Photodegradation of Polypropylene with sorbitol-based nucleating agent

ROMAN ČERMÁK, JANA NAVRÁTILOVÁ, LEOŠ VAŠEK
Department of Polymer Engineering
Tomas Bata University in Zlín, Faculty of Technology
nám. T. G. Masaryka 275, 762 72 Zlín
CZECH REPUBLIC
cermak@ft.utb.cz   http://www.ft.utb.cz

Abstract: - The paper deals with the effects of nucleation on photodegradation of isotactic polypropylene. The starting polymer was modified by a specific α-nucleating/clarifying agent Millad 3988 based on 1,3;2,4-bis(3,4-dimethylbenzylidene) sorbitol. Several concentrations were applied. Samples prepared by compression moulding were then exposed to UV-irradiation. Infrared spectroscopy showed that the degradation kinetics is similar for all the samples. Melting and crystallization behaviour of irradiated samples was followed using a differential scanning calorimetry. In all cases UV-irradiation led to decrease of melting/crystallization temperature as a result of polymer degradation. The surface cracking was observed using polarized light microscopy. The network of the surface cracking was significantly different for neat and nucleated samples.

Key-Words: - polypropylene, nucleating agent, sorbitol, photodegradation, polymorphism

1 Introduction

Macroscopic behaviour of polymeric materials within their lifecycle is generally determined by their chemical nature. However, processability, applicability and durability of plastics can be essentially influenced by several smart ways. Namely, the modification of supermolecular structure of semicrystalline polymers is particularly important. The morphology can be controlled by several methods, however, one of the most important and widely applied in the plastics industry is the application of nucleating agents. The heterogeneous nuclei influence crystallization kinetics, size of spherulites and, consequently, resulting properties.

The nucleation of isotactic polypropylene (PP) is of particular interest due to its commercial importance and, consequently, intensive efforts are directed towards developing efficient nucleators and clarifiers for this polymer.

Isotactic polypropylene is polymorphic polymer; it can crystallize into three phases: monoclinic α-phase, trigonal β-phase and orthorhombic γ-phase. Commonly, it crystallizes into α-phase [1]. However, specific α-nucleating agents are often added into the material, primarily to improve the transparency, whilst the shortening of processing time and some improvement of mechanical properties are bonuses. For this purpose, powders of various compounds such as sodium benzoate, sorbitol derivatives and organophosphate salts have been developed.

One of the often used α-nucleating agent is 1,3:2,4-bis-(methylbenzylidene)sorbitol [2, 3]. Sorbitol-based nucleating agents are soluble in concentration below 2 wt.% in molten PP at elevated temperatures [4]. Upon cooling, the sorbitol-based compounds are capable of self-organizing in the polymer melt in the form of a three dimesional fibrillar network with characteristic dimensions in the nanometer range that causes the nucleation of PP, presumably due to epitaxial growth. The sorbitol derivatives improve optical properties with respect to clarity and haze dramatically. However, due to its sugar-based structure they has pure thermal stability during processing [5].

The weathering of polymeric materials plays an important role for their service performance. The presence of tertiary carbon in the backbone of isotactic polypropylene is the reason of its high sensitivity to UV light, which is the most severe component of solar radiation. As generally accepted, degradation reactions of semicrystalline polymers proceed predominantly in the amorphous regions; nevertheless, morphology factors, such as the size, arrangement and distribution of the crystalline regions, play an important role in the degradation process as well. Thus, degradability of semicrystalline polymers is significantly influenced by their supermolecular structure. Many works deal with photodegradation of polypropylene [e.g. 6-10]. However, the effect of 1,3:2,4-bis-(methylbenzylidene)sorbitol nucleating agent on photodegradation of PP has not been complexly described yet. Thus, in this work, the pohotooxidation behaviour of PP containing several concentrations of this nucleating agent and neat PP is compared.

2 Experimental

2.1 Materials and Specimens

The basic material used throughout this study was isotactic PP homopolymer Mosten GB 005 manufactured by Chemopetrol Litvínov a. s., the Czech Republic. The materials was characterized by a melt flow index of 5 g/10 min (2.16 kg, 230 °C, ISO 1133), a weight average molecular weight of 360 000 (GPC) and an isotacticity index of 98 % (ISO 9113). The material was stabilised by a standard package based on phenol-phosphite stabilizers.

The starting material GB 005 was modified by α-nucleating agent Millad 3988 based on 1,3:2,4-di(3,4-dimethylbenzylidene) sorbitol. This nucleating agent was produced by Milliken Chemical. The concentrations applied were 0, 0.2, 0.5 and 0.8 wt. %. Blends were processed using twin-screw extruder Brabender DSK 42/6D and finally pelletized.

