

Empirical Models for End-Use Properties Prediction: Application to Injection Molding of Some Polyethylene Resins

M. C. B. Costa,¹ A. L. Jardini,¹ N. M. N. Lima,¹ M. Embiruçu,² M. R. Wolf Maciel,¹ R. Maciel Filho¹

¹Department of Processes Chemical Development, School of Chemical Engineering, State University of Campinas, UNICAMP, Campinas-SP 13083-970, Brazil

²Department of Chemical Engineering, Polytechnical School of Federal University of Bahia, Salvador, Bahia, Brazil

Received 21 December 2006; accepted 4 June 2009

DOI 10.1002/app.30911

Published online 17 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A great challenge related to polymers research has been the development of reliable models enabling prediction of polymer end-use properties according to the initial operational conditions—either during the polymerization process or the transformation process phases. These models can be utilized to produce final devices with specified properties in a more economic and faster way. The first step for building up such kind of model is the information about the relationship between the intrinsic properties, which is a convenient way to develop the models. The intention is to optimize the operational conditions of transformation systems, resulting in better products with lower costs. Empirical models are suitable workable solutions to represent complex systems in which it is difficult and expensive or too time-consuming to develop a detailed deterministic model. Bearing this in mind, this article aims to build-up empirical models relating intrinsic

and end-use properties of polymers, which can be applied in the injection plastic molding. The development was carried out through resins characterizations together with the impact quantification of process operating variables including their interactions. Polyethylene resins produced in a second generation petrochemical industry were used as a case study. The first generation industries include the production of basic products from naphtha, whereas the second generation involves the transformation of basic petrochemicals, such as ethane and propane, into thermoplastic resins, polyethylene, and polypropylene. The developed models were compared to experimental data and good predictions were obtained. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3780–3792, 2009

Key words: polyethylene; modeling; mechanical properties; density; simulations

INTRODUCTION

When producing polymer, the properties must be tailored toward the final characteristics of the product. Moreover, with the enormous competition of polyolefins market, the knowledge about those properties and their relations with operating conditions and the effect of additives become very important for the industry. In fact, the polymer supply industries must be able to produce resins with desired characteristics to satisfy customers of polymers transformation industries.¹ The desired characteristics are defined by the properties of polymer, operating conditions of transformation machines and additives.

The final characteristics of polymers vary according to their application as well as to the type of processing used. Each polymer structure influences directly on its density and mechanical properties. Therefore, there is a large number of different properties combinations that a polymer can present, leading to significant difficulties to correlate intrinsic and end-use properties.² Empirical models can describe the process behavior, based on experimental evidence, with a suitable procedure to cover all possible range of operating conditions.

Deep knowledge about correlations between end-use properties (regarding to resulting properties of the product obtained in the polymer production industries) and polymer intrinsic properties could be a possible way to define the operational conditions of each processing unit in the industry to achieve the desired properties. Among several properties, the fluidity index (FI) and the density are properties that exert strong influence in the polymer final characteristics.³

It is always welcome to be able to develop relationships or correlations taking into account the

Correspondence to: M. C. B. Costa (mcarol@feq.unicamp.br).

Contract grant sponsor: State of São Paulo Foundation (Fapesp); contract grant number: 05/52580-4.

Contract grant sponsor: Finep.

intrinsic polymer properties as morphology, orientation, and residual stresses. However, for the easy to use industrial implementation, it is helpful to have correlations-based properties that are easier to measure. Properties as FI and density may be used to identify the main polymer characteristics, useful for the polymer production industries, even as an early state of the polymer manufacturer process. To become the procedure more general and able to be used in industrial conditions in which on line properties measurement are important source of information to interfere in the process aiming to obtain the product with the desired characteristics, FI and density are good candidates as monitored properties.

There are many other molecular and structural characteristics that influence processability and molded product properties, but they are not considered here because of measurement difficulties for industrial sake. Processing variables, the cooling process, and sample dimensions also are very important; however, the models presented here intend to be useful for polymer production industries and then to satisfy customers necessities of polymer transformation industries. Thus, tests were performed in samples that were not transformed in the final products; hence do not presenting crystallinity distributions, so that the results are general and useful to any transformation operation.

The objective of this work is to develop empirical models able to predict end-use properties of polyethylene resins as functions of intrinsic properties of the polymer resins. The development was carried out through resin characterizations and variable determination used on empirical models. Polyethylene resins that can be applied in the injection plastic molding, produced in a second generation petrochemical industry, were used as a case study, because nowadays it is an important commodity.

THE PROPOSED PROCEDURE

The product quality is one of the preliminary reasons for using advanced controls in the polymer production industry. The material without specification must be sold by reduced price, be mixed with another material, or be wasted, leading, all the three alternatives, in lower profits.⁴ However, the main problem is to obtain the required set of reactor operational conditions based on feedback information from the polymers desired properties. This is not easy to be done but important insight can be seen if the end-use properties of the polymer are expressed as function of the intrinsic properties of the polymeric chains. Finally, it is necessary to find out a way to relate the polymeric chain properties or even the desired properties with easy to measure operational variables. A possible scheme of the feed-

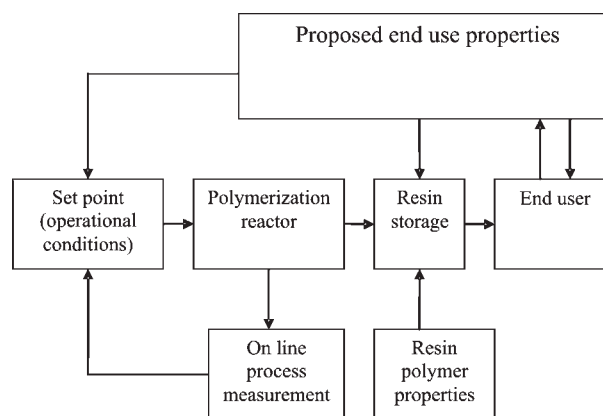


Figure 1 Simplified scheme of the feedback flow of structure polymer information.

back flow of structure polymer information is proposed in Figure 1.

Among several properties, the FI, stress exponent (SE), and density are those relatively easy to measure and, as they exert a significant influence in the final polymer, it is convenient to use them as a basis for model development.

The FI may be defined as the mass of polymer that flows in 10 min through an orifice at a defined temperature when subject to a specified pressure. It is essentially an indirect measurement of viscosity and weight-average molecular weight (MW). The larger the FI, the lower the weight-average MW. Because FI measurements are much cheaper and faster than other techniques used to evaluate average MWs, FI evaluations are very popular at plant sites. SE is a type of ratio between values of FI obtained when different loads are used to force the melt flow through the standard orifice, and it is a measure of the non-Newtonian character of the polymer melt and may be used to evaluate the processability of the polymer resin, which may be closely related to polydispersion.⁵ Although it is known that the correlation between the molecular weight distribution (MWD) and the flow behavior of polymer melts may be rather complex,⁶ a typical empirical model used at plant site for FI has the following form^{7,8}:

$$FI = \alpha * M_w^\beta, \quad (1)$$

where, $\alpha = 4.195 * 10^{19}$ and $\beta = -3.9252$.

