

Effect of the Processing Conditions on the Microstructure and Properties of Rotational Molded Polyamide 11

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ABSTRACT: Rotomolded containers for solvents and hydrocarbons require the use of high-permeability resins such as polyamide (PA). The published studies with this material are very scarce. In this work, a commercial grade of PA11 was rotational-molded using different processing temperatures and characterized with a range of techniques. The study aims at investigating the influence of the processing conditions on the microstructure and properties of molded parts. The results showed that the spherulitic morphology and the mechanical properties are affected by the processing temperature, the optimum processing range being between 220°C and 240°C. Overheating causes a decrease of the impact strength and a severe increase in

the formation of pinholes at the outer surface due to polymer degradation and formation of volatile products. The thermo-oxidation reactions occurring at the inner surface of the samples result in the formation of products that absorb in the UV and visible light regions and cause the microhardness and the melt viscosity of the material to increase. The extent and severity of the degradation at the inner surface may be easily assessed by fluorescence microscopy. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 939–946, 2008

Key words: polyamides; processing; microstructure; degradation; mechanical properties

INTRODUCTION

The rotational molding process is one of the fast growing technologies used with plastic, with recent growth rates above 12% in Europe and USA.^{1,2} This process is ideal for large hollow products, as deposits and containers made from thermoplastics that may not be produced by any other method.^{3–5} Polyethylene is the material that accounts for more than 90% of the applications in rotational molding and is also the better-studied material in this context. A selection of publications related to the rotational molding of polyethylene is included herein.^{6–8} In spite of its widespread use, polyethylene bears some weaknesses, namely the low barrier properties for gases and volatile organic liquids. Therefore, a demand for other polymers with lower permeability toward those agents exists and widens the research interests in rotational molding. Polyamides (PAs) are known by their excellent barrier properties to gases and organic vapors and may well overcome the weakness of polyethylene in products where these properties are relevant, as is the case of diesel and gasoline fuel tanks.

Therefore, the combination of PAs with polyethylene in containers for volatile products opens a new and important field for application of rotational molding that is already being explored with PA11.

During the rotational molding process, the material, generally in powder form, is heated by contact with the internal metal surface of a mold that is kept rotating in a hot oven until a homogeneous molten layer is formed. The mold is then moved into a cooling zone and the rotation maintained until the material is solidified and the part can be handled. During the heating period and the first part of the cooling stage, when the molten material is kept at temperatures well above the melting point and in the presence of air, degradation of the polymer may occur and affect deeply the material properties. Previous work with polyethylene⁷ showed that degradation at the inner free surface of the parts is likely to occur when the melt is overheated. The degradation causes the melt viscosity to increase because of the crosslinking of the polymer molecules, and results in evident modifications of the crystalline morphology and severe deterioration of the mechanical performance of the products. Consequently, the maximum temperature reached by the air inside the mold [peak internal air temperature (PIAT)] is a fundamental processing parameter that must be controlled to avoid degrada-

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TABLE I
Properties of Rilsan PA11

Specific gravity ASTM D 792	1.05
Melting point ASTM D 3418	185°C
Zero shear viscosity at 210°C	150 Pa s
Tensile stress at yield ASTM D 638	36 MPa
Elongation at break ASTM D 638	270%
Izod impact strength ASTM D 256	123 J/m

tion of the polymer and to obtain optimum properties of the parts.

The degradation reactions in rotational molding are specific for each polymer and may affect differently the morphology and properties of the molded parts. For instance, in the case of polyethylene, the dominant degradation reactions lead to molecular crosslinking and may suppress the crystallization of the polymer or at least change its nucleation behavior in such a way that the resulting morphology reveals very clearly the thermal history of the polymer.⁷ In contrast to this, the degradation of polypropylene, which is dominated by chain-scission reactions, is more difficult to access by observing the crystalline morphology. This results from the modifications in the spherulitic morphology at the inner surface being small and only a slight increase in the birefringence of the α -form spherulites is detected in the degraded polymer.⁹

The detection of degraded polymer or of incomplete powder sintering in the molded parts, which may be done by light microscopy, is crucial in terms of quality control because these are the two main causes for deterioration of the mechanical properties. However, before applying that technique to a particular polymer, a detailed study must be done to establish the relationship between the processing conditions, the morphology, and the properties of the molded parts.

Studies on rotational molding of a reactive liquid nylon (Nyrim) were published,^{10,11} but to our best knowledge there are no publications related to rotomolding of PA powders. This paper reports on a study where a powder grade of a commercial PA11 was used with the objective of gathering a better knowledge of the rotational molding behavior of this material. A wide range of experimental techniques were envisaged, aiming at establishing the morphology-processing-properties relationship for that material. From hereon the optimum processing window and the best testing methods could be selected for quality control of the molded parts.

