

On the Vickers Microhardness and Wide-Angle X-Ray Line Width for Characterization of the Oxidative Stability of Poly(ethylene-co-propylene) Pipes

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Abstract

The purpose of the current study is to evaluate the ageing of poly(ethylene-co-propylene) fittings produced by several manufacturers. The fittings were aged for varying times as follows: 0, 2, 13, 23, 45, 106, 225 and 391 days at 100°C. In a previous paper, the oxidation induction time (OItime) and oxidation induction temperature (OItemp) were evaluated with respect to every single step of the ageing process [1]. Here, the Vickers microhardness and wide-angle X-ray line width were used for characterization of the oxidative stability of poly(ethylene-co-propylene) pipes. Both the Vickers microhardness and wide-angle X-ray line width as evaluated from a certain reflex of the diffractogram generally increase with ageing for most samples. The higher microhardness is most likely related to higher fragility of the pipes. The increase of the X-ray line width with ageing indirectly proves that reducing the crystallite size as well as increase of the crystallite defectiveness take place.

Keywords

Poly(ethylene-co-propylene), Ageing, Microhardness, X-Ray Line Width

1. Introduction

During the last few decades, the old iron pure water pipes and fittings are being replaced with plastic ones. Usually the polymer used is poly(ethylene-co-propylene) where the ethylene content is in much smaller quantity. Together with a few advantages, these materials suffer from thermooxidative degradation that is the

main factor that substantially decreases the service life of the piping systems [1]. The common way to assess the pipes life under the field conditions is to measure the OItime and OItemp. For this purpose for the first time, poly(ethylene-co-propylene) specimens were subject of prolonged ageing (more than an year). In our previous study [1], the inhomogeneity of the antioxidant distribution was found to be the main factor that compromises the values of OItime and OItemp obtained by conventional differential scanning calorimetry (DSC). This stronger dependence of OItime on the antioxidant distribution urged us to look for other quantities describing the process of artificial ageing with time and temperature. Thus, in the present work, an attempt was made to describe the ageing by changes in microhardness and 040 X-ray PP line width. Due to the degradation, the tubes and fittings become more brittle hence their microhardness is expected to increase. For the same token, the size and perfectness of the crystallites decreases hence an increase of the X-ray line width is expected.

2. Experimental

2.1. Specimens

A total of 7 commercial specimens of poly(ethylene-co-propylene) were taken “as they are” from the respective fitting that was believed to be representative for the manufacture typical production run. The specimens (designated P1, P2, P3, ..., P7) were supplied by various producers. The main material information in our case is the oxidation induction time, but as stated and shown in [1]: “...some pipes and fittings may degrade much faster than others, hence the initially measured OItime may not be reliable enough to characterize the polymer”. That is why we decided to act somewhat “blindly”, *i.e.*, without having in mind any preliminary information concerning the samples. This did not restrict the scope of our investigation. All specimens were proved to be copolymers where only α -iPP crystallizes [1].

2.2. Ageing of the Specimens

Thermal ageing was conducted at 100°C in air in an oven for 0, 2, 13, 23, 45, 106, 225 and 391 days, respectively. These numbers do not bear any special meaning but are chosen on the assumption that in the beginning of the ageing changes take place more quickly and the maximum duration should also be reasonable from a practical viewpoint. Several pieces from any single specimen were put initially into the oven. Periodically, at each time interval, one of them was taken out of the oven and cooled. Several samples were taken from various parts of each piece and characterized.

2.3. Methods for Characterization

2.3.1. Microhardness

The microhardness H of the samples was derived with an apparatus for Vickers microhardness measurements (Leica VMHT, Leica Mikrosysteme GmbH, Wien,

Austria) at three different loads. 30 indentations were made for each load and the results obtained for both diagonals of the indentation marks were averaged. The microhardness was received following Krumova *et al.* in order to minimize the elastic recovery error [2]. Regardless the relatively high number of indentation, the relative error was not as low as desired due mainly to the fact that the samples were taken from convex specimens.

2.3.2. X-Ray Diffraction

A Siemens D500 diffractometer, Germany, with a secondary monochromator and $\text{CuK}\alpha$ radiation was used to scan the 040 reflection, situated at $16.92^\circ 2\theta$ over the range $13^\circ - 21^\circ 2\theta$. Lorentzian function was used to fit this reflection in order to get the line width at half height $\beta_{1/2}$.