The density is typically used as a measure of polymer crystallinity and degree of branching of polymer chains. In copolymer grades, it may be related to the final copolymer composition, as comonomer molecules introduce short branches into the polymer chain and cause a reduction of polymer crystallinity and bulk density. As polymer crystallinity also depends on the average MWs and polydispersion, it

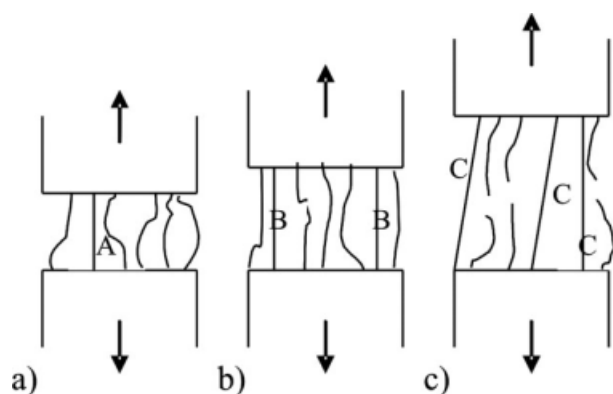


Figure 2 Tie molecules in the “amorphous” layer between crystal blocks. At low strain (a) a single tie molecule (A), at medium strain (b) two tie molecules (B), and at the highest strain (c) three molecules (C) are stretched up to the rupture point.

may be concluded that density is not an unequivocal measurement of polymer composition, but depends on the availability of FI and SE measurements. It is important to emphasize that the independent variables selected for the density model describe the MWD and composition of the final polymer resin in an indirect manner.⁵

$$\rho = \alpha + \beta * \log(\text{FI}) + \gamma * \text{SE} + \delta * [\text{CM}]_e^\varepsilon, \quad (2)$$

where, $\alpha = 0.9424$, $\beta = 4.08 * 10^{-3}$, $\gamma = 1.094 * 10^{-2}$, $\delta = -56.37$, and $\varepsilon = 0.4668$.

Because polymers cannot be completely crystalline (cannot have a perfectly regular crystal lattice) the concept “crystallinity” has been introduced. The meaning of this concept is still disputed. Solid polymers can be distinguished into the amorphous and the semicrystalline categories. The traditional model used to explain the properties of the (partly) crystalline polymers is the “fringed micelle model.” Although the coexistence of small crystallites and amorphous regions in this model is assumed to be such that polymer chains are perfectly ordered over distances corresponding to the dimensions of the crystallites, the same polymer chains include also disordered segments belonging to the amorphous regions, which lead to a composite single-phase structure. The fringed micelle model gives an extremely simple interpretation of the “degree of crystallinity” (X_c) in terms of fractions of well-defined crystalline and amorphous regions. Many excellent correlations have evolved from this model through the years, so that it has long been popular.⁹

In another model used to explain the crystalline structure of semicrystalline polymers, the main feature is that the crystalline regions disturb the amorphous phase and reduce its segmental mobility. This reduction is at its maximum in the immediate vicinity of the crystallites; at large distances from the

crystallites, the properties of the amorphous phase will become equal to those of the bulk amorphous material.⁹ The main consequence of this reduced mobility is an extension of the glass transition region toward the high temperature side.

The majority of the physical, mechanical, and thermodynamic properties on semi crystalline polymers, as the polyethylene case, depend largely on the X_c , which is directly related to resin density.

Figure 2 illustrates the mechanical behavior of semicrystalline polymers and the role of the small percentage of tie molecules.

The high MW has an intense influence on its processing. It is well known that MW can markedly affect the mechanical properties of a polymer. For many mechanical properties and polymers this effect reaches a limiting value at some relatively high MW, where there is no longer any appreciable change on mechanical properties increasing the MW. Generally, as the MW raises, the mechanical properties, toughness, and melting’s viscosity increase. The current classification of highly durable materials is based on polymers with increased MW.^{10,11}

POLYETHYLENE PRODUCTION AND PREPARATION

The process considered here is typical of many industrial processes for obtaining polyethylene and it is composed of two tubular reactors and a non-ideal stirred tank reactor. The operation is adiabatic and cooling devices are not used. The basic process configuration is shown in Figure 3. Different operation modes may be used in this system, as all reactor vessels are equipped with injection points for all chemical species. Usually, monomer, comonomer, solvent, hydrogen, catalysts, and cocatalysts are fed into the first reactor of the series (which may be reactor PFR or reactor CSTR), and hydrogen is injected along the reactor train to modify the resin grade. Reactor PFR_{trim} is used as a trimmer to increase monomer conversion and reduce the amounts of residual light gases at output stream. Besides, the agitators of

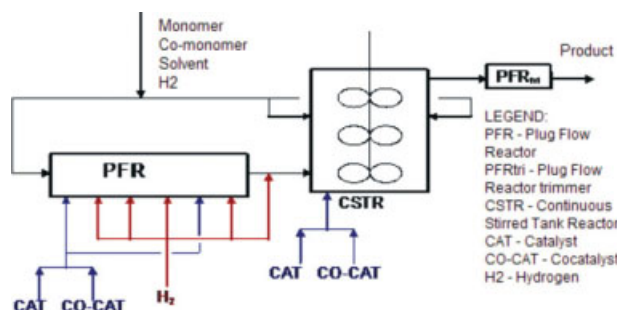


Figure 3 Basic process configuration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

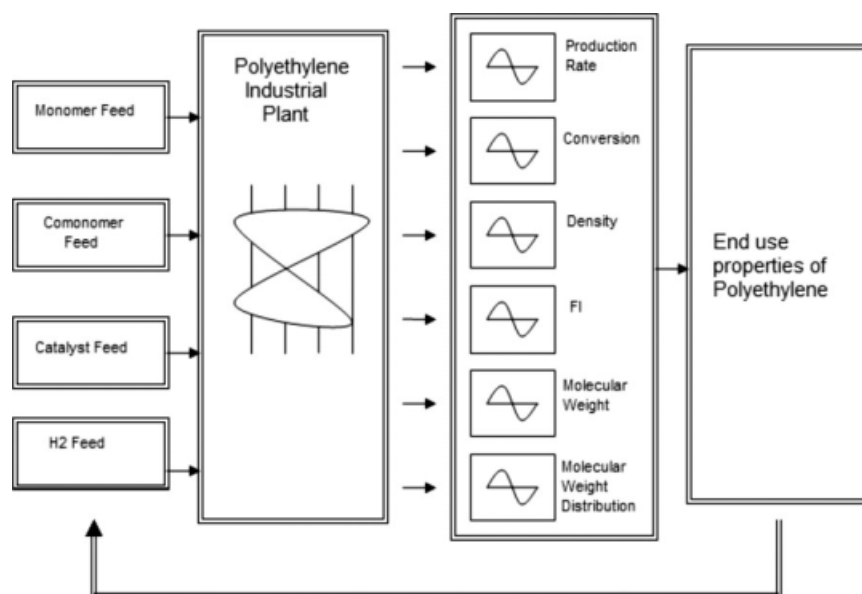


Figure 4 End-use properties related with reactor output variables.