EXPERIMENTAL

Material and equipment

The material used in this study is a powdered PA11, Rilsan RDG-238, from Arkema Inc. (France). This PA

is being applied in rotomolded fuel tanks, and some of their properties, as quoted by the supplier, are shown in Table I.

The material was molded using a prototype rock and roll rotational molding machine, developed at the Polymer Engineering Department of University of Minho and described elsewhere.¹² The heating system consists of a cubic oven with an internal volume of $\sim 400^3$ mm³ provided with electric resistances with total power of 7.5 kW. The molding is a 700-mL bottle with flat sides that allow impact and tensile test specimens to be taken for mechanical testing. Prior to molding, the polymer powder was dried for 14 h at 90°C.

In the molding cycle, the powder is charged manually into the mold and all the other operations follow automatically. Once the mold is closed and the cycle started, it moves into an electrically heated oven while is rotated and rocked at predefined speeds and amplitudes. When the predefined heating time is complete, the mold moves into the cooling chamber where it can be cooled using forced air, water spray, or a combination of the two.

In this study, the oven temperature was set at 400°C, the rotation speed was 8 rpm, and rocking frequency of the mold 2 cycles per minute. During a rocking cycle, the mold rocks upwards up to an angle of +45°, downwards to -45°, and comes back to the initial horizontal position. The cooling was done by forced air (fan rotation: 1300 rpm).

For each molding, the temperature at different locations inside and outside the mold were recorded throughout the cycle using thermocouples connected to a radio signal emitter fitted to the rotating arm of the mold. The signal from the emitter was transmitted every 2 s to a computer for recording. Figure 1 gives an example of the temperature profiles

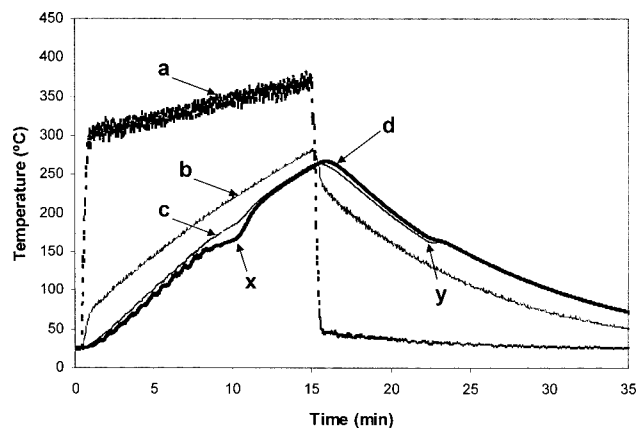


Figure 1 Plot showing the temperature profiles at different locations during a molding cycle: (a) oven air; (b) outer surface of the mold; (c) inner surface of the mold; (d) air inside the mold. The melting of the polymer occurred at zone (x) and the crystallization at zone (y).

obtained at different locations during a complete cycle of a part molded to a PIAT close to 270°C. This figure shows that the inner air temperature is very close to the inner mold surface, and also reveals very clearly the melting and crystallization zones of the polymer. The PIAT was identified for every molded part and used as its reference. Eight sets of bottles were produced, with PIATs varying from 205°C up to 270°C.

Characterization methods

The crystalline morphology of the samples was analyzed on microtomed cross-sections of 15 µm thickness with a Olympus BH2 polarized light microscope fitted with a digital camera. Fluorescence microscopy was also used for detecting degradation of the polymer in cross-sections of 25 µm mounted with a nonfluorescent liquid. The fluorescence intensity was measured across the thickness of the part with a Leitz MPV photometer.

UV-vis spectroscopy was carried out onto the internal and external surfaces of the moldings with a Shimadzu UV-240 IPC apparatus fitted with an integrating sphere. FTIR analyses were performed on the internal surface of the samples with a Shimadzu-IR Prestige-21 apparatus fitted with a diffuse reflectance accessory.

The rheological behavior of the molded material was assessed using a Paar Physica MCR300 parallel plate rheometer. The specimens were thinned down to 1 mm, leaving the inner surface intact, and cut into discs of 25-mm diameter. The tests were done at 200°C with a frequency sweep from 0.5 to 100 Hz. The overall testing time was of ~ 25 min. Before testing, the discs were dried at 90°C for 12 h.

Thermal gravimetric measurements were done in a TGA Q500 of TA Instruments. The powder was predried overnight at 90°C and heated at 10°C/min under air or nitrogen flow (50 cm³/min).

