Modeling and simulation for correlation between operational conditions and end-use properties of high density polyethylene resins
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Modeling and simulation for correlation between operational conditions and end-use properties of high density polyethylene resins

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Abstract

The development of mathematical relationships to allow the prediction of end-use properties of polymer resins as functions of the polymerizations conditions may be very useful for the production of resins with consumer specified properties. The problem, however, is that there is a lack of theoretical knowledge regarding how end-use properties are influenced by process operation conditions. The approach used here to bridge this gap is to develop relationships between the molecular, morphological and end-use properties first and then to correlate operation conditions with molecular and morphological resin properties. Bearing this in mind, the first step in this work is to build-up empiric models relating intrinsic and end-use properties of high density polyethylene (HDPE). Statistical correlation analysis was performed for all variables and used as the basis for proper choice of inputs to each outputs model. Subsequently, a process composed of two tubular reactors and a non-ideal stirred tank reactor, representative of many industrial plants, where different operational modes may be used as case study. Polyethylene resins produced in a second generation petrochemical industry and applied in the injection plastic molding were evaluated experimentally, since it is an important commodity nowadays. The developed models were compared to experimental data and good predictions were obtained.

Keywords: modeling, empirical models, polymerizations conditions, end-use properties, polyethylene

1. Introduction

The injection molding process involves taking plastic in the form of pellets or granules and heating this material until a melt is obtained. Then the melt is forced into a split-die chamber/mold where it is allowed to "cool" into the desired shape. The mold is opened and the part is ejected, at which time the cycle is repeated. Figure 1 shows schematically the injection plastic molding process.
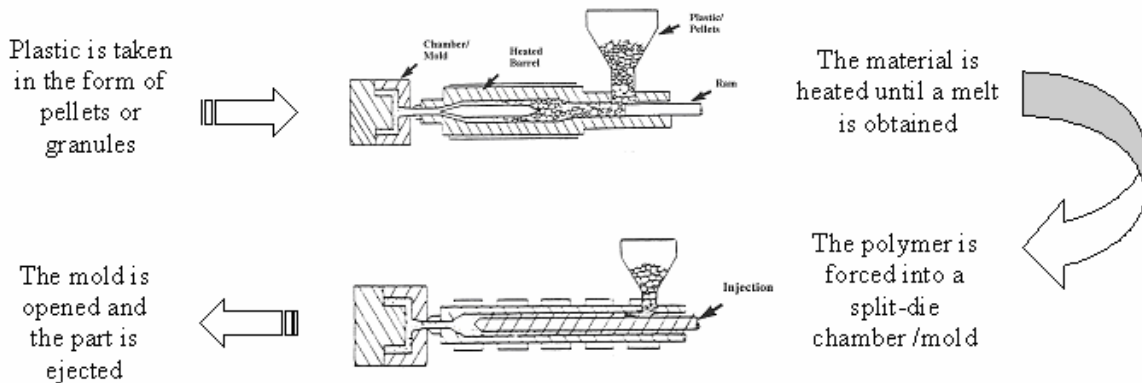

Figure 1 – Schematic diagram of the injection plastic molding process.

The final use properties 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 an enormous amount of different properties combinations that a polymer can present, leading to significant difficulties to correlate basic and final polymers properties (Costa *et. al*, 2006).

Resins produced in a polymerization process are approved by industrial quality control routines only if they meet a package of specifications needed for certain applications. Specifications are usually defined in terms of end-use properties, such us tensile strength and stiffness. If resin properties do not meet the defined specifications, resin lots are discarded, reprocessed or used for other applications, bringing some disadvantage to the company. Therefore, the development of mathematical relationships to allow the prediction of end-use properties of polymer resins as functions of the polymerizations conditions may be very useful for the production of resins with assured specified properties. The problem, however, is that there is a lack of theoretical knowledge regarding how process operation conditions and end-use properties are related. The approach used here to bridge this gap is to identify the relationship between the some molecular and morphological properties (FI and density) of polyethylene resins and then to accommodate the desired end-use properties with those properties to develop suitable correlations. Continually, it is necessary to correlate operation conditions with FI and density of resins. According to this strategy, the first step may be regarded to be the most important one, as the second step may be performed with the help of process simulators.

Empirical models are possible and useful solutions to represent complex systems in which is hard, expensive or too time consuming to develop a detailed deterministic

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model. Empirical models can describe the process behavior, based on experimental evidence, with a suitable procedure to cover all possible range of operating conditions.