reactor CSTR may be turned off to allow the operation of this vessel as a tubular reactor of large diameter. Therefore, depending on the operation mode, the process may be composed of a series of tubular reactors, a continuous stirred tank reactor, or some other type of mixed configuration. By changing the operation mode, significant changes of the MWD of the final polymer may be obtained, allowing the production of many resin grades.

Two operation modes are most often used:

Configuration 1: Agitated mode—Reactor PFR is not used and the agitators of reactor CSTR are turned on. Two monomer feed points and one catalyst feed point are used. Lateral feed points are used to improve the degree of mixing inside the stirred tank reactor. The degree of mixing is controlled through the manipulation of the agitator speed and the lateral feed flow rate. Back mixing inside the stirred tank reactor is forced by the agitator work, but relatively distinct mixing zones are present and axial temperature gradients may be observed. The process is composed of a no ideal stirred tank and a tubular reactor in series is used to produce polymer grades with narrower MWDs.

Configuration 2: Tubular mode—Monomer and catalysts are injected into reactor PFR and hydrogen is injected along the reactor train to control the MWD. The agitators of reactor CSTR are turned off, so that the process is composed of three tubular reactors in series. The proper control of the feed temperature is of fundamental importance in this mode, to avoid polymer precipitation inside the reactor. This operation mode is used to produce polymer grades with broader MWDs.

In this work, both configurations are considered for resins production utilized as case study. After models development that correlate end-use and intrinsic properties, the next step is to relate polymers intrinsic properties with the reactor operating conditions, through the models encountered previously [eqs. (1) and (2)]. Figure 4 illustrates this scheme. Basically, the two first blocks are related to reactor operating conditions, which will affect the polymer properties. Such intermediate properties as density and FI impact the quality of the final products represented by the last block. If such properties are well defined and related to the intermediate properties is possible to define reactor operating policies so desired products are achieved.

EXPERIMENTAL

In this work, 13 polyethylene resins were used for the models development. The most important properties to several applications and experiments involving those resins properties were evaluated. Such properties are as follows: tensile strength (TS), yield strength (YS), elongation at break (EB), stiffness, hardness, Vicat softening point (VP), melting temperature (T_m), crystallization temperature (T_c), degree of crystallinity, and impact strength (IS). Among general plastic injection molding applications are as follows: aerospace components, automotive components, avionics components, cable assemblies, computer electronics, electronics components, encapsulations, engineering prototypes, instrumentation, marketing samples, material quality testing, medical and dental products, medical

TABLE I
Operational Conditions Maintained Constants

Operational conditions	Values
CSTR agitation rotation (Amp.)	0.00
Pressure (Kgf/cm ²)	200.821
Mass percentage of lateral feed in the CSTR	0.00
Deactivation agent 1	0.00
Deactivation agent 2	0.00
Mass percentage of ethane	17.7
H ₂ (PFR)	0.00

laboratories, model shops, toys, hobby, new product design and development, test specimens, and more. Tables I and II show an average of operational conditions values for resins production. Resins present the following characteristics:

- Eight resins of high-density polyethylene (HDPE)—Homopolymers and copolymers of buthene-1, produced by solution process, with application in the injection plastic molding, which present high stiffness, IS, and environmental stress cracking, in addition to easy processability. They are additived with antioxidant.
- Two resins of linear medium-density polyethylene—Copolymers of buthene-1, produced by solution process, with application in the injection plastic molding, which present high fluidity and easy processability. They are additived with antioxidant.
- Three resins of linear low-density polyethylene—Copolymers of buthene-1, produced by solution process, with application in the injection plastic molding, which present great fluidity, flexibility, and toughness. They are also additived with antioxidant.

For the accomplishment of the experimental analysis, the samples were obtained through compression molding, which is a method in which the molding material, generally preheated, is first placed in an open heated molted cavity. The mold is closed with a top force or plug member, pressure is applied to force the material into contact with all mold areas, and heat and pressure are maintained until the molding material has cured. After compression molding of the samples, analysis were performed. For the cases in which the preservation was required, samples had been kept in the following conditions: $(23 \pm 2)^\circ\text{C}$ and $(50 \pm 5)\%$ of relative humidity, for minimum time of 40 h before the test.

A data treatment was made and empirical models correlating end-use and intrinsic properties were developed. This was carried out through STATISICA¹² software as it follows: some important correlations between all properties were found through

correlations tables and then the chosen inputs for the models were as follows: FI and density. Using a set of experiments, it was possible to built-up correlations expressing for instance performance properties (end-use properties as TS) as function of density and FI. Subsequently, the empirical models were built-up for the most usual end-use properties.

The FI is an indication of the polymer flow properties in low shear rates. The flow rates determination consists of an automatic register of the time necessary to extruder a specific volume of polyethylene through an orifice. The weight used was 6480 g, followed by the weight of 2160 g. The extrusion time, volume, temperature, and the molten polymer density were used to calculate the FI. The equipment used for measurement of FI was a Tinus Olsen Plastometer.

The polyethylene density is determined by the measured of its mass in distilled water. The density is calculated using the "Principle of Archimedes." The Principle of Archimedes states that a floating body is buoyed up by the weight of liquid it displaces. Consequently, an object floating in a liquid denser than water will not be submerged to the same extent as in water. The equipment used to determine the density was a Toyoseiki Areometer, model D-1.

The end-use properties were determined in accordance to specific analysis methods, normally used by the resin suppliers which are based on standard methods as described later.

Tensile mechanical properties were determined in accord to the ASTM D 638 norm. The TS is the maximum resistance to fracture. It is equivalent to the maximum load that can be carried by one square inch of cross-sectional area when the load is applied as simple tension. TS is the ratio between the maximum load and the area of original cross-section.