The mechanical characterization included tensile testing at 23°C in an Instron 4505 machine and an impact testing at -40°C using a Ceast Fractovis instrumented falling weight impact tester. The number of specimens tested for each sample was 5 and 8, respectively.

Microhardness tests were carried out at room temperature on the internal surface of the moldings with a Leica VMHT 30A microhardness tester, using a Vickers diamond indenter. A square of 20 mm side was cut from a flat area at the middle of the bottles for the testing. All the specimens were tested with a load of 980.7 mN applied for 30 s. The microhardness (H) was derived from the residual projected area according to $H = kF/d^2$, where d is the length of the impression diagonal, F the contact load applied, and k a factor equal to 1.8544. For each sample, the

value of H was calculated as the average of 10 indentations (standard deviations between 0.4 and 0.6 MPa).

RESULTS AND DISCUSSION

Morphology and degradation behavior

The polarized light microscopy revealed that the processing conditions affect the morphology of the PA11, particularly at the inner surface layer. By increasing the PIAT, the cooling rate at the inner part of the molding reduces and simultaneously more favorable conditions are created for polymer degradation to occur at that zone. Both the cooling rate and the degradation state of the polymer appear to influence the size and the perfection of the spherulitic morphology. The photomicrographs shown in Figure 2 illustrate the morphology of samples molded with the lowest, medium, and highest PIAT. Although the changes in the spherulitic morphology resulting from the increase of the processing temperature are not as outstanding as in the case of polyethylene,⁷ it is clear that it was affected by the processing temperature. The sample heated up to a relatively low PIAT (205°C), as shown in Figure 2(a), depicts a fine texture consisting of imperfect spherulites, probably because of the fast cooling rate that was experienced by this sample. The sample molded with the PIAT of 240°C, shown in Figure 2(b), where polymer degradation is still absent and the cooling rate was slower, presents a well-defined and homogeneous spherulitic texture with concentric rings. The sample processed at the highest PIAT (270°C), shown in Figure 2(c), developed spherulites of bigger size and with well-defined rings except near the edge, indicated by the arrow, where the melt contacted the inner atmosphere of the mold. As it is revealed by the fluorescence micrograph shown in Figure 2(d), polymer degradation occurred at the inner surface zone of this sample, and this relates well with the changes observed in the spherulitic texture. The fluorescence microscopy is used to detect degradation in processed polymers.^{7,9,13} It enables the visualization of zones where the polymer chains formed double bonds because they absorb ultraviolet radiation and reemit it at longer visible wavelengths.¹³ In the case of the sample molded with a PIAT of 270°C, the fluorescence is confined to a layer of width around 200 µm, where the oxygen of the air kept inside the mold could diffuse.

The fluorescence intensity plots, in Figure 3, evidence that above 250°C the degradation at the inner surface increases strongly. In this figure, it is also evident that the fluorescence intensity at the outer surface is very low and has a reduced dependence from the processing temperature. Thus, it may be