The objective of the present work is to develop empiric models to predict end use properties of polyethylene resins as functions of more fundamental molecular and morphological properties of the polymer resins. The development was carried out through resin characterizations and variable determination used on empirical models. Polyethylene resins applied in the injection plastic molding, produced in a second generation petrochemical industry, were used as a case study, since it is an important commodity nowadays.

2. The Proposed Procedure

The product quality is one of the preliminary reasons for using advanced controls in the polymer industry. The material without specification must be sold by reduced price, be mixed with another material, or be wasted, resulting all the three alternatives in lower profits (Latado *et. al*, 2001). However the main problem is to obtain the required set of reactor operational conditions based on feedback information from the desired properties of end-use of the polymers. This is not easy to be done but important insight can be seen if the final properties of the polymer are expressed as function of the intrinsic properties of the polymeric structure. Finally, it is necessary to find out a way to relate the intrinsic properties or even the end-use desired properties with easy to measure operational variables.

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. The FI is essentially an indirect measurement of viscosity and weight average molecular weight. The larger the FI, the lower the weight average molecular weight. Because FI measurements are much cheaper and faster than other techniques used to evaluate average molecular weights, FI evaluations are very popular at plant sites (Embiruçu *et. al*, 2000). Although it is known that the correlation between the molecular weight distribution (MWD) and the flow behavior of polymer melts may be rather complex (Carrot *et. al*, 1996), a typical empirical model used at plant site for FI has the following form (Gahleitner *et. al*, 1995, 1996):

$$FI = \alpha * Mw^{\beta} \tag{1}$$
where, $\alpha = 4,195*1019$ (g/10min) and $\beta = -3,9252$ (g/10min)

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 molecular weights and polydispersion, it may be concluded that density is not an unequivocal measurement

of polymer composition, but depends on the availability of FI and *"stress exponent"* (SE) measurements. 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. 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 (Embiruçu *et. al,* 2000).

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

where, $\alpha = 0{,}9424$ (g/ml), $\beta = 4{,}08*10^{-3}$ (g/ml), $\gamma = 1{,}094*10^{-2}$ (g/ml), $\delta = -56{,}37$ (g/ml), $\varepsilon = 0{,}4668$ (g/ml)

3. Process Description

The process studied here 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 1. As shown in Figure 1, 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 #3 or reactor #1), and hydrogen is injected along the reactor train to modify the resin grade. Reactor PFR_{tri} is used as a trimmer, to increase monomer conversion and reduce the amounts of residual light gases at output stream. Besides, the agitators of reactor #1 may be turned off in order 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.
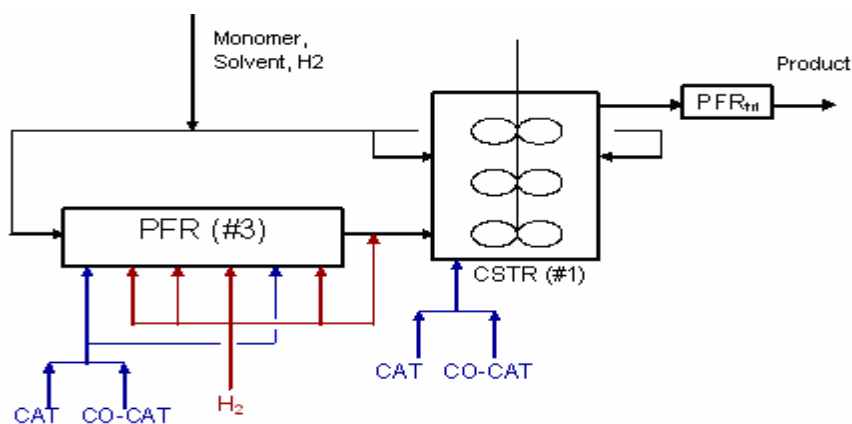

Figure 2 – Basic Process Configuration.

Two operation modes are used most often:
Configuration 1: agitated mode. Reactor #3 is note used and the agitators of reactor #1 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 and is used to produce polymer grades with narrower MWDs.

Configuration 2: tubular mode. Monomer and catalysts are injected into reactor #3 and hydrogen is injected along the reactor train to control the MWD. The agitators of reactor #1 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.

