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The WAXD and Tensile Stress and Elongation at the Yield Point of Polypropylene Additived Films

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Summary: The study of some properties of commercial polypropylene additived films, that were submitted to UV radiation, has been done for samples that were produced as a prototype for synthetic grass. In the present work, was analyzed by WAXD the area of diffraction peak at 2θ around 17°, that is correlated with the monoclinic crystalline phase in PP, and its reciprocal width at half weight, and also the tensile stress and the elongation in the yield point. All these properties were analyzed as a function of the sample exposure time under UV radiation in the accelerated mode. To clarify the behavior found for these properties were also analyzed by WAXD some samples that have been heated at 200 °C and cooled at room temperature. These studies show that the samples could undergo some modification on their photo-degradation profile that is correlated with the modification of the PP macromolecular and supramacromolecular structures.

Keywords: mechanical properties; photo-degradation; polypropylene; WAXD

Introduction

The UV-photo-oxidation of polypropylene (PP) has been treated in several works,[1–14] especially for isotactic PP samples (iPP) without pigments.[1–7] Some of them deal with the heterogeneity of the photo-oxidation process throughout the sample thickness.[1,2,5,6] This heterogeneity is correlated with: **a)** change in the polymer macromolecule physicochemical structure, by branching[1] and by the incorporation of other chemical groups generated in the photo-degradation process, for example, carbonyls from esters and carboxylic acids, hydroperoxides, etc.;[1,2]**b)** chain scission,[1–5] by preferential and initial formation of tertiary macro radicals and subsequent crosslinking in the last stage of photo degradation;[3,4]**c)** change in the degree of crystallization[1,2,4,6,7] or crystal phase modification;[2,7]**d)** crystallization of macro-radicals[1] also called chemi-crystallization, that occurs after tie chain scission during the first stages of the photo-degradation. Differently of some papers related in the above described literature, the aim of this work is to analyze and correlate some properties of PP films, that are at constant thickness and produced with a commercial PP, that is additived with UV absorber and colored masterbatch. These films were submitted to UV radiation, in the accelerated mode, for several different times in the interval of zero to 450 hours. The correlations were made, between WAXD and mechanical properties behavior, to understand how the photo-degradation affects the macromolecular and the supramacromolecular structure of the commercial and additived PP films.

Experimental

Sample Production

The polypropylene used is a commercial one from Polibrasil, named PPY6300,

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which has as additive the UV radiation stabilizer Tinuvin-FDL 783. The colored films, in the moss-green color, were produced as following. First, one colored masterbatch, in the moss-green color, was prepared in an extruder machine with three zone temperatures of 180 °C, 210 °C and 210 °C, and produced with the PPY6100 and Brazil Cromex-Brancolor colored masterbatches. Second, with the moss-green masterbatch and PPY6300, it was prepared a second mixture in a concentric cylinder mixer, at 180 °C. Third, by thermopressing process the films were produced, in the thickness of 150 microns, at 180 °C and cooling up to 50 °C under pressure followed by a quenching in water at 25 °C.

Sample Aging under UV Radiation

The sample aging was carried out, by the accelerated mode, in a chamber with a Lamp of Hg vapor, 290 nm and 6W-model-GERMITEC. The samples were disposed in the chamber at 17 cm from the UV lamp so that both faces could be submitted to UV radiation. These samples were in the form of strips cut from the films in the dimensions of the sample for mechanic test.

Sample Thermal Treatment

The same sample was also treated thermally, before WAXD analysis, to elucidate the morphological change that was detected by the behavior of the first diffraction curves analyzed as a function of the sample UV aging time. This thermal treatment was done by heating the samples in an oven at 200 °C under vacuum for 15 min and subsequent cooling at room temperature.

WAXD Analysis

The X-R diffraction was in a Spectrometer – model: RIGAKU/Dam 2500 PC; K_α-Cu, Repeat Count of 1, room Temperature, start angle at 5°, stop angle at 35°, sampling width of 0.03 degree, scan speed of 7 degree/min, voltage of 40 KV, current of 150 mA.

Mechanical Test

The sample tensile mechanical properties were analyzed in a machine model EMIC DL200, cell load of 200 Kgf and a cross-head rate of 5 mm/min., on strips with 80 mm length and 0,8 mm width and L_0 of 40 mm.

Results and Discussion

In Figure 1 the WAXD shows that the sample has well defined diffraction peaks correlated with the α phase, that has a monoclinic crystal structure of PP,[7,9] with the stronger one located at 2θ around 17°.[2,7,9] There is also a weaker peak observed around 20° that indicates that a small fraction of orthorhombic γ phase[2,7,9] can be generated in commercial PP films without UV radiation.