2.3.3. DSC Measurements

The DSC curves, obtained in [1] were used, in order to get the enthalpy of melting ΔH_m . The built-in program in the DSC apparatus Q200 of TA, USA, was applied. Subsequently, the DSC degree of crystallinity, w_c was calculated.

3. Results and Discussion

3.1. Evaluation of the Piping Systems Ageing Using Microhardness

The oxidative degradation was estimated by measuring the microhardness of the specimens after ageing. The dependence of the microhardness vs. the aging time for all specimens P1 to P7, is shown in **Figure 1**.

As the antioxidant concentration is generally very low—in the order of parts of a percent [3], the inhomogeneous antioxidant distribution, established in [1], could hardly be the reason for the observed relatively high scattering of the

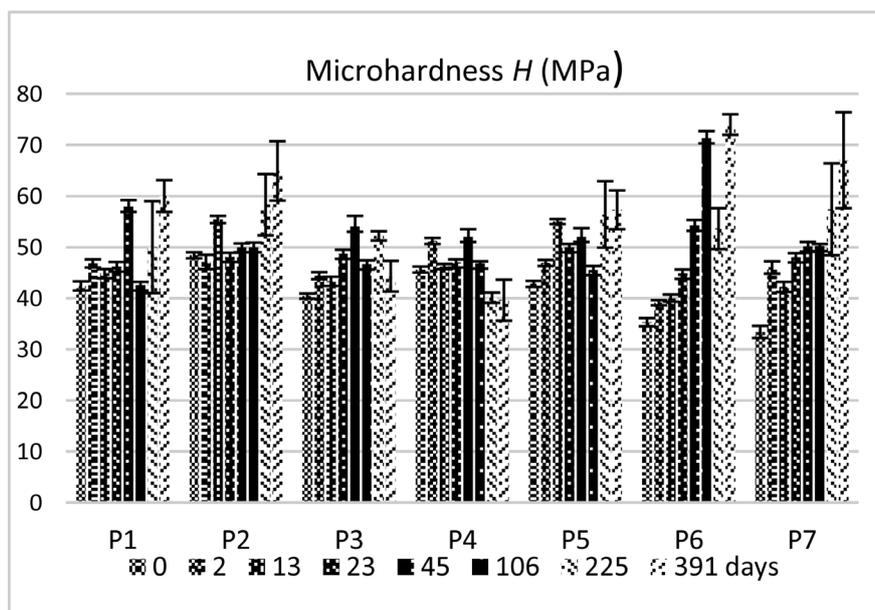


Figure 1. Dependence of the microhardness on the ageing time for the seven specimens P1 to P7.

microhardness values within each specimen. Generally, the increase of the microhardness is not very high in comparison to the statistical error but for five out of the seven specimens a tendency of increasing the microhardness may be noticed (Figure 1). This is expected since the degradation leads to lower molecular weight but also to densification of the structure as the used ageing temperature is quite high (100°C). In addition, embrittlement of PP during the thermooxidative ageing occurs [4]. It also leads to increase of the microhardness. Its increase in the first days of ageing, observed for some of the specimens, may be partially attributed to an increase of the degree of crystallinity since the microhardness of the crystalline phase is higher than that of the amorphous one [5].

In order to check if the microhardness increase with ageing originates from additional crystallization, the enthalpy of melting vs. the aging time was also drawn (Figure 2). The DSC curves used as a sources of determination of the enthalpy of fusion are very similar ordinary melting curves and for this reason as well as for lack of space are not given here. There is a big scattering of the data mainly due to the uncertainty of the melting peak area determination in the DSC thermogram. As a rule, the melting peak lower temperature boundary is not sharp and that complicates the peak integration. There is not any indication of additional crystallization. Based on the enthalpy of melting and degree of crystallinity (as measured by DSC), the lower and the higher theoretical PP microhardness H_{PP} was calculated, according to the additivity law [5]:

$$H_{PP} = w_c H_{PP}^c + (1 - w_c) H_{PP}^a \quad (1)$$

where H_{PP}^c and H_{PP}^a are the microhardnesses of the crystalline and amorphous PP phases, respectively. The volume degree of crystallinity w_c was calculated on the basis of the weight degree of crystallinity (by DSC), the overall density and the density of the crystalline phase [5].