4. Experimental

For this work, thirteen polyethylene resins applied in the injection plastic molding were used for the models development. The most important properties to several applications and experiments involving those resins properties were evaluated. Subsequently, a data treatment was made and empiric models developed, correlating end-use and intrinsic properties.

The fluidity index (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 6480g, followed by the weight of 2160g. 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 final properties were determined in accordance to specific analysis methods, normally used by the resin suppliers.

Tensile mechanical properties were determined in accord to the ASTM D638 norm. The tensile strength 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. Tensile strength 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 yield strength. The yield strength 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 yield strength. To find yield strength, the predetermined amount of permanent strain is set along the strain axis of the graph, to the right of the origin (zero).

The elongation at break of a material is the percentage increase in length that occurs before it breaks under tension. Elongation at break 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 tensile strength and high elongation at break leads to materials of high toughness.

The stiffness was determined in accordance with the ASTM D742 norm, procedure A, in an Instron instrument, model 5565. Five injection molded test pieces were used for each resin, with thickness of 3 mm, width of 12,5 mm and length of 200 mm. Samples 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 upon 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 D2240 describes the test.

The vicat softening point was determined in accordance with the ASTM D1525 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 10N or 50N is applied to the specimen. The specimen is then lowered into an oil bath at 23 degrees C. The bath is raised at a rate of 50^0 or 120^0 C per hour until the needle penetrates 1 mm.

Melting temperature, Crystallization temperature and degree of crystallinity were determined by the ASTM D3895 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 top of a

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heater. The computer turns on the heaters, at a specific rate, usually something like 10^0C per minute. Degree of crystallinity 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 impact strength was determined through the ASTM D256 norm. Six injection molded test pieces 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.

The experimental data of the properties were normalized and representative equations were found for the final properties. Thus, the model parameters were found in such way that each final property is connected to the intrinsic properties (used as entrance variable in the models).

Standard correlation analysis was performed for all variables in order to detect the existence of significant correlations. The *Statistica* software was used for this purpose and for models development. Some of the correlations obtained, significant within the 95% confidence limits, are presented in the discussion of the results. The model parameters were obtained in such way that each final property is connected to the intrinsic properties (used as entrance variable in the models). The proposed general procedure is presented in Figure 3.
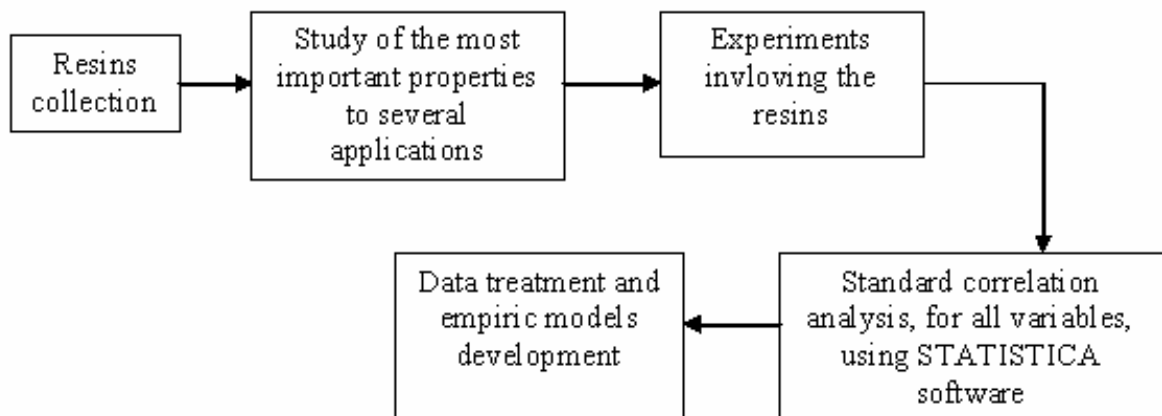

Figure 3 – Schematic Diagram of experimental procedure.

The next step is to relate polymers end-use properties with the reactor operating conditions, which may be performed with the help of process simulators.

