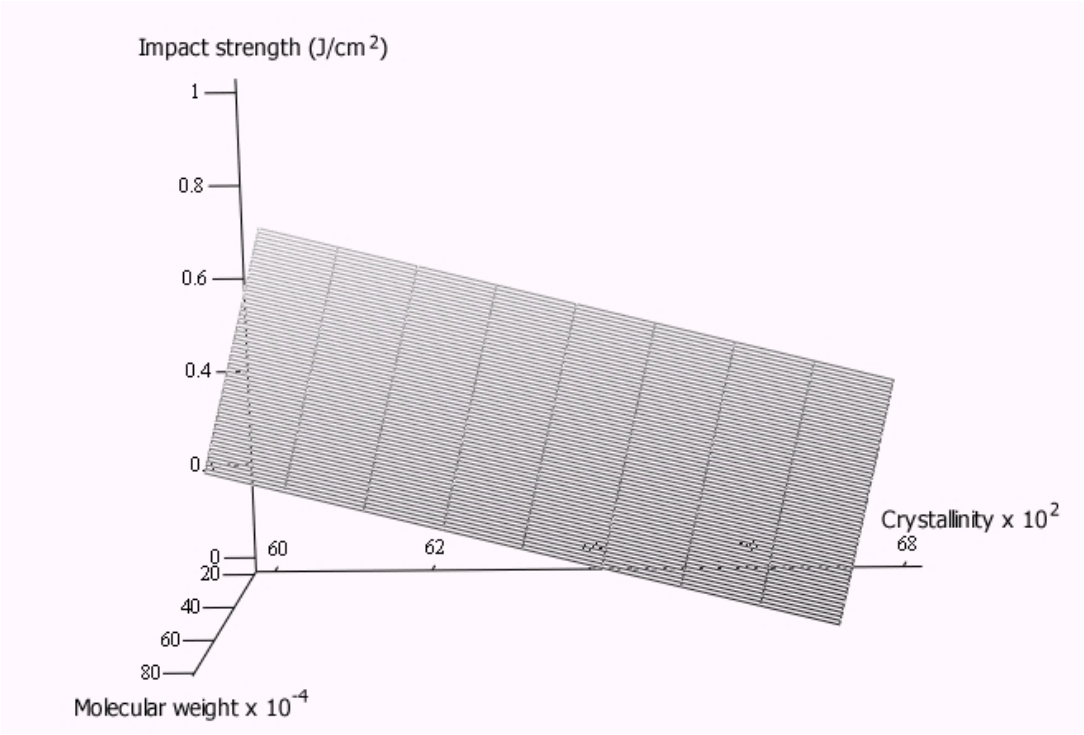

Fig. 1: Impact strength as a function of the molecular weight and crystallinity for PP.

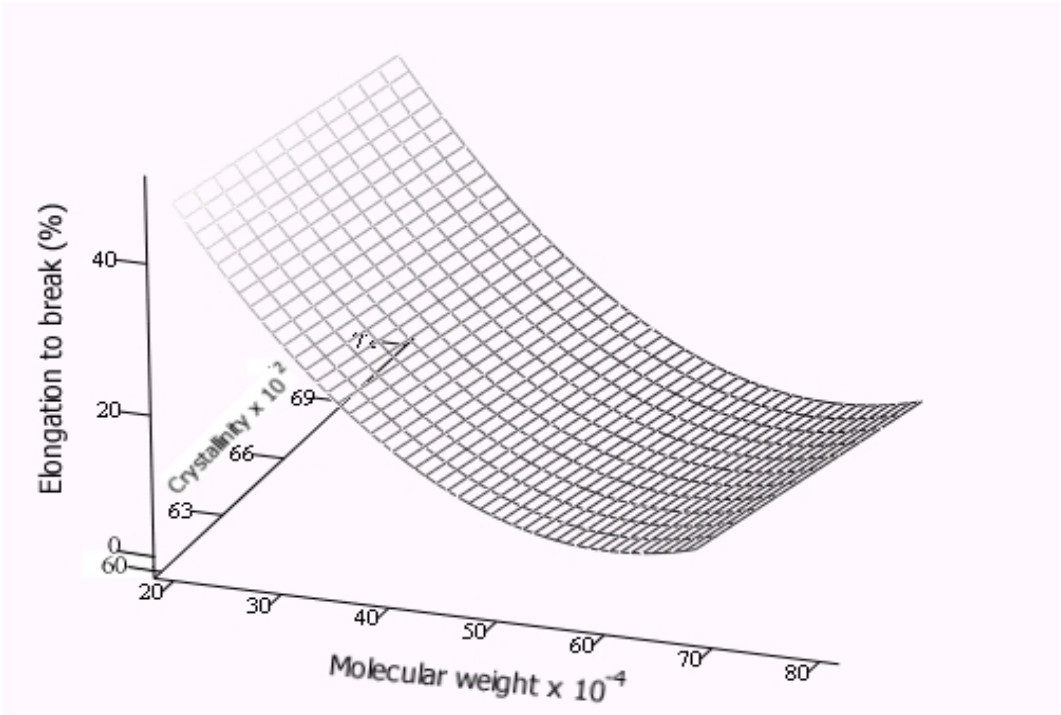

Fig. 2: Elongation to break as a function of the molecular weight and crystallinity for PP.