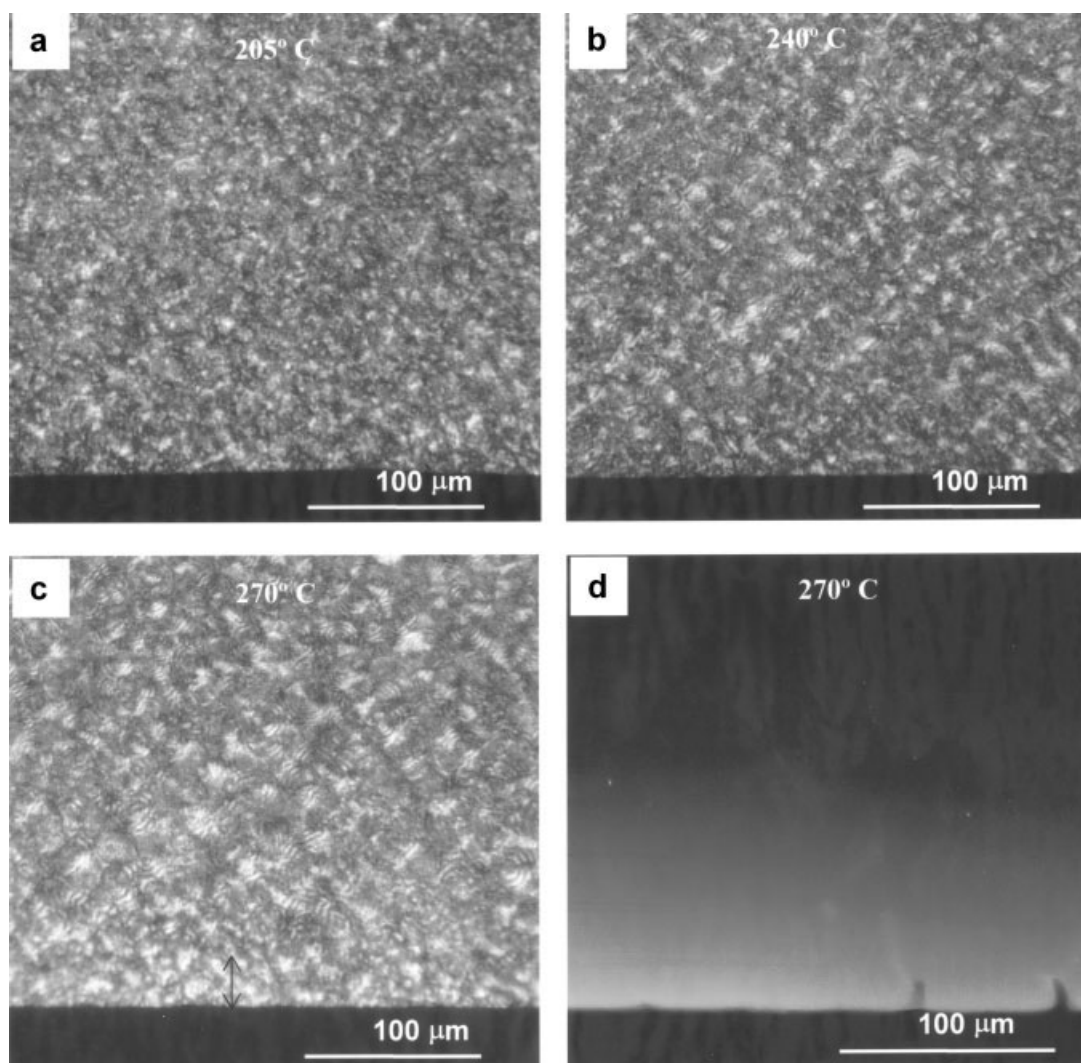


Figure 2 Pictures of microtomed cross-sections taken from the internal layer of molded samples. Polarized light microscopy (a), (b), and (c); Fluorescence microscopy (d). (a) PIAT of 205°C; (b) PIAT of 240°C; (c) and (d) PIAT of 270°C (the arrow in picture (c) defines the depth of layer with imperfect spherulites).

concluded that if polymer degradation occurs at the outer surface it does not lead to the formation of new double bonds in the polymer molecules as it happens at the inner surface.

The visual observation of the samples molded with PIAT above 250°C revealed yellowing at the inner surface and a high number of pinholes at the external surface (Fig. 4). The number of pinholes reduced slightly with the increase of PIAT up to 230°C and then increased strongly with the temperature, especially above 250°C.

It is known that one of the shortcomings of rotational molding is the formation of pinholes at the outer surface, and several authors studied the formation of bubbles and the mechanisms for their removal and minimizing.^{14–19} Factors such as the powder characteristics (shape, size, and distribution), the viscosity of the polymer melt, the surface tension of

the plastic melt, and the mold affect the pinhole formation. The incorporation of bubble releasing additives¹⁵ or the use of internal pressure¹⁷ were used to

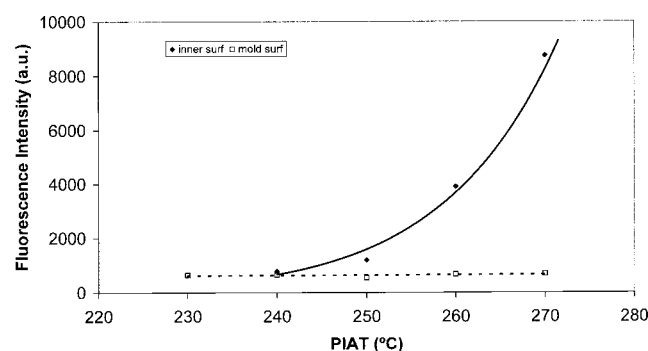


Figure 3 Plots of the fluorescence intensity of samples molded with different PIAT measured at the inner and outer surface, respectively.