A number of terms have been defined for the purpose of identifying the stress at which plastic deformation begins. The value most commonly used for this purpose is the YS. The YS is defined as the stress at which a predetermined amount of permanent deformation occurs. The graphical portion of the early stages of a tension test is used to evaluate YS. To find YS, the predetermined amount of permanent strain is set along the strain axis of the graph, to the right of the origin (zero).

TABLE II
Changeable Operational Conditions

Operational conditions	Utilized range
Rate of flow of catalyst	10–30
Cocatalyst/catalyst ratio	1.3–1.9
Buthene/ethene ratio	0.03–0.09
Main feed temperature	100–130

TABLE III
Experimental Values of Resins

Resin	FI	Density	Tensile strength	Yield strength	Elongation at break	Stiffness	Hardness
RI-1	0.555	0.133	0.037	0.120	0.098	0.005	0.045
RI-2	0.543	0.233	0.037	0.255	0.152	0.226	0.136
RI-3	0.863	0.342	0.048	0.255	0.003	0.310	0.454
RI-4	0.882	0.328	0.052	0.800	0.018	0.293	0.500
RI-5	0.0002	0.672	1.000	1.000	0.740	0.805	0.773
RI-6	0.108	0.858	0.604	0.950	0.943	0.956	0.909
RI-7	0.107	0.823	0.633	0.750	0.867	0.680	0.818
RI-8	0.122	0.667	0.419	0.905	0.553	0.945	0.682
RI-9	0.386	0.753	0.241	0.970	0.302	0.991	0.955
RI-10	0.606	0.810	0.304	0.700	0.128	0.903	1.000
RI-11	0.404	0.133	0.074	0.750	0.051	0.142	0.318
RI-12	0.990	0.753	0.156	0.010	0.068	0.960	0.909
RI-13	0.0918	0.800	0.556	0.050	0.998	0.856	0.909

The EB of a material is the percentage increase in length that occurs before it breaks under tension. EB values of several hundred percent are common for elastomers and film/packaging polyolefins. Rigid plastics often exhibit values under 5%. The combination of high ultimate TS and high EB leads to materials of high toughness.

The stiffness was determined in accordance with the ASTM D 742 norm, procedure A, in an Instron instrument, model 5565. Five samples were used for each resin, with thickness of 3 mm, width of 12.5 mm, and length of 200 mm, and they were deformed until a total deflection of 3 mm.

Hardness is the resistance of a material to penetration of its surface. It is related to the crystallinity and hence the density of the material. The typical hardness tests are either the Shore or the Rockwell. The hardness value determined by the shape, size, and time of the indenter used to penetrate the specimen. Depending on the hardness of the material to be tested, each hardness test has several scales to

cover the entire range of hardness. For polyethylene, the Shore D scale or Rockwell L scale is used. ASTM D 2240 describes the test.

The VP was determined in accordance with the ASTM D 1525 norm. This property is the temperature at which a flat-ended needle penetrates the specimen to the depth of 1 mm under a specific load. The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application. A test specimen is placed in the testing apparatus so that the penetrating needle rests on its surface at least 1 mm from the edge. A load of 10 or 50 N is applied to the specimen. The specimen is then lowered into an oil bath at 23°C. The bath is raised at a rate of 50 or 120°C/h until the needle penetrates 1 mm.

T_m , T_c , and X_c were determined by the ASTM D 3895 norm, through differential scanning calorimetry (DSC) technique. In this technique, there are two pans. In one pan, the polymer sample is placed, and the other one is the reference pan. Each pan sits on

TABLE IV
Experimental Values of Resins (Continuation)

Resin	Vicat softening point	Melting temperature	Crystallization temperature	Degree of crystallinity	Izod impact strength
RI-1	0.015	0.009	0.027	0.003	1.000
RI-2	0.108	0.597	0.657	0.499	–
RI-3	0.115	0.612	0.740	0.379	–
RI-4	0.112	0.606	0.683	0.291	0.456
RI-5	0.362	0.944	0.893	0.875	0.581
RI-6	0.369	0.975	0.960	0.888	0.528
RI-7	0.385	0.966	0.970	0.956	0.369
RI-8	0.346	0.819	0.840	0.678	0.006
RI-9	0.333	0.919	0.837	0.957	0.117
RI-10	0.335	0.944	0.840	0.953	0.125
RI-11	0.071	0.237	0.223	0.221	0.247
RI-12	0.315	0.809	0.880	0.988	–
RI-13	0.354	1.000	0.843	0.782	–

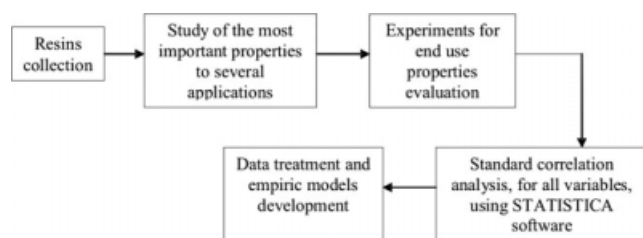


Figure 5 Schematic diagram of experimental procedure.

top of a heater. The computer turns on the heaters, at a specific rate, usually something like $10^{\circ}\text{C}/\text{min}$. X_c was evaluated from DSC measurements as the ratio between the amount of heat required to melt the sample and the heat of fusion for 100% crystalline PE.

Izod IS was determined through the ASTM D 256 norm. Six samples were tested for each resin, with thickness of 3 mm, width of 12.7 mm, and length of 62 mm, in a TMI instrument, model 4302.

Tables III and IV show the normalized experimental results obtained for resins utilized in this study. The experimental data of the properties were normalized and representative empirical models are showed. Thus, the model parameters were found in such way that each end-use property is connected to the intrinsic properties (used as entrance variable in the models).

The proposed general procedure is presented in Figure 5. After the resins collected at the reactor exit with well-known operating conditions, an extensive investigation of the resin properties is carried out for each particular application. Experiments to obtain the end-use properties of the resins are realized having as inputs the intermediate properties (FI and density, for instance), which are related to the reactor operating conditions. Statistical analysis is performed to identify which are the impacts of the intermediate properties, and hence the operating

conditions on the end-use properties. The whole procedure allows to develop the empirical models described in the next section.

RESULTS AND DISCUSSION

After characterization of the resins used as case study, the construction of the empirical models was developed using statistical tools, as factorial design and experimental planning, through the commercial software Statistica. Tables V and VI illustrate the determination coefficient R^2 , the parameter values found for each model and the statistic correlation coefficient (P) for each parameter. For the majority of the equations, the higher " P " assumed was the standard deviation normally used which is 0.05. It signifies that the probability of a calculated value for a correlation factor (or for a parameter) becomes repeated in further experiments (or data sets) are either higher than or equal to 95%. However, in specific case of some properties, the considered " P " was a little higher than 0.05, because a satisfactory multiple correlation coefficient of the model is assumed. It is important to point out that models presented here were build-up with normalized parameters. A summary of the equations obtained is shown in Table VII. Subsequently, the predictions from the empirical models were compared to the experimental values. Figures 6 and 7 illustrate the performance of the empirical models which, in fact, is quite satisfactory. It is possible to conclude that the empirical models developed may be useful to be used in either product development or for the definition of operation strategy to obtain the products with the desired property.