Therefore, the literature[2,7,9,11] pointed out that in PP sample crystallization can be generated a polymorphism, that comprises three phase crystal forms (monoclinic α, trigonal β and orthorhombic γ). The most common is the α phase, but the relative amount of β phase can be observed by crystallization under shear fields, temperature gradients or by incorporation of specific nucleating agents.[7,9,14] It is believe that the γ phase could only be generated from the recrystallization of PP with low molecular weight,[11] and PP fractions in random copolymers.[12] More recently was found that this γ phase also appears in commercial PP with high molecular weight, when the crystallization goes under high pressures or under high orientation,[14] and that the presence of defects favors the γ phase crystallization.[2]

The diffraction curves of Fig. 2 reveal that not only the crystalline α phase has modified the degree of sample crystallization, as a function of radiation time or thermal treatment, but also that there is some modification in the peak intensity corresponding to γ phase (2θ around 20°). These results show that both the α phase and the γ phase can coexist in additived commercial PP films, and more, the γ phase

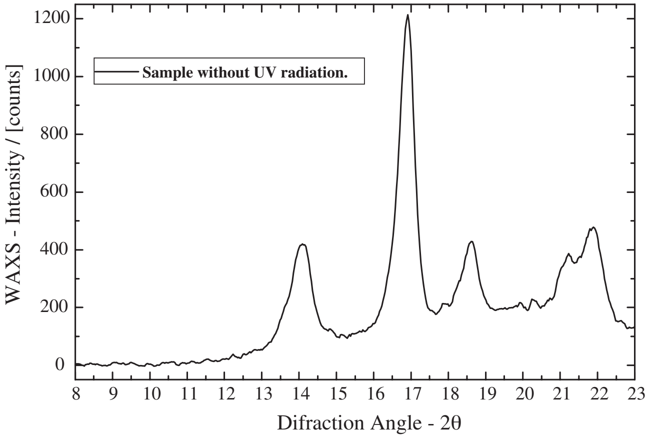

Figure 1.
WAXD curve of the sample without UV radiation.

has less imperfection for samples that are submitted to an UV radiation time up to 100 h and treated thermally at the condition used here (heating at 200 °C for 15 min and cooling at room temperature). As one knows, 200 °C is a temperature over the melting point of PP crystalline sample, and high enough for the destruction of the pre-existing supramacromolecular structure. An important result shown in Figure 2 is that the intensity peak of the α and γ phases increase as a function of the photo-degradation time but not as shown in literature,[2,7] where it is pointed out that the appearance of the γ phase occurs only after long times of exposure to UV radiation. Therefore, in our case the γ phase seems to be more perfect (Fig. 2 (e) and (f)) after thermal treatment over samples that have been submitted to UV radiation up to 100 h.

The results of Fig. 3 show the behavior of two parameters that can be related to the degree of crystallization (the peak area (A)) and the crystalline particle size or order into crystalline structure (reciprocal of the half-height width (1/A)). These results show that between 0 and 100 h the peak area increases slightly, and the increase of 1/A is more accentuated up to 55 h and then becomes constant up to 150 h. In the range 0 and 100 h the increase of both parameters can be related to secondary crystallization of pre-existing crystal structures that can growth for short time of UV radiation or due to some effects of the inorganic pigments that are present in our samples. For example, formation of crystalline structure lager than the pre-existent ones. It is important taking into account that in some literature[2–5,7] it has been pointed out that in the first stages of PP sample photo-degradation, the chain scissions are the main process, but these authors have worked with iPP without pigments.

In the range from 100 to 350 h, two crystallinity recoveries were observed (one from 100 to 250 h and the second one from 250 to 350 h) when the peak area falls down and increases again.

Nevertheless, the decay and increase in the first range is more accentuated than the second decay and increase. The observed first decrease in the peak area may be related to chain scission in the range from 100 to 150 h. This process, that not affects the particle size in these range time of UV exposure, under our point of view, can generate macro radicals, that present its own orientation and can act as nucleation sites for recrystallization; so, this behavior can justify the first increase in the peak area (A) in the range from 150 to 250 h and in the