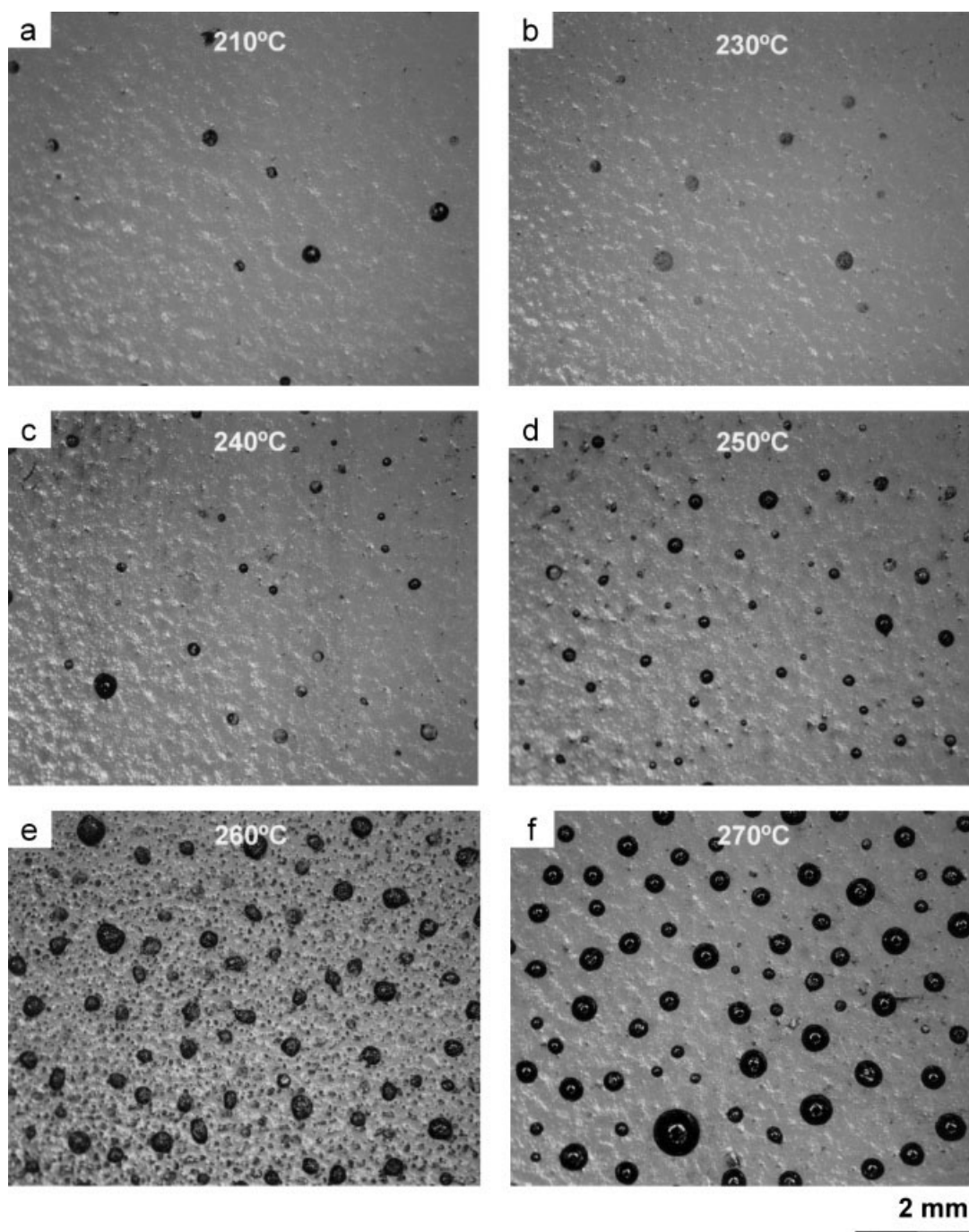


Figure 4 Stereomicroscope pictures of the external surface of PA11 molded with different PIAT: (a) 210°C; (b) 230°C; (c) 240°C; (d) 250°C; (e) 260°C; and (f) 270°C. The dark spots are pinholes.

ease the diffusion of air from the melt diminishing the formation of pinholes at the surface of polyethylene parts.