For the validation of the models, the equations developed using data of commercial resins were also tested using resins quoted in literature. According to the difficulty of finding data among the literature for all the properties discussed here, the cited validation

TABLE V
Parameters of Tensile Strength, Yield Strength, Elongation at Break, Stiffness, and Hardness Models

	Independent variable	Parameter	P
Tensile strength ($R^2 = 0.980$)	FI	-0.080879	0.000006
	Density	0.587494	0.000458
	FI*Density	-0.304551	0.005068
	Independent parameter	-0.079653	0.005409
Yield strength ($R^2 = 0.966$)	Density	13.22961	0.000000
	Independent parameter	-1.65495	0.000000
	FI	-0.810032	0.000260
Elongation at break ($R^2 = 0.863$)	Density	0.505505	0.016969
	Independent parameter	0.446983	0.029290
	Density	1.237417	0.000001
Stiffness ($R^2 = 0.903$)	Independent parameter	-0.074494	0.000001
	Density	1.097995	0.000001
Hardness ($R^2 = 0.906$)	Independent parameter	0.029724	0.000004

TABLE VI
Parameters of Vicat Softening Point, Melting Temperature, Crystallization Temperature, Degree of Crystallinity, and Izod Impact Strength Models

	Independent variable	Parameter	P
Vicat softening point ($R^2 = 0.976$)	FI	-0.070876	0.010801
	Density	0.441700	0.000000
	Independent parameter	0.030225	0.000000
Melting temperature ($R^2 = 0.843$)	Density	1.005198	0.000010
	Independent parameter	0.160989	0.000129
Crystallization temperature ($R^2 = 0.736$)	Density	0.858845	0.000224
	Independent parameter	0.239849	0.002333
Degree of crystallinity ($R^2 = 0.884$)	Density	1.118922	0.000002
	Independent parameter	0.022485	0.000004
Izod impact strength ($R^2 = 0.832$)	FI	-0.37229	0.166626
	Density	-1.23377	0.024028
	Independent parameter	1.37656	0.021676

was not realized for some properties. Through the results presented in Figures 8–12 can be observed that the correlations are useful for others resins, besides resins used in this work. Table VIII shows normalized experimental values of literature resins, which are used for validation of some models.

The way as each end-use property is connected to the intrinsic properties (used as independent variable in the models) is all illustrated in Table IX. With the empirical models, an analysis of the final properties behavior related to the intrinsic properties was carried out.

TS presents negative correlation with the FI, according to the model equation. This means that TS increases as FI decreases and MW increases. On the other hand, the decrease of MW leads to a smaller number of tie chains; thus, the materials become physically less interconnected, so that the applied load become more concentrated in fewer points among the microfibrils surfaces. The connections number has a stronger effect under the failure resistance (in comparison to the microfibril size), because the failure is preferably initiated over the microfibril border. According to the models, the TS and the YS

depend strongly on the polymer density. This fact is justified by stronger interaction forces between molecules as the density increases. YS does not present considerable dependence with the FI.

A viable conclusion for the EB was not possible because of the wide variations, with possible experimental errors. However, through the developed model, in the linear polyethylene and HDPE, the EB is highly and positively correlated with the density. Probably, this occurs because in these polymers (linear polyethylene and HDPE), only short branches are present, causing increase in the intermolecular forces because the chains are very packed. Moreover, long branches cause chain entanglement increase. Thus, the absence of long branches does not inhibit the chain straightening before break. In the model found the EB decreases as the FI increases. Large molecular chains can be stretched and straightened. Moreover, the greater number of intercrystalline tie chains linking the microfibrils, as the increase of MW, resists the separation which leads to fracture. The low MW HDPE contains fewer and shorter intercrystalline tie chains leading to less extension before the breaking stress is reached.

TABLE VII
Empirical Models with Representative Parameters

Properties	Empirical models	R^2
Tensile strength	$-0.080879 * \ln(\text{FI}) + 0.587494 * \text{Density} - 0.304551 * \text{FI} * \text{Density} - 0.079653$	0.980
Yield strength	$13.22961 * \text{Density} - 1.65495$	0.966
Elongation at break	$-0.810032 * \text{FI} + 0.505505 * \text{Density} + 0.446983$	0.863
Stiffness	$1.237417 * \text{Density} - 0.074494$	0.903
Hardness	$1.097995 * \text{Density} + 0.029724$	0.906
Vicat softening point	$-0.070876 * \text{FI} + 0.441700 * \text{Density} - 0.030225$	0.976
Melting temperature	$1.005198 * \text{Density} + 0.160989$	0.843
Crystallization temperature	$0.858845 * \text{Density} + 0.239849$	0.736
Degree of crystallinity	$1.118922 * \text{Density} + 0.022485$	0.884
Impact strength	$-0.37229 * \text{FI} - 1.23377 * \text{Density} + 1.37656$	0.832

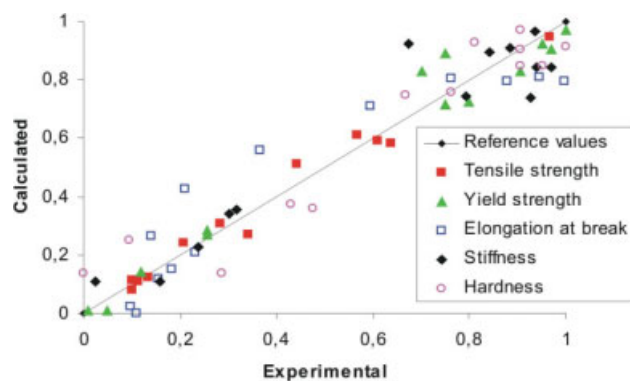


Figure 6 Comparison between experimental values and calculated values for tensile strength, yield strength, elongation at break, stiffness, and hardness. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The stiffness model demonstrates that it presents strong and positive correlation with the density. Stiffness can be expressed by the flexion elastic module (flexural modulus), which supplies a strain strength measure while forces are applied. The module is the ratio between the applied tension and the resultant deformation. In the International System of Units, stiffness is typically measured in newtons per meter and it increases according to module increases. The MW influence over the stiffness will depend on its relation to the X_c and the degree of molecular orientation. For this reason, the stiffness can increase or decrease as the FI reduces.⁴ In the proposed model, the FI does not present considerable effect in the stiffness. This could have occurred because the two mentioned factors (the X_c and the degree of molecular orientation) presented considerable influence, beyond the influence exerted by the MW. Therefore, the effect of the MW could be confounded to the