Plates with dimensions of 125x60x0.2 mm were compression-moulded from all the materials. The material was put into preheated mould and after 5 min pressing at 210 °C, the plates were cooled at 20 °C.

2.2 UV-exposure

Rectangular specimens cut from the compression-moulded plates were irradiated at 50 °C in Original Hanau XENOTEST® 150. The exposure times varied from 0 to 528 h.

2.3 Infrared Spectroscopy

A Nicolet Impact 400 spectrometer with nominal resolution of 2 cm^{-1} was employed in transmission mode with a 64-scan summation. Molecular degradation was characterized by carbonyl index A_C/A_R where A_C is the area of the carbonyl absorption bands (in the range from 1 700 to 1 800 cm^{-1}) and A_R is the area of a reference band not affected by photooxidation and varying crystallinity (in the range from 2 700 to 2 750 cm^{-1}) [10].

2.4 Differential Scanning Calorimetry

A Perkin-Elmer Pyris 1 differential scanning calorimeter was used to observe melting, re-crystallization and re-melting of the specimens. Thermograms were recorded at a rate of ±10 °C/min under nitrogen purge (20 cm^3/s). Approximately 4 mg of irradiated materials were heated to 220 °C. Then the samples were held at 220 °C for 5 min, cooled to 100 °C and finally heated to 190 °C.

2.5 Optical Stereomicroscopy

In order to study surface of the degraded samples, a Zeiss Stemi 2000-C microscope was used. Micrographs of the observed surface were taken using a SONY F-717 digital camera.

3 Results and Discussion

3.1 Melting

The evolution of melting curves of neat and nucleated samples under study is presented in Figure 1. The exposure times of 0, 60, 120, 192, 336, 432, 480 and 528 hour are chosen as representatives. The interval of the melting is similar for all nucleated samples. Neat PP melts in slightly broader interval and also the shape of the peak is different as compared to nucleated samples; the peak is flat without distinct top. This points to formation of crystallites with narrower distribution of the size in heterogeneously nucleated materials. During the UV-irradiation the melting endotherms do not significantly change up to the 336 hours. However, at prolonged exposure time the interval of melting gradually shifts to lower temperatures in all cases. Moreover, the splitting of the peaks occurs. Finally, they are very flat with several maximums. The decrease of melting temperature of the materials upon the UV-irradiation is caused by erosion of the surfaces of the crystallites decreasing their thermodynamic stability [10].
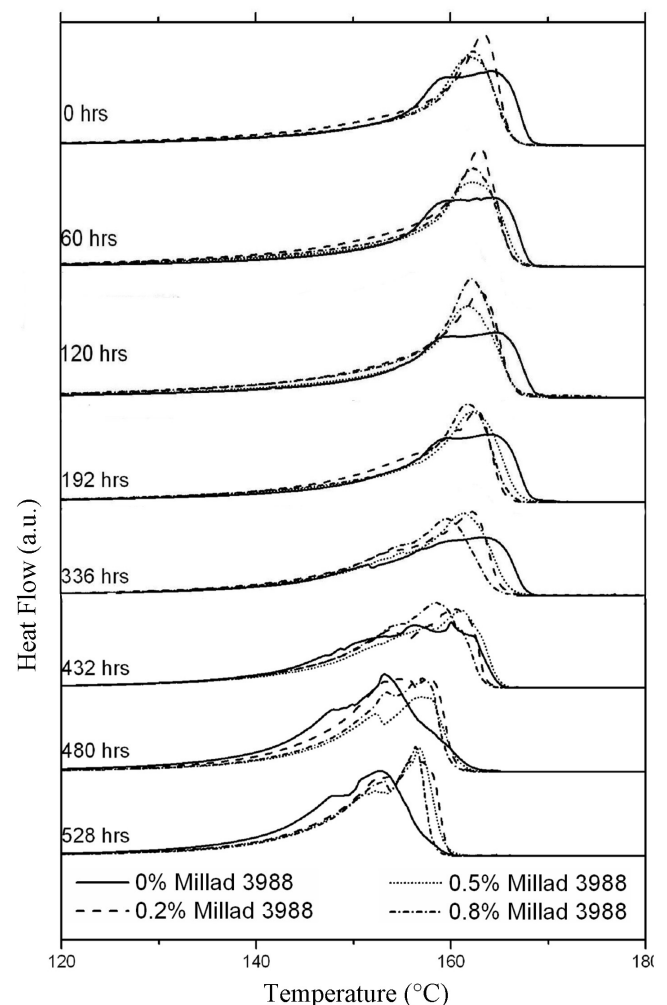