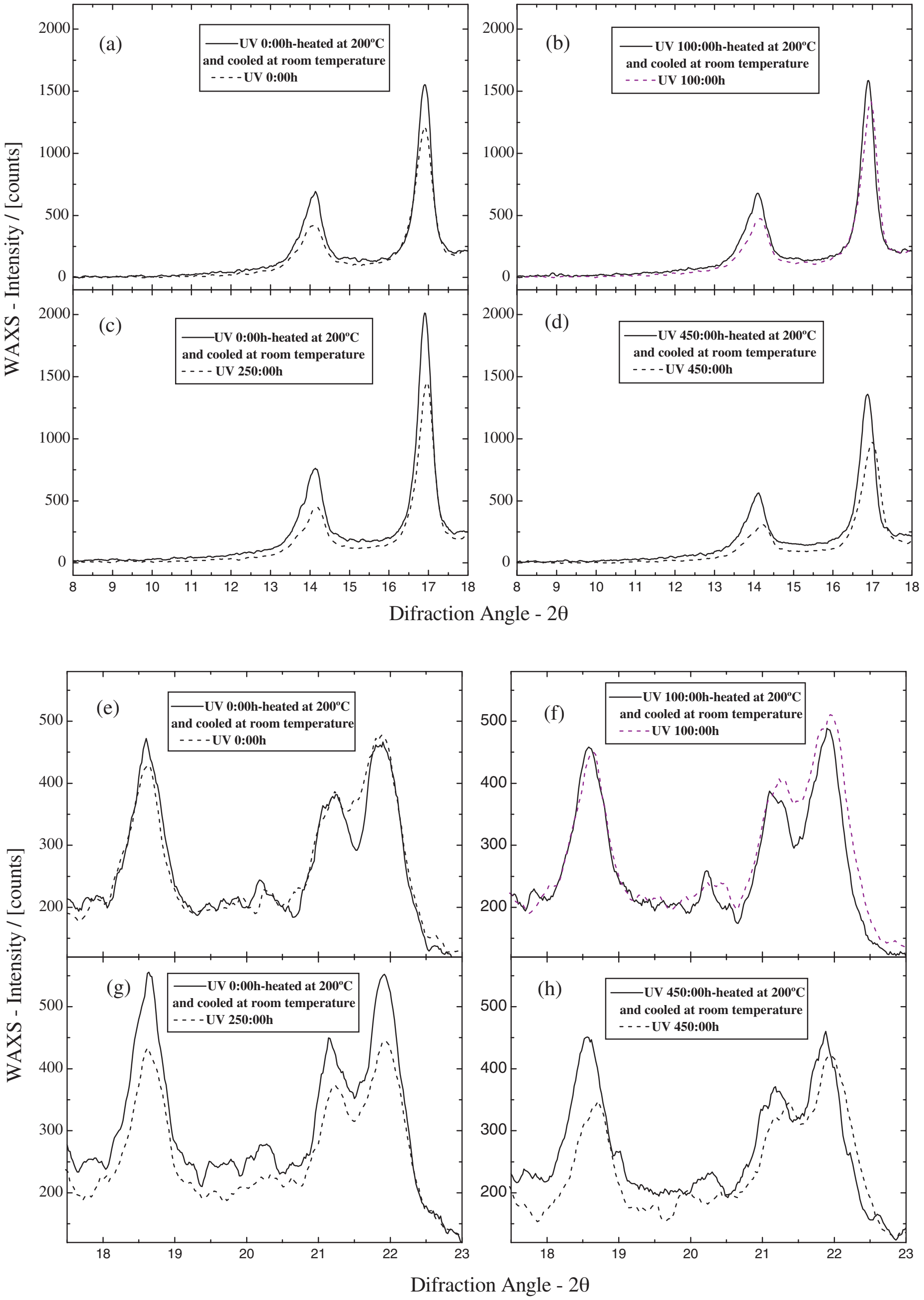

Figure 2.

WAXD curve of the sample, without thermal treatment (···) and treated at 200 °C (---), as a function of sample time under UV radiation.

1/A value in the range 150 to 200 h. In the range from 250 to 350 h, the decrease of the peak area, observed in the range 250 to 300 h, can be related to scission of molecules that could be more resistant to UV radiation. Again, under our point of view, these molecules can be the tie molecules between crystal structures. Therefore is