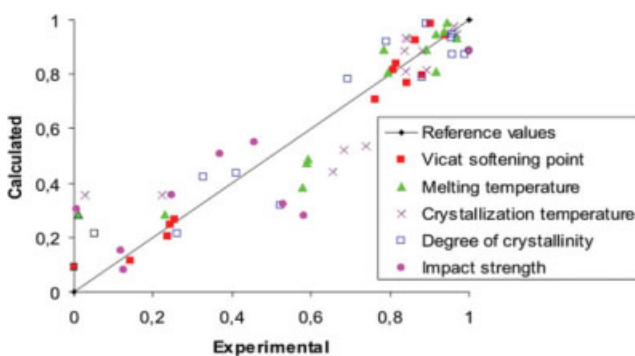


Figure 7 Comparison between experimental values and calculated values for Vicat softening point, melting temperature, crystallization temperature, degree of crystallinity, and impact strength. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

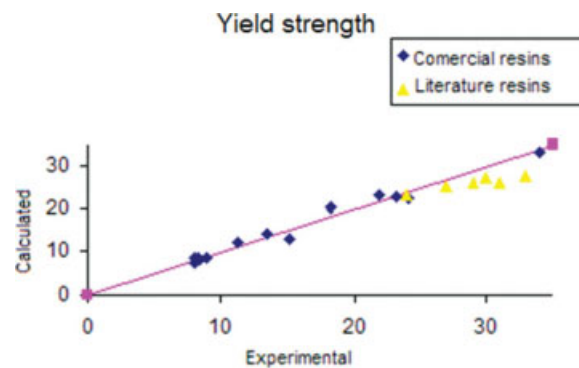


Figure 8 Calculated results for yield strength of commercial resins and literature data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

effect exerted by these two mentioned factors. The density presented strongly and positively correlation with this property.

Latado (2000) tested many grades of polypropylene and propylene/ethylene copolymers for to develop empirical models to predict the stiffness. The best result obtained for this property was as follows:

$$\text{Stiffness} = \frac{a1}{MW} + a2XS + a3, \quad (3)$$

where, $a1 = -1.45 \cdot 10^5$, $a2 = -3.37 \cdot 10^{-2}$, $a3 = 2.2530$, MW, molecular weight, and XS, xylene soluble (weight percent).

It is important to emphasize that some properties not used for this model formulation are usually assumed to be important to describe variations in the stiffness models. The density is one of them. One may wonder whether the experimental range of variation observed for crystallinity is too narrow,

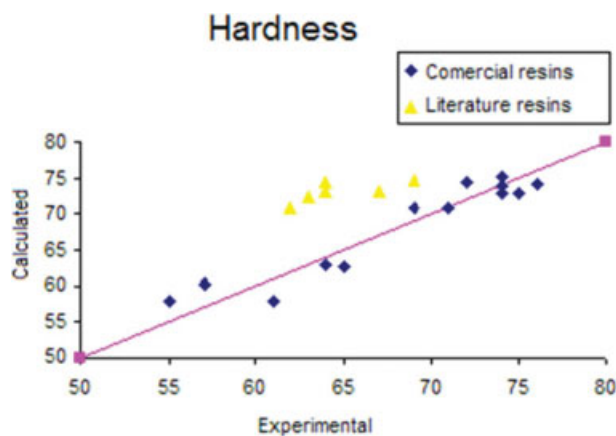


Figure 9 Calculated results for hardness of commercial resins and literature data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

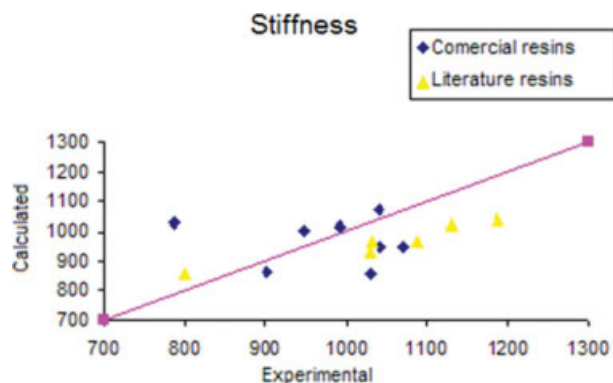


Figure 10 Calculated results for stiffness of commercial resins and literature data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

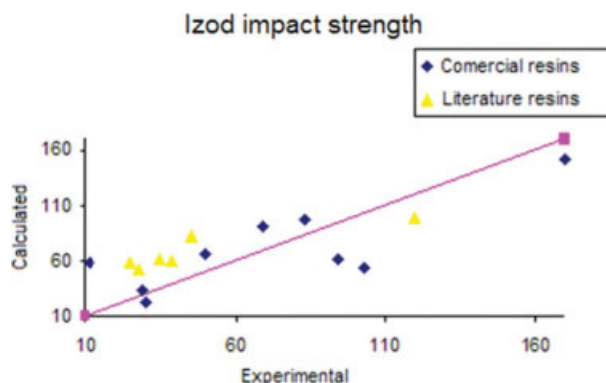


Figure 12 Calculated results for Izod impact strength of commercial resins and literature data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

although the X_c certainly depends on both X_S and MW , which are used as model inputs.⁴

The hardness tends to increase because of density increases in function of a lower distance between the polymer chains, when this property increases. This fact is explained by a stronger compacting over the polymeric chains. The FI is not a property that presents strong influence on the hardness; however, in the proposed model, the hardness tends to increase as the MW increases (lower FI).

The VP increases strongly as the density increases and it decreases as the FI increases. As cited previously, the density increase and the high MW cause the polymer resistance increase to the raised temperatures. On the other hand, the wide MWD can cause the reduction of this property, because the landslide between polymeric chains is facilitated, reducing the polymer softening temperature.

The T_m is related to overcoming secondary forces and supporting mobility to the polymeric chains.

Thus, the factors that increase secondary forces and stiffness chains will increase the T_m . In this sense, the density increase affects the T_m . The T_m had also presented strong and positive correlation with the density because as the density increases, the forces between chains increase, raising the necessary energy for the polymeric chains mobility. Although in the model encountered, the FI did not present considerable influence in the T_m , generally the T_m is positively correlated with the MW , because as larger the MW , greater will be the temperature for the beginning of the viscous draining. Thus, samples with larger MW possess larger physical interaction between the chains, leading to reduction of the chains flexibility in case of molten polymers. The expected overall trend for homopolymers is such that lower MW polymers are to melt at lower temperatures than higher MW samples.