In the case of the PA used in this work, the pinhole formation is likely to be a problem if the processing temperature rises above the optimum value. In this context, the PA contrasts with polyolefins that show a decrease in the formation of pinholes with the rising of PIAT.⁷

The thermogravimetry curves, in Figure 5, show that the thermal decomposition of the material under a flow of air or nitrogen occurs mainly above 400°C. However, there is some release of volatiles in the rotational molding temperature range (slightly higher when air is used). The weight loss reaches a value around 5% for the temperature of 270°C in the presence of air. As was already shown in Figure 1, the temperature of the internal surface of the mold

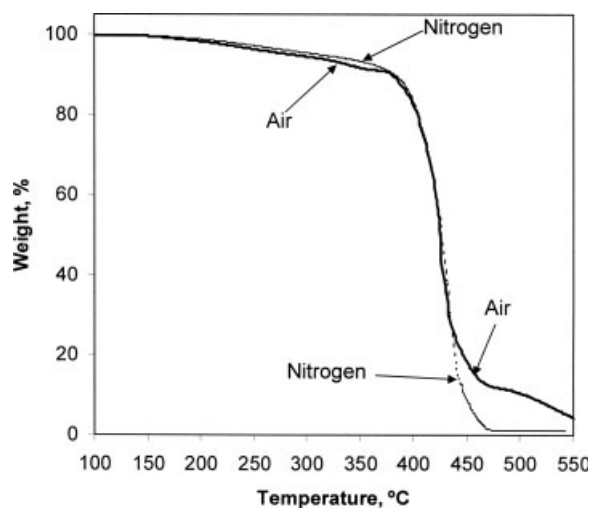


Figure 5 Thermogravimetry curves obtained during the heating of PA11 powder in air (—) and in nitrogen (---); heating rate, 10°C/min.

in contact with the polymer melt is very close to the internal air temperature. During the heating stage, the temperature at the internal surface of the mold is slightly higher than the internal air but, as soon the mold is removed from the oven, the situation is reversed. In fact the maximum temperature reached by the internal mold surface is lower than the PIAT.

Thus, it appears that for PA11 there are two different causes for the pinhole formation: at low PIAT the surface pinholes are caused by the trapping of air between the powder particles during the coalescence stage that will reduce in number and size when the melt temperature increases and the viscosity decreases; at high PIAT the pinholes are certainly associated to the release of volatile degradation products. The formation of different types of volatile products were identified during the thermal decomposition of PAs,^{20,21} namely H₂O, CO₂, CO, unsaturated hydrocarbons, and methane. Although the thermal environment is less severe in rotational molding than in these studies, the release of similar volatiles substances is likely to occur in the samples processed with PIAT above 250°C. This is suggested from the TGA results and is in close agreement with the evidence of degradation given by the fluorescence microscopy analysis results.

Further evidence of degradation at the inner surface of the samples molded with the higher PIAT is given by the UV/vis spectrum [Fig. 6(a)]. The curves show a noticeable increase of the absorbance in the UV near visible region with PIAT, confirming the presence of double bonds, probably of the conjugated type. This would explain the yellowing and fluorescence observed at the internal surface of the moldings. At the outer surface [Fig. 6(b)], the increase of absorbance with PIAT is very low.

The studies on thermooxidative degradation of PA11 are scarce and generally refer to more severe conditions than those used in normal processing. Levichik et al.²⁰ reviewed the thermal decomposition of aliphatic nylons and suggested that UV/vis active chromophores may be produced as a result of aggregative reactions of azomethines, giving rise to sequences with conjugated double bonds. Yellowing of PA11 films after thermooxidation at 90°C was also observed by Fromageot et al.,²² who attributed it to the formation of unsaturated aliphatic aldehydes.

The rheometry tests on the effect of the processing temperature on the rheological behavior of the material showed clearly that the melt viscosity increases with PIAT (Fig. 7). Li et al.²³ reported that chain scission and extension reactions of end groups (—COOH and —NH₂) were observed in PA 6 in the presence of ultrasonic radiation. Although further studies are necessary for a better understanding of the degradation mechanisms of PA11 under rotational molding conditions, the results herein suggest that the degradation reactions cause chain extension and, as a consequence of that, the viscosity increases.

Mechanical properties

The already mentioned increase in the viscosity of the inner layer material with PIAT was accompanied by a similar increase in the microhardness, as can be