5. Results and Discussion

The predictions from the empirical models were compared to the experimental values. Figures 4 – 13 illustrate the performance of the empirical models, which in fact is quite satisfactory, the models with representative parameters obtained for resins applied in the injection plastic molding and the multiple correlation coefficients for each model. 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. With the empiric models, an analysis of the final properties behavior related to the intrinsic properties was carried out.
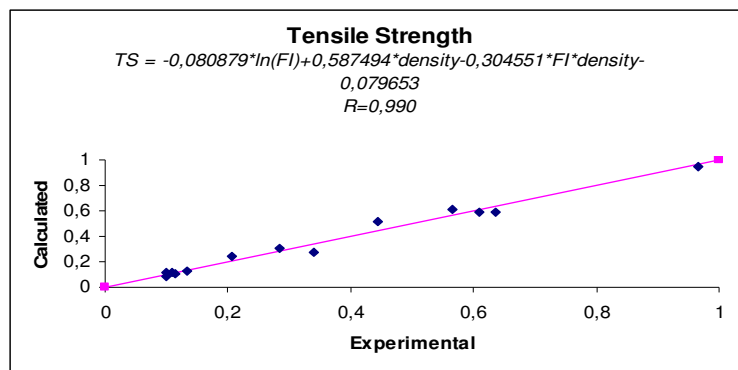
Tensile Strength
TS = -0,080879*ln(FI)+0,587494*density-0,304551*FI*density-0,079653
R=0,990

Figure 4 – Comparison between experimental values and calculated values for tensile strength.

Yield Strength
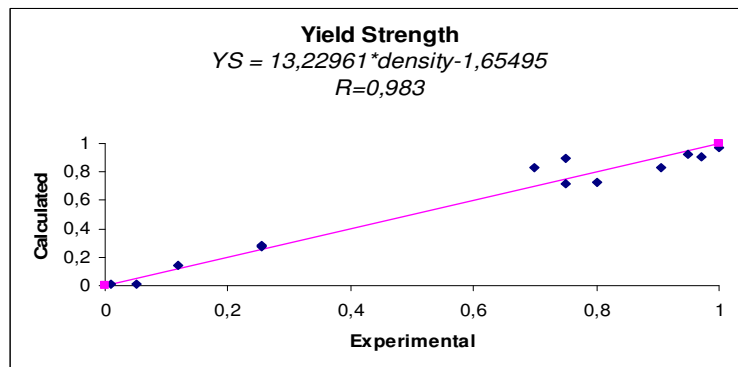*YS = 13,22961*density-1,65495*
R=0,983

Figure 5 – Comparison between experimental values and calculated values for yield strength.

Tensile strength presents negative correlation with the fluidity index, according to the model equation. Thus, tensile strength increases as fluidity index decreases and molecular weight increases. The decrease of molecular weight originates decrease of the number of tie chains; thus the materials become physically less interconnected – then, the applied load become more concentrated in fewer points among the microfibrils surfaces. The connections density 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 tensile strength and the yield strength depend strongly on the polymer density. This fact is justified by

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stronger interaction forces between molecules as the density increases. Yield strength doesn't present considerable dependence with the fluidity index.
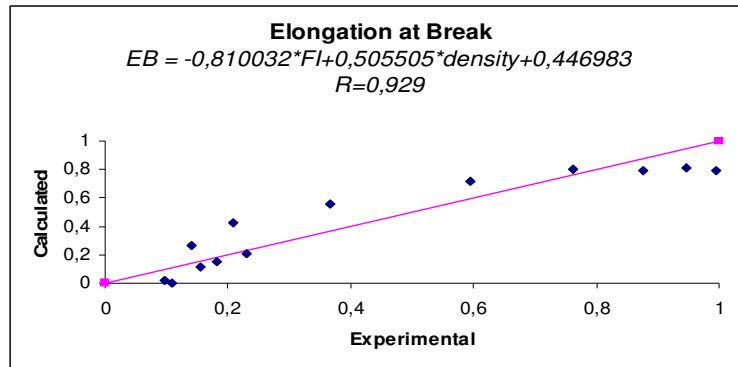
Elongation at Break
EB = -0,810032*FI+0,505505*density+0,446983
R=0,929

Figure 6 – Comparison between experimental values and calculated values for elongation at break.

A viable conclusion for the elongation at break was not possible. Probably, this occurred because the experimental values for this property presented wide variations, with possible and considerable experimental errors. Thus, the repetition of these experiments is indicated. However, through the developed model, in the linear polyethylene (LDPE) and high density polyethylene (HDPE), the elongation at break is highly and positively correlated with the density. Probably, this occurs because in these polymers (linear polyethylene and high density polyethylene), 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 prior to break. In the model obtained the elongation at break decreases as the FI increases. Big molecular chains can be stretched and straightened. Moreover, the greater number of intercrystalline tie chains linking the microfibrils as the increase of molecular weight 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.