Polymers which crystallize at high temperatures have a higher density, in comparison to polymers which crystallize at low temperatures. This fact occurs because at high T_c s, the crystals are more perfectly formed. According to the model for T_c , this property did not present considerable correlation

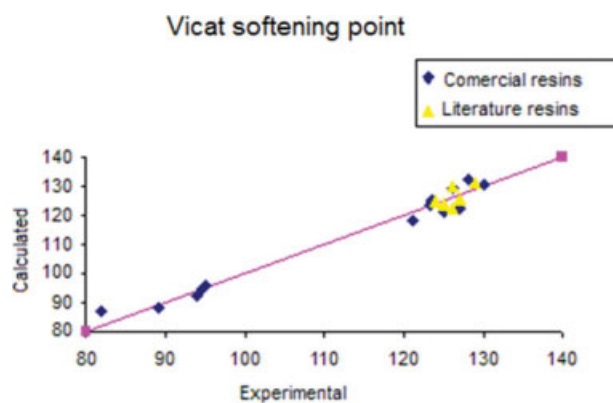


Figure 11 Calculated results for Vicat softening point of commercial resins and literature data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VIII
Experimental Values of Literature Resins, Which are Used for Validation of Some Models

Resins	Yield strength	Stiffness	Hardness	Vicat softening point	Izod impact strength
RL-1	0.600	0.78	0.400	0.143	0.050
RL-2	0.700	0.86	0.400	0.429	0.150
RL-3	0.400	0.66	0.300	0.571	0.250
RL-4	0.100	0.2	0.200	0.429	1.000
RL-5	1.000	0.976	0.900	0.857	0.190
RL-6	0.800	0.664	0.700	0.286	0.080
RL-7	0.600	0.78	0.400	0.143	0.050

TABLE IX
Correlation Between Intrinsic Properties and Final Properties

Properties	FI (↑)	Density (↑)
Tensile strength	Decreases	Increases
Yield strength	Little influence	Increases
Elongation at break	Decreases	Increases
Stiffness	Little influence	Increases
Hardness	Little influence	Increases
Vicat softening point	Decreases	Increases
Melting temperature	Little influence	Increases
Crystallization temperature	Little influence	Increases
Degree of crystallinity	Tends to increase	Increases
Impact strength	Decreases	Decreases

with FI; however, T_c tends to increase when the FI reduces (for crystallized polymers). Polymers with low MW (high MI) have a better mobility, crystallizing at lower temperatures than polymers with higher MW. In the same way, polymers with wider MWD will crystallize more easily, because smaller chains move more easily between the higher chains, facilitating the crystallization. Thus, the T_c tends to decrease as the MWD widens.

As stated previously, the X_c presents strong and positive correlation with the density. The X_c can decrease as MW increases. Larger chains are more difficult to compact, becoming the polymer more amorphous. On the other hand, polymers whose chains possess low MW form a more perfect crystalline arrangement in function of the higher chains mobility, and the higher facility for its compacting.

The IS increases as the FI and density decrease, and it is strongly correlated to the weight-average MW; in fact, it is basically a function of MW.¹ As the density increase, the X_c increases and the polymer becomes more rigid, causing low IS. On the other hand, an increase in the MW tends to increase toughness. The lower MW polymer tends to collect at the boundary between microfibrils, reducing the number of the "tie molecules." The type of crystal morphology and extent of spherulitic structure also may change with MW; hence, the behavior of crystalline polymers is affected by both MW and a variable X_c which may change with MW.

Latado (2000) developed a model to predict IS of poly(ethylene/propylene):

TABLE X
Values of the Resin Intrinsic Properties

FI	Density
21.7	0.9552

TABLE XI
Factorial Design Utilized for the Simulations

Simulation	FI	Density
1	-1	-1
2	+1	-1
3	-1	+1
4	+1	+1

$$\text{Izod} = a1 * MW + a2 * D_{RP}^2 + a3 * D_{RP} + a4 * \frac{DPP_{RP}}{D_{RP}} + a5 * \text{HDPE} + a6, \quad (4)$$

where, $a1 = 5.8 * 10^{-5}$, $a2 = -7.005 * 10^3$, $a3 = 7.056 * 10^3$, $a4 = -9,52 * 10^2$, $a5 = 57.46$, $a6 = 8.3748$, MW, molecular weight, D_{RP} , mean diameter of rubbery phase particles (μm), DPP_{RP} , mean distance between rubbery phase particles (μm), and HDPE, high-density polyethylene (weight percent).

To explore the models behavior, the technique of experimental design was used. For the application of this technique, only one resin was used in the simulations. Thus, to obtain the experimental design, it was necessary to choose a resin with intermediate values of the independent variables. Table X shows the values of the resin independent variables, and Table XI shows the experimental design used for the simulations.

The objective is not show which of the four simulations is better. They are useful for resins producers, because it is possible to observe how a variation on intrinsic properties affects end-use properties—allowing, so, a higher effective control on operational conditions, according to clients (polymers transformation industries) needs and expectations.

Intending to facilitate the analysis of the influence exerted by simultaneous variations of intrinsic

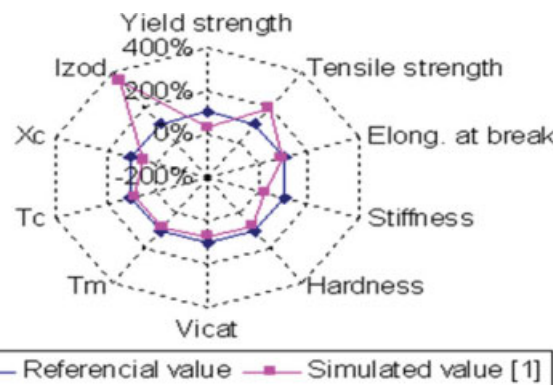


Figure 13 Variation of the final properties for simulation 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

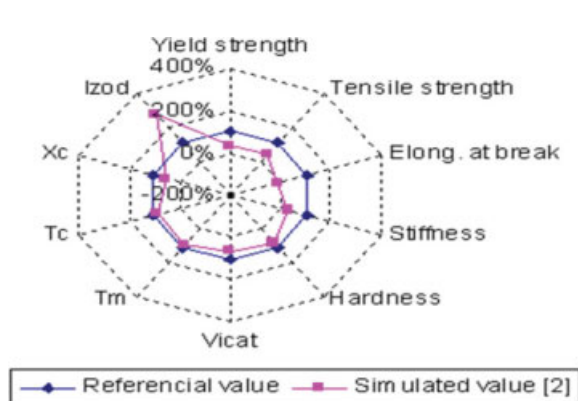


Figure 14 Variation of the final properties for simulation 2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

properties on final properties, it is proposed the use of graphics type “radar”—in which the reference values (—◆—) for each final property were calculated (by the constructed models) using values of intrinsic properties of the resin chosen to construct the factorial design (Table X). Varying the intrinsic properties, the simulated values (—■—) could be compared to the reference values. Each simulation presents a different combination of higher and lower values for the entrance variables of the models.