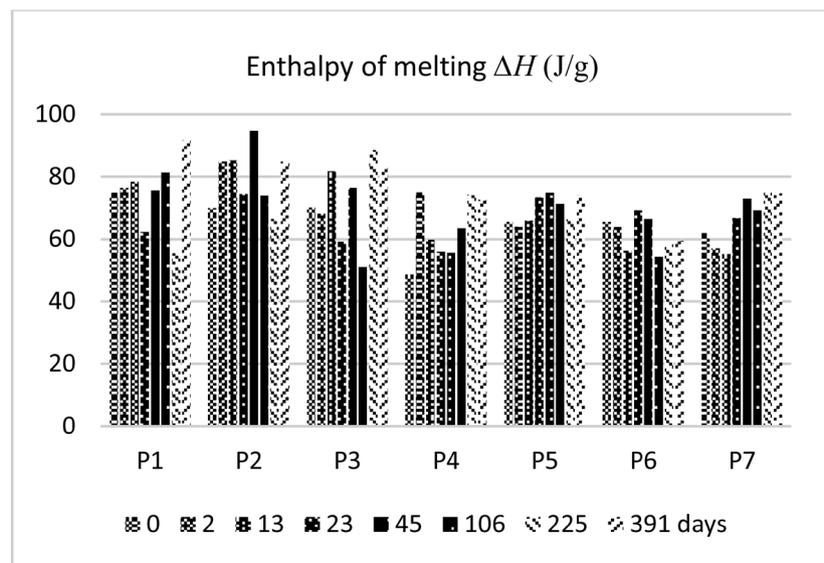


Figure 2. Dependence of the enthalpy of melting on the ageing time for the seven specimens P1 to P7.

Strictly speaking, w_c should be calculated as:

$$w_c = \frac{\Delta H_m}{C \cdot H_0} \quad (2)$$

where C is the PP concentration in the copolymer. However, as it is not known exactly, we applied here the conclusions drawn by Wening and Schoeller from their study of a similar to our system. They have investigated blend of PE and PP and have shown that for concentration of the PE below 10%, its maxima do not appear on the diffractograms [6]. We have also shown [1] that the PE blocks in the studied copolymer are very short; since only PP crystallizes and its blocks are significantly longer. Thus, the content of PE should be no more than c.a. 10%, *i.e.*, $0.9 < C < 1$ and we simply took it unity for the sake of comparison between the samples thus adding a systematic relative error in H of no more than 10%.

The calculated after Equation (1) microhardness of PP is between 57 и 82 MPa varying with the degree of crystallinity. This is in accordance with the value between 30 and 88 MPa, measured by other authors, e.g. Martinez-Salazar *et al.* [7] as well as in general agreement with the measured microhardness of the initial and aged specimens, **Figure 1**.

3.2. Evaluation of the Ageing Using the Width of X-Ray Diffraction Line

For the first time the oxidative degradation was estimated by measuring the width of a certain diffraction line of the specimens after a prolonged ageing. It is well known that the diffraction lines width might be used for evaluation of the crystallite size and microstress. The former generally is expected to increase during the ageing due to the eventual additional crystallization taking place in the process of annealing at 100°C. For instance, for polyethyleneterephthalate the degree of crystallinity reaches maximum values for only 6 hours due to an annealing process [8]. PP is expected to crystallize even faster. Since the ageing times in our case are much longer, the process of crystallization can be neglected. A main and opposite process of decreasing the size due to polymer degradation with time is to be expected. On the other hand, due to the low number of clearly expressed maxima (see **Figure 1** in [1]) it is impossible to separate the effect of the crystallite size and microstress on the line width so we restricted ourselves by following the change of the width $\beta_{1/2}$ of the best expressed 040 line with the ageing time (**Figure 3**).

The width does not change unambiguously mainly due to the small sample size, irregular shape of the samples (they were cut from tubes and fittings) and uneven sample surface. Since the chain length decreases with the ageing, not all molecules enter the crystallites, so the crystallite size also decreases and the defectiveness increases. As a result the line width increases and this is clearly seen as a tendency for most samples. Thus, the decreasing of the crystallite size is generally registered. As already stated, an increasing of this size due to the annealing and subsequent recrystallization is not probable due to the fast PP crys-

tallization.