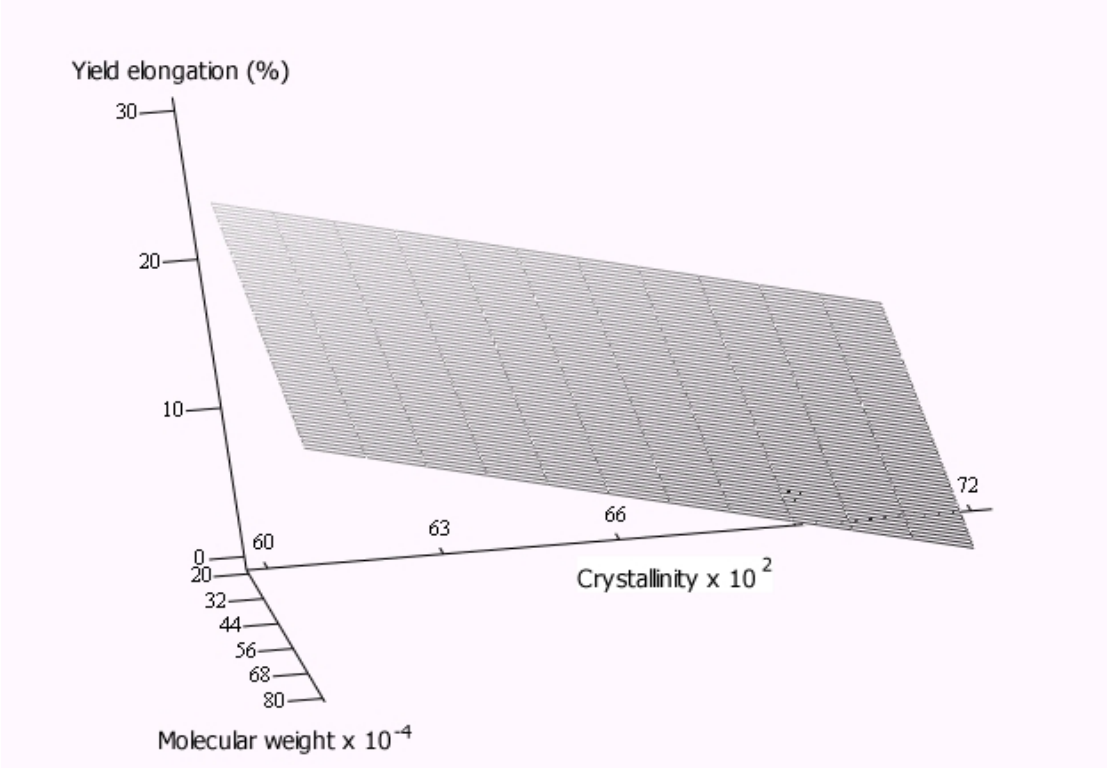

Fig. 3: Yield elongation as a function of the molecular weight and crystallinity for PP.