Margolies (1971), working with HDPE, found that the ultimate tensile elongation increased rapidly to a maximum at an MW of $5*10^5$ to $7,5*10^5$. However, further increases in MW caused a steady decrease in ultimate elongation. Two possible explanations for this behavior can be given. First, it was considered the molecular chain in the vicinity of MW $\approx 5*10^5$. Here the molecular chains are long enough to be stretched and straightened and yet short enough so that substantial entanglement, as compared to that which occurs in the ultra-high molecular weight region, does not occur. In the ultra-high molecular weight region, chain entanglement increases to a point where chain straightening is substantially inhibited prior to break, therefore resulting in lower elongation values. The second explanation was that in addition to increasing chain entanglements, intermolecular forces between very high MW molecules become significant. In low MW PE the intermolecular forces between small molecules are weak in comparison to the primary valence forces. Therefore,

chain slippage is the primary factor affecting elongation. In high MW samples, however, it becomes easier to break primary valence bonds (chain scission) than to overcome the chain entanglements and significant intermolecular forces. The net effect again is a reduction in ultimate elongation. Perkins and Porter (1976), examined ultra-drawn HDPE and found that the ultimate elongation increased with increasing MW. They stated that this was due to the greater number of non-extended intercrystalline tie chains linking the microfibrils and resisting the separation which leads to fracture. The fibers made from low MW HDPE would contain fewer and shorter intercrystalline tie chains leading to less extension before the breaking stress is reached.
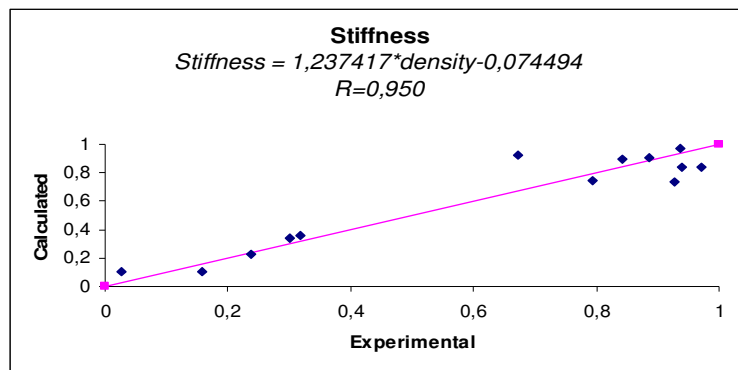

Figure 7 – Comparison between experimental values and calculated values for stiffness.

The stiffness model demonstrates that it presents strong and positive correlation with the density (Latado *et. al*, 2001). Stiffness can be express by the flexion elastic module, which supplies a strain strength measure while forces are applied. The module is the ratio between the applied tension and the resultant deformation. The stiffness increases according to module increases. Strength and stiffness are, in theory, closely related - but in practice, a high modulus does not necessarily guarantee high strength (W. Wu and Black, 1979).

The molecular weight influence over the stiffness will depend on its relation to the degree of crystallinity and the degree of molecular orientation. For this reason, the stiffness can increase or decrease as the fluidity index (FI) reduces. In the proposed model, the fluidity index does not present considerable effect in the stiffness.
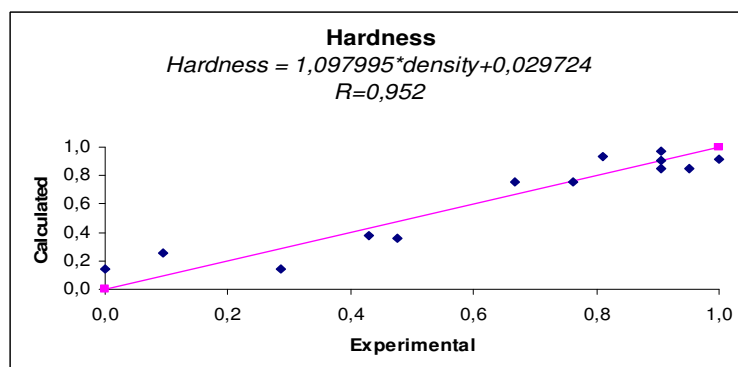

Figure 8 – Comparison between experimental values and calculated values for hardness.