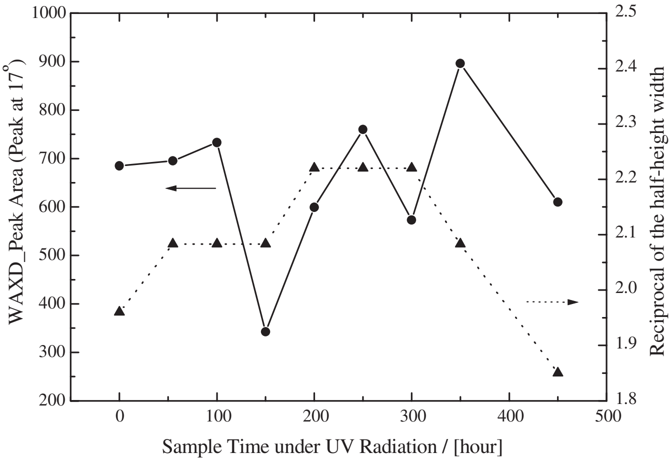

Figure 3.
The WAXS peak Area (2θ at 17°) and its reciprocal half width increase, as a function of the sample UV radiation time.

important taking into account, that scission of tie molecules promotes disorder into the crystal structure. If these hypotheses are true, then the observed increase in the peak area and the decrease in the 1/A value, in the range from 300 to 350 h, can be explained respectively by crystallization of tie molecules and disorder into the crystal structures previously present in the sample.

All these considerations are consistent with the argument used by Rabello[13] that also observed mechanical property recovery in commercial grade PP without pigment and exposure by 25 weeks under UV radiation. Is important to elucidate that Rabello[13] worked with bar samples 3.1 mm thick, and in our case we have films 0.15 mm thick.

As pointed out by Rabello[13] the degree of photo-degradation in PP samples is a function of the defect gradient along sample thickness. So, due to the fact that Rabello has worked with sample in the

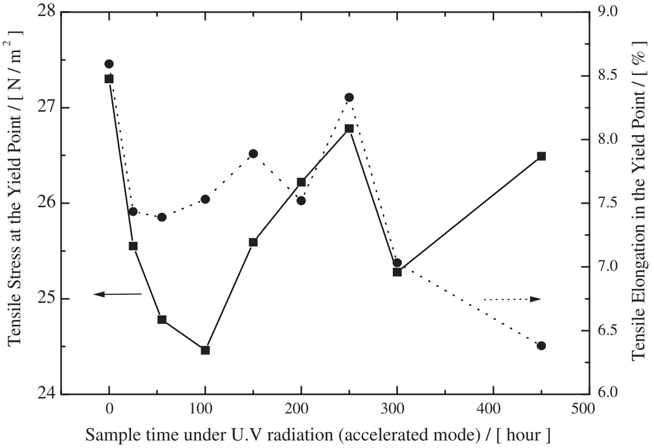

Figure 4.
Tensile stress and elongation, in the yield point, as a function of sample time under UV radiation.

order of 20 times ticker than our samples, this probably explains the larger difference found in the recovery time.

All the discussion given for Fig. 3 is also supported by the results of Fig. 4. In this figure the elongation at yield point decreases between 0 and 55 h, as expected, due to the fact that the PP chain structure becomes more rigid as the secondary crystallization or takes place. Nevertheless, in the time interval from 55 to 150 h for both properties, stress and elongation at Yield Point, there are some recoveries, that are connected with disorder into the crystalline region of the sample, in accordance with the results of Fig. 3, showing that the main process is the chain scission.

The results of stress at yield point show two decays and two recoveries. The two decays are also in accordance with was just discussed for Fig. 3, but with some difference between 100 and 150 h, what shows that, instead of decay what has happened was a recover of the strength, with continuous grow up to 250 h.

If we return to the discussion of Fig. 3, the recover between 100 and 250 h leaves to a greater number of chain ends due to the chain scission (between 100 and 150 h), this can generate more entanglement, then, the stress and elongation in the yield point increase. This same argument can explain the increasing of tensile strain in the range of 200 to 250 h.

Finally for the time range from 350 to 450 h the increasing in stress versus the decreasing in elongation can only be explained by chain crosslinking.

In our previous work,[8] with the same samples used here, the degradation thermal properties investigated, as a function of the time UV radiation, have shown similar behavior of those in this work.

Conclusion

The results of this work show that:

1. In commercial PP additived, fibber grade, where the samples are thermo-pressing films, it can be generated the polymorphism that comprises the monoclinic α and orthorhombic γ phases. This is improved by both photo-degradation and thermal treatment after photo-degradation, for short times of sample UV radiation.
2. The commercial PP films photo-degradation, in accelerated mode, following the UV sample radiation time at short time intervals, permitted to observe two recoveries in mechanical properties consistent with the analysis of the WAXD.
3. The confrontation of the samples WAXD analysis and the tensile stress and elongation at Yield Point, allowed to suggest that the degradation process, that occur at sample UV radiation time higher than 350 h, promotes the PP chain crosslinking.

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