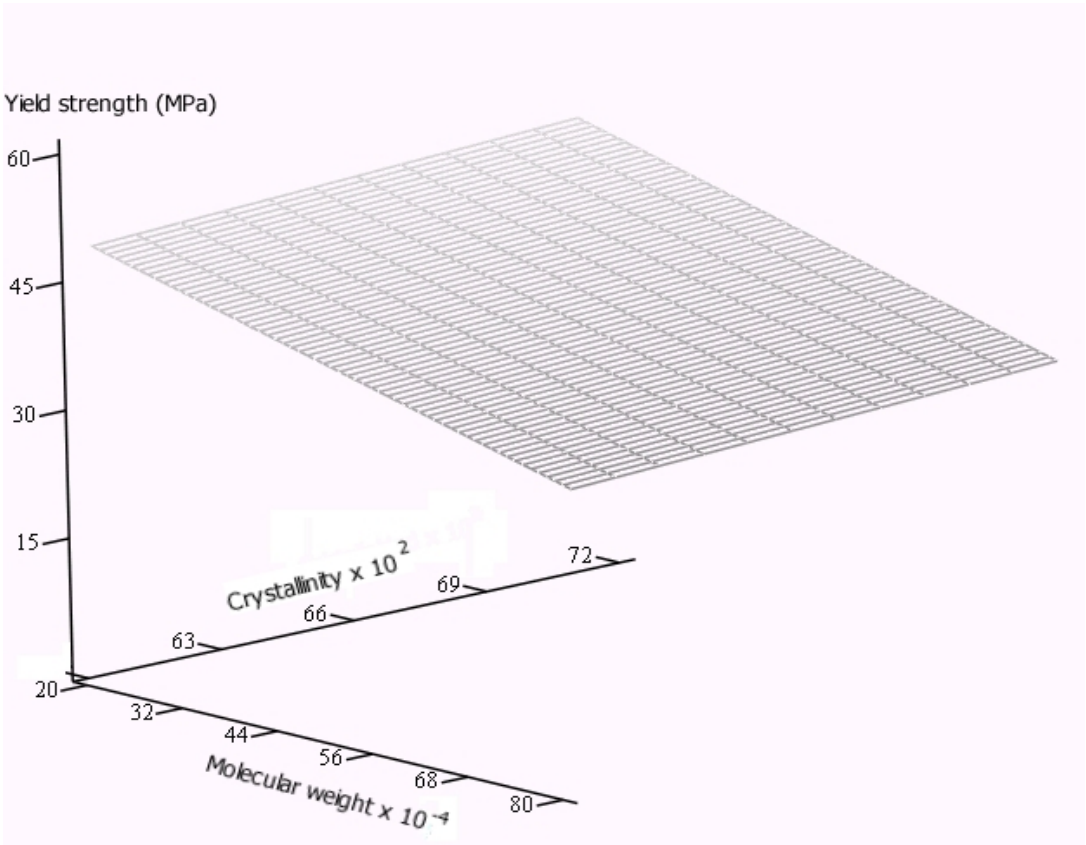

Fig. 4: Yield strength as a function of the molecular weight and crystallinity for PP.

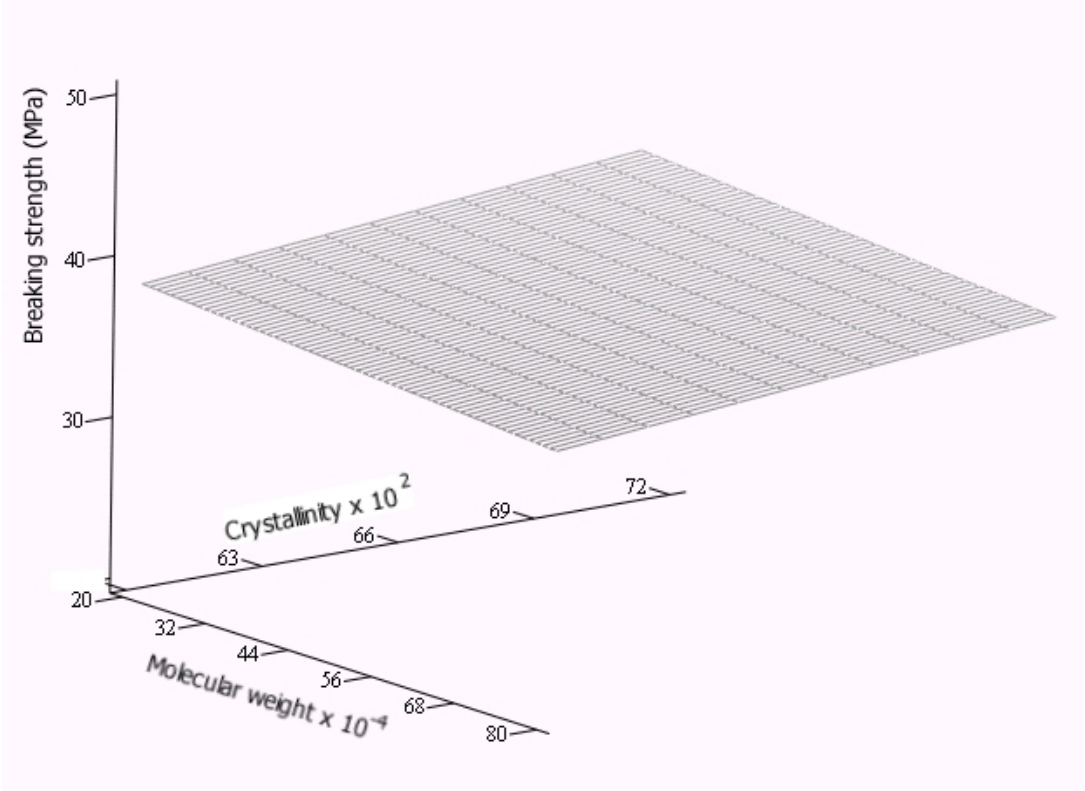

Fig. 5: Breaking strength as a function of the molecular weight and crystallinity for PP.

On the other hand, yield elongation and yield strength models (Figures 3 and 4) together with breaking strength (Figure 5) were found to be fairly well adjusted to experimental data, since their relative deviations are under 15%.

CONCLUSIONS

In spite of the existence of other variables that were not quantified, mainly those related with the distribution of the molecular weight and the crystalline morphology of the polymers, the models could be reasonably well adjusted to the experimental information. Therefore they represent an important tool to estimate the mechanical behavior of these polymers with regard to the degree of crystallinity and the molecular weight, particularly for the industry that is always demanding products that meet specific requirements.

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