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The hardness tends to increase due to density increases in function of a lesser distance between the polymer chains, when this property increases. This fact is explained by a stronger compacting over the polymeric chains. The fluidity index is not a property that presents strong influence on the hardness. Margolies (1971), found that with the Rockwell type R tests, hardness of PE decreased with increasing MW up to $1,75*10^6$, beyond which no further change occurs. On the other hand, Schollenberger and Dinbergs (1979), found no systematic change in hardness with increasing polyurethane MW when measured by Shore A durometer. A slight trend toward lower Shore D hardness in the lower MW samples was observed. Deanin *et al.* (1971), showed that indentation hardness of plasticized PVC was moderately dependent on MW. Their data suggest that the high MW fraction was controlling and that hardness depended upon disentanglement of the longest chains rather than on segmental mobility.

Vicat Softening Point
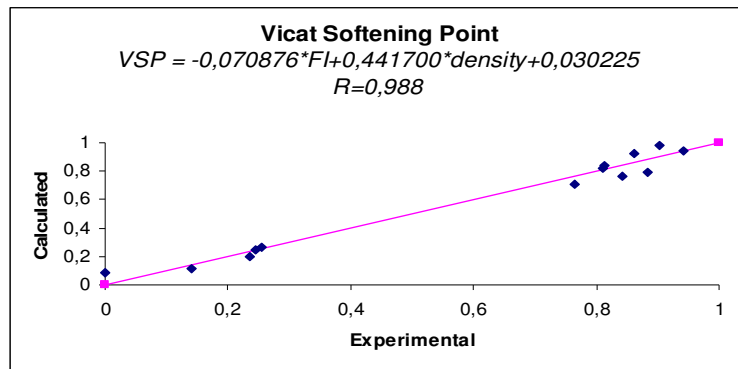*VSP = -0,070876*FI+0,441700*density+0,030225*
R=0,988

Figure 9 – Comparison between experimental values and calculated values for Vicat softening point.

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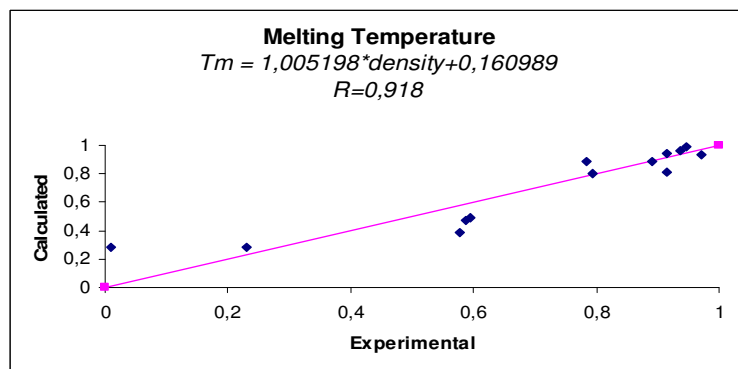

Melting Temperature
Tm = 1,005198*density+0,160989
R=0,918

Figure 10 – Comparison between experimental values and calculated values for melting temperature.

The Tm 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 Tm. In this sense, the density increase affects the melting temperature. The melting temperature had also presented strong and positive correlation with the density because as the density increases, the forcers between chains increase, raising the necessary energy for the polymeric chains mobility. Although in the model encountered, the FI hadn't presented considerable influence in the Tm, generally the melting temperature is positively correlated with the molecular weight, because as larger the molecular weight, greater will be the temperature for the beginning of the viscous draining. Thus, samples with larger molecular weight possess greater physical interaction between the chains, causing 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. Clements *et. al* (1979) and Perkins and Porter (1976), found the melting point of drawn PE to increase with increasing MW. The softening temperature increases in a manner proportional to MW (Margolies, 1971).
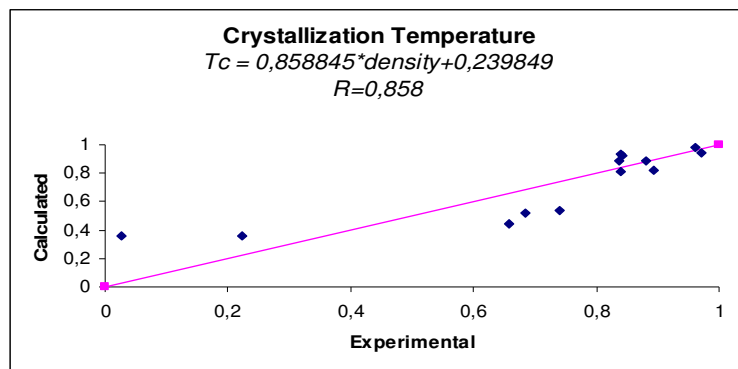

Figure 11 – Comparison between experimental values and calculated values for crystallization temperature.