For FI, values +1 and -1 indicate the variation in the values -90 and +90%, and for density, this variation is -4 and +4%. The graphs showing the final properties variation, for each simulation carried through experimental design, are illustrated in Figures 13–16.

Tables XII and XIII show the percent variation of increase (+) or decrease (-), in relation to the initial experimental value of each final property, for each simulation. These simulations are of great interest to resins producers, once, through them, it is possible

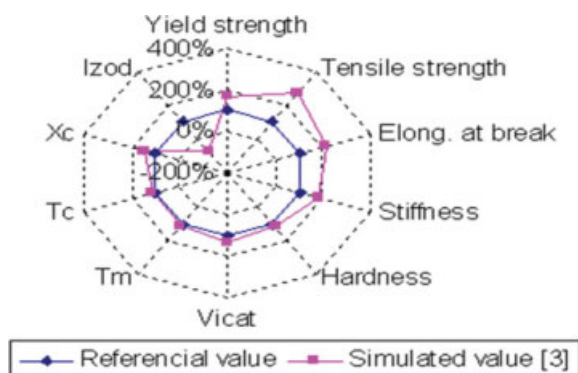


Figure 15 Variation of the final properties for simulation 3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

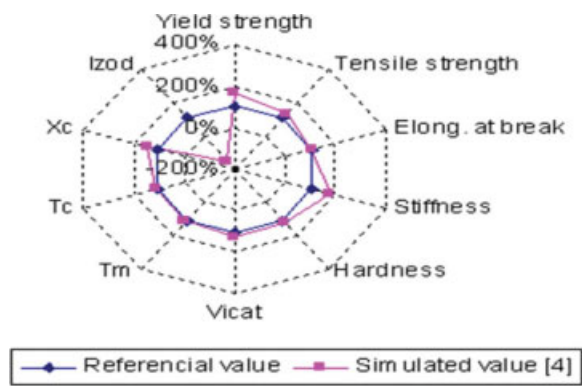


Figure 16 Variation of the final properties for simulation 4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to control process variables, to obtain resins with the specified properties.

It can be observed that TS decreases as the FI increases, and it is strongly correlated with the density. YS, EB, stiffness, hardness, and X_c increase significantly as density increases. Elongation at break decreases as the FI increases. The VP decreases as the FI increases, and it increases as the density increases. The T_m and T_c tend to increase as the density increases. IS decreases with the increase of the FI and density.

CONCLUSIONS

Empirical models have been developed to predict end-use properties of polyethylene resins. The modeled properties were TS, YS, EB, stiffness, hardness, Vicat softening temperature, T_m , T_c , X_c , and IS. According to the results presented, all the properties are a function of the density and they are correlated strongly and positively with this property. TS, EB, Vicat softening temperature, and IS are a function of the FI. The results presented allow to conclude that final properties can be affected by several factors. However, it may also be concluded that it is possible to model polymer end-use properties as functions of

TABLE XII
Percentual Variation for TS, YS, EB, Stiffness, and Hardness

Simulations		End-use properties				
FI	Density	TS (%)	YS (%)	EB (%)	Stiffness (%)	Hardness (%)
-1	-1	+96	-66	-2	-75	-21
+1	-1	-55	-66	-113	-75	-21
-1	+1	+170	+66	+113	+75	+21
+1	+1	+25	+66	+2	+75	+21

TABLE XIII
Percentual Variation for VP, T_m , T_c , X_c and IS

Simulations		End-use properties				
FI	Density	VP (%)	T_m (%)	T_c (%)	X_c (%)	IS (%)
-1	-1	-27	-15	-14	-45	+254
+1	-1	-32	-15	-14	-45	+176
-1	+1	+32	+15	+14	+45	-176
+1	+1	+27	+15	+14	+45	-254

FI and density in a simple manner, which may have an impact on the company sales strategy of polymer manufacturers. As suggestion for future works, which certainly will contribute for deepening the knowledge in this area contributing to the competitiveness increase in the polymers transformation industries, is the consideration of other molecular and structural characteristics that influence processability and model product properties, processing variables, sample dimensions, and properties, such as morphology, orientation, and residual stresses. Also, it is worthwhile to consider the distributions of crystallinity and density in the injection molding part, depending on the shape and molding conditions, the cooling process, which determines the density, mechanical properties, morphology, shrinkage, etc. With the proposed procedure, it is also possible

to correlate density, FI, and other molecular and structural properties with processing conditions.

References

- Hinchliffe, M.; Montague, G.; Willis, M. *AIChE J* 2003, 49, 2609.
- Meijer, H. E. H.; Govaert, L. E. *Prog Polym Sci* 2005, 30, 915.
- Costa, M. C. B.; Jardini, A. L.; Embiruçu, M.; Wolf Maciel, M. R.; Maciel Filho, R. In *17th European Symposium on Computer Aided Process Engineering (ESCAPE17)*; Plesu, V., Agachi, P. S., Eds.; Elsevier B.V.: Bucharest, Romania, 2007.
- Latado, A.; Embiruçu, M.; Mattos Neto, A. G.; Pinto, J. C. *Polym Test* 2001, 20, 419.
- Embiruçu, M.; Lima, E. L.; Pinto, J. C. *J Appl Polym Sci* 2000, 77, 1574.
- Carrot, C.; Revenu, P.; Guillet, J. *J Appl Polym Sci* 1996, 61, 1887.
- Gahleitner, M.; Bernreitner, K.; Neißl, W.; Paulik, C.; Ratajski, E. *Polym Test* 1995, 14, 173.
- Gahleitner, M.; Wolfschwenger, J.; Bachner, C.; Bernreitner, K.; Neißl, W. *J Appl Polym Sci* 1996, 61, 649.
- Van Krevelen, D. W. *Properties of Polymers—Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*; University of Technology: Delft, The Netherlands, 1990.
- Trotignon, J. P.; Verdu, J.; Dobraczynski, A.; Piperaud, M. *Précis de Matières Plastiques—Structures-Propriétés mise en Oeuvre et Normalisation*; Paris, Tour Europe, 1982.
- Lucas, F. E.; Soares, B. G.; Monteiro, E. E. C. *Caracterização de Polímeros—Determinação de Peso Molecular e Análise Térmica*; E-papers serviços Ltda.: Rio de Janeiro, 2001; p 194.
- Statsoft, Inc *STATISTICA'98 Edition, Version 6.0*; Statsoft, Inc.: 1998.