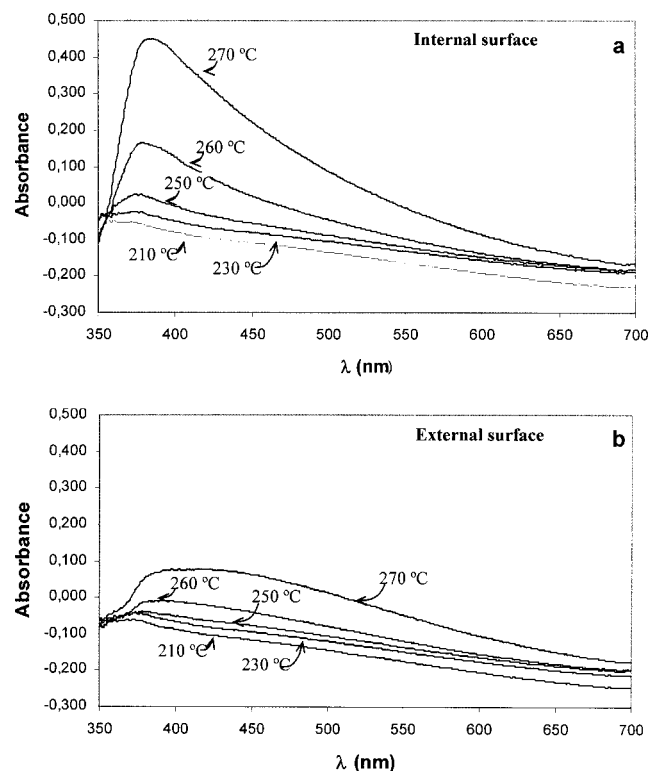


Figure 6 UV spectra of samples molded with different PIAT: (a) inner surface; (b) external surface.

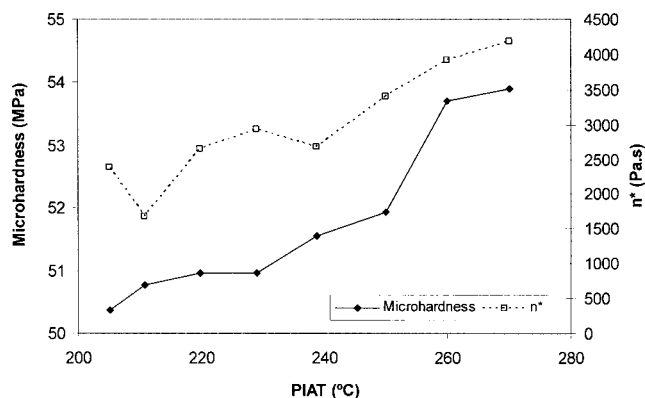


Figure 7 Influence of PIAT on the microhardness and the viscosity (n^*) of the internal layer of the rotationally molded samples. The viscosity values correspond to a frequency of 0.5 Hz.

seen in Figure 7. The microhardness was measured on the internal surface where great changes in the chemical structure of the polymer may occur during the processing. Although the reasons for the increase of the microhardness with PIAT are not fully understood, the variations observed are so significant that this testing method appears to be very adequate for quality control purposes. A clear advantage of this method is the simplicity of the sample preparation and quickness of the measurements.

The effect of the processing temperature on the impact behavior of PA11 is shown in Figure 8. The samples molded at moderate temperatures, from 210°C up to 240°C, show the expected ductile behavior of this semicrystalline polymer, with the total fracture energy being about twice the peak energy.

In the samples molded at extreme temperatures a brittle behavior was observed. This is reflected in the lower values of the energy and in the high values for the standard deviation, which denotes the existence of ductile and brittle regions in the same molding. The brittle behavior has different causes, for the

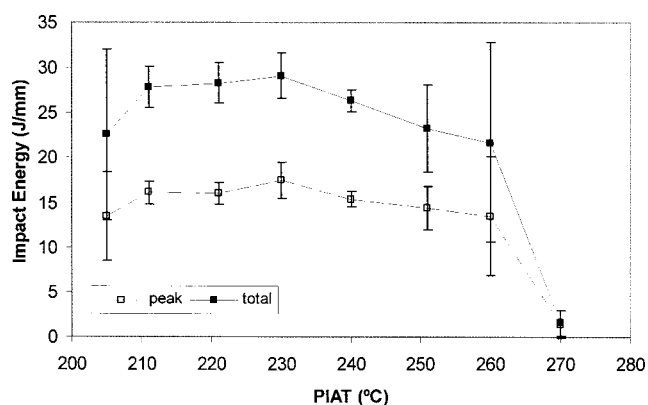


Figure 8 Effect of PIAT on the impact strength of rotationally molded samples.

TABLE II
Tensile Properties of Rotomolded PA11 Samples^a

Sample PIAT (°C)	σ_y (MPa)	ϵ_y (MPa)	σ_r (MPa)	ϵ_r (%)
205	41.0 (4.1)	25.9 (1.7)	36.6 (13.6)	124 (95)
210	40.5 (5.4)	24.6 (2.1)	31.4 (16.2)	154 (83)
220	41.2 (7.2)	25.6 (2.3)	41.0 (6.8)	216 (25)
230	39.8 (2.2)	24.9 (2.5)	37.4 (8.9)	207 (44)
240	38.1 (3.4)	27.0 (2.4)	39.8 (3.5)	220 (6)
250	38.8 (4.4)	24.5 (1.7)	37.5 (11.2)	179 (42)
260	41.9 (2.3)	27.5 (1.9)	35.8 (6.2)	180 (38)
270	39.9 (0.5)	25.3 (1.6)	26.5 (12.5)	125 (56)