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 crystallization temperatures, the crystals are more perfectly formed. According to the model for crystallization temperature (Tc), this property didn't present considerable correlation with FI, however crystallization temperature (Tc) tends to increase when the fluidity index reduces (for crystallized polymers). Polymers with low molecular weight (high FI) have a better mobility, crystallizing at lower temperatures than polymers with higher molecular weight. In the same way, polymers with wider molecular weight distribution will crystallize more easily, because smaller chains move more easily between the higher chains, facilitating the crystallization. Thus, the crystallization temperature tends to decrease as the molecular weight distribution widens.

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Degree of Crystallinity
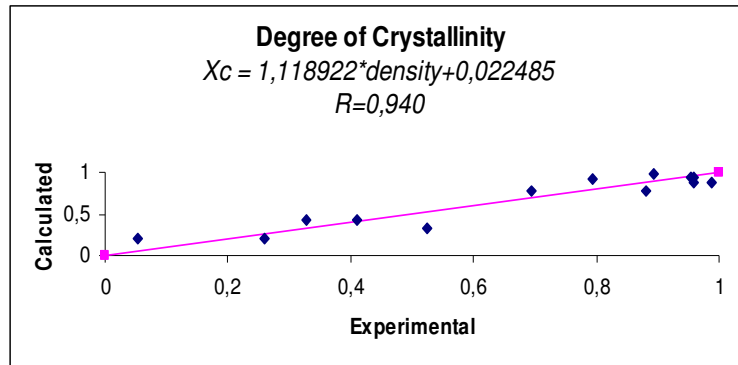*Xc = 1,118922*density+0,022485*
R=0,940

Figure 12 – Comparison between experimental values and calculated values for degree of crystallinity.

As stated previously, the degree of crystallinity presents strong and positive correlation with the density. The degree of crystallinity can decrease as MW increases. Larger chains are more difficulty 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.

Impact Strength
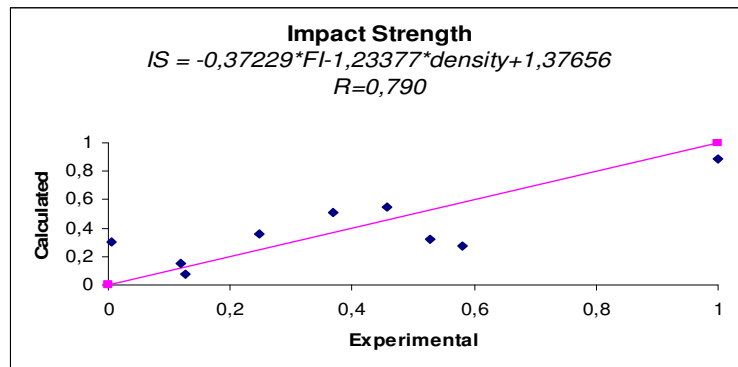*IS = -0,37229*FI-1,23377*density+1,37656*
R=0,790

Figure 13 – Comparison between experimental values and calculated values for impact strength.

The impact strength increases as the FI and density decrease. With the density increase, the degree of crystallinity increases and the polymer become more rigid, causing low impact strength. 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". Therefore, low MW polymers tend to brittle and have low impact strength. 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 degree of crystallinity which may change with MW.

6. Conclusions

Empirical models have been developed to predict end-use properties of polyethylene resins. According to the results presented, all the properties are positively and strongly correlated with the density, unless impact strength. Tensile strength, elongation ate break, Vicat softening point and impact strength decrease as the FI increases. The results presented allow us to conclude that final properties can be affected by several factors. It may also be concluded that it is possible to model polymer end-use properties as functions of fluidity index and density in a simple manner, which may have an impact on the company sales strategy of polymer manufacturers. Beyond this, the equations obtained may be used to define process operation in order to obtain a product with desired properties.

7. Acknowledgments

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