3.3. Evaluation of the Ageing Using the Melting Temperature

In order to check if any additional crystallization takes place (irrespective of the ageing time) the melting temperature of the specimens was followed with the ageing (Figure 4). It has been established for PE that its melting temperature increases with the ageing time since additional crystallization occurs, defined by the linearity of the molecules [9]. However, in our case (Figure 4) such an additional crystallization is hardly probable since the PE blocks in the copolymer are

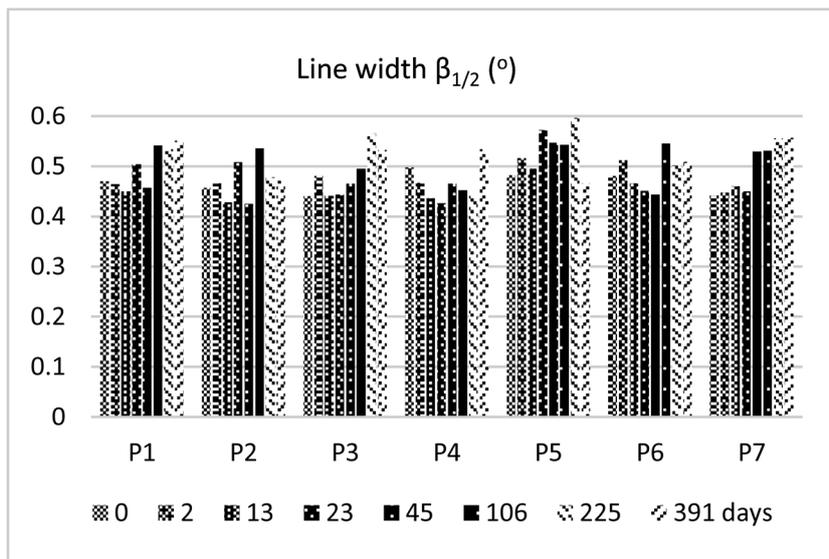


Figure 3. Dependence of the line 040 width on the ageing time for the seven specimens P1 to P7.

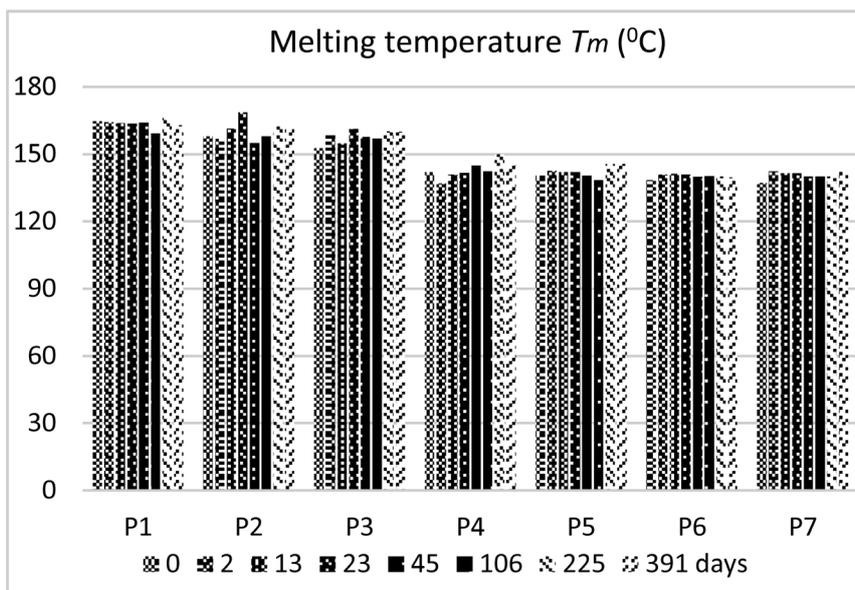


Figure 4. Dependence of the melting temperature on the ageing time for the seven specimens P1 to P7.

so short that they remain as defects in the PP crystallites. This was confirmed by X-ray investigations of the line width (see above) whence it can be concluded that even though larger PP crystallites are formed with the ageing time, they still appear imperfect. The observed changes in the melting temperature are comparable with the experimental error, hence this temperature cannot be taken as a parameter, describing the ageing.

In summary, the fact that the melting temperature does not depend on the antioxidant distribution and changes only a little within each specimen once again indirectly proves that the high scattering of OItime (**Figure 1** in [1]) is due to the inhomogeneous antioxidant distribution, as well as that no additional crystallization takes place during the ageing.

4. Conclusions

1) The oxidative degradation was estimated by measuring the Vickers microhardness in a long lasting ageing experiment. The microhardness generally increases with the process of ageing. The observed higher microhardness is most probably connected to higher fragility of the fittings.

2) The oxidative degradation was estimated for the first time by measuring the width of a certain diffraction line of the specimens in a long lasting ageing experiment. This width generally increases with the process of ageing. The higher width indirectly proves a reducing of the crystallite size as well as an increase in their defects, which both are expected to result in poorer mechanical properties.

3) The constancy of the melting temperature with the ageing indirectly proves that no additional crystallization takes place during the ageing.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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