^a Standard deviation values are in parentheses.

underheated and overheated samples. In the sample molded at the lowest PIAT, 205°C, the sintering of the powder particles is certainly poor, and this reduces the strength of the material. Furthermore, the voids close to the inner surface promote the brittle behavior, acting as sites for fracture initiation. In the case of the moldings obtained with high values of PIAT, the hard degraded internal layer induces the brittle behavior. For the samples molded at the utmost condition, PIAT of 270°C, all the specimens have broken in a brittle manner, which is reflected in the low impact energy data, both for the average and for the standard deviation. The pinholes at the outer surface are not critical in this test for the dart hitting the external surface of the specimens, and it is the inner layer that is subjected to the higher tensile stress.

The tensile properties of the molded samples are summarized in Table II. The differences observed in the structure of the samples are reflected mainly in the strain at break, as can be seen in the Figure 9. The tensile strength of the samples molded at low temperatures show the poorest performance. The incomplete sintering of the powder resulted in low values of the strain at break. Upon increasing the PIAT, the strain at break reaches a maximum

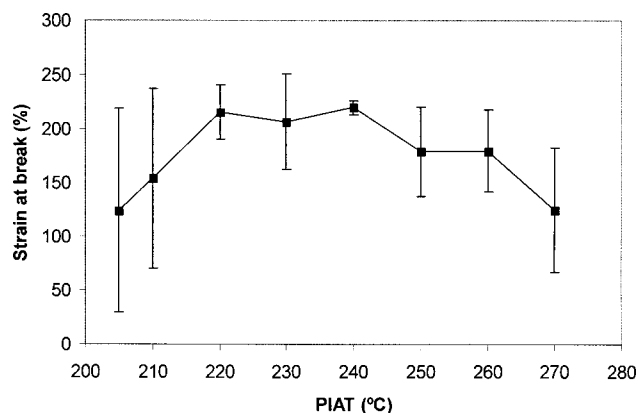


Figure 9 Effect of PIAT on the tensile strain at break of rotationally molded samples.

plateau for the samples molded at PIATs between 220 and 240°C. For higher processing temperatures, the strain at break decreases and, again, there is an increase in the data scattering, this being certainly a result from the degraded material at the inner surface and the pinholes at the outer surface. Under this test, the two sides of the specimens are subjected to identical stresses, and thus both defects contribute to reduction of the tensile strength. The larger scatter observed within the samples results probably from the very small size of the specimens used that are more prone to have a nonuniform distribution of defects.

CONCLUSIONS

In this work, the relationship between the processing conditions, the microstructure, and the properties of rotational molded PA11 was investigated. The results obtained showed that the morphology of the moldings is spherulitic with concentric rings that may be absent if the molding temperature was too low or if the polymer is degraded.

The maximum temperature of the air inside the mold (PIAT) is a fundamental parameter of the rotational molding process that must be optimized for obtaining the best product performance, as it affects not only the mechanical performance but also the pinhole formation. For the PA 11 grade studied in here, in order to obtain the best impact strength and the lowest pinhole formation at the outer surface, the PIAT ought to be around 230°C.

Thermooxidative degradation of PA11 may occur at the inner surface when the internal air temperature goes above 240°C. In this situation, there is formation of products that absorb UV radiation and fluoresce in the visible region. The degradation severity and the extension of degraded zone are very easily assessed by fluorescence microscopy on cross-sections microtomed from the molded part.

The formation of pinholes at the outer surface decreases with the increasing PIAT up to the optimum temperature range. Above that optimum PIAT a reverse behavior takes over as a result of the release of volatiles products originated by the polymer degradation. Thus, the presence of pinholes must be looked with care as it may be a sign of overheating and not underheating, as in the case of rotomolded polyolefins.

The degradation of the material at the inner surface of rotationally molded PA11 causes an increase of the viscosity that might be associated to an

increase of the chain length. This change in the material structure also affects the impact strength and the elongation at break.

The molecular modifications caused by degradation may be assessed by rheometry or by microhardness testing. The microhardness test appears to be very adequate for quality control purposes, because it is simple, fast, and does not require elaborated sample preparation. Furthermore, as the required sample size is small (about 20 mm × 20 mm), the samples may possibly be machined from nonfunctional zones of the molding that are trimmed after the process. In this way, the whole part is not affected by the quality control test.

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