Figure 1. Melting thermograms of UV-irradiated polypropylenes

3.2 Evolution of Carbonyl By-Products

The evolution of the carbonyl index of all samples upon UV-irradiation is shown in Figure 2. Generally, two steps can be distinguished. First, an induction period occurs and second, after an induction period the slope of the curves dramatically increases. The results indicate that the degradation of all samples is not dramatically different. In initiative time of exposure (0-150 hours) carbonyl index values are zero and they are not marked in the graph. After this period carbonyl index begins slightly increase. After this induction period (approx, 250 hours of UV-exposure) carbonyl index rapidly increases. This rapid growth starts quite earlier in the case of neat PP and PP with 0.8 wt. % of nucleating agent. Final values of carbonyl index of these samples are consequently about one point higher than that of PP with o 0.2 and 0.5 wt. % of nucleating agent. Nevertheless, the difference in degradation kinetics of neat and variously nucleated samples is not significant and the presence of nucleating agent seems to not influence the process of carbonyl by-product formation during photooxidation.
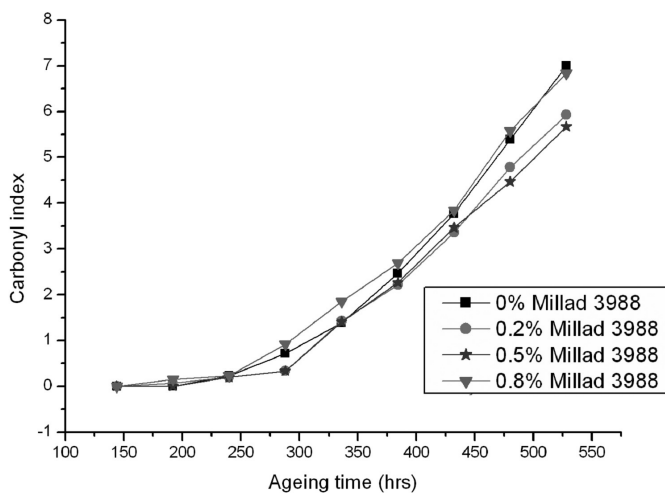

Figure 2. Evolution of carbonyl index upon UV-irradiation

3.3 Surface Cracking

Upon UV-irradiation the creation of surface cracking was observed. The cracks were not observed until 228 hours of irradiation. With prolonged exposure the cracks were more pronounced. The micrographs of surfaces of the samples after 336 and 528 hours of irradiation are shown in Figure 3 and 4, respectively. The surface of UV-irradiated neat PP shows dense network of cracks. This network is more distinct, the number of cracks is higher and they are wider with increasing time of exposure. The cracks of nucleated PP are significantly different as compared to neat PP. They extend in parallel lines. The number of cracks is not markedly higher with increasing irradiation time. As degradation proceeds wide and relatively short cracks associate to long splits which extend across the whole sample. Finally, the sample breaks down, however, not in the orientation of the cracks. This process is the same for all nucleated samples. The difference of crack formation in neat and nucleated PP is caused by different morphology. Actually, cracks in neat PP copy the spherulite boundaries. In the case of nucleated materials the crystallites are too small, thus, different effect such as processing conditions plays a role in the shape of cracks.
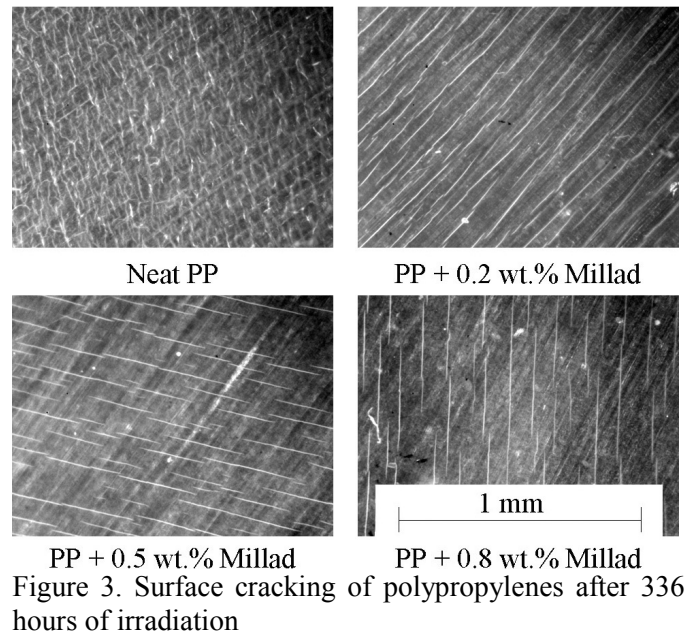

Neat PP   PP + 0.2 wt.% Millad

PP + 0.5 wt.% Millad   PP + 0.8 wt.% Millad

Figure 3. Surface cracking of polypropylenes after 336 hours of irradiation

Neat PP   PP + 0.2 wt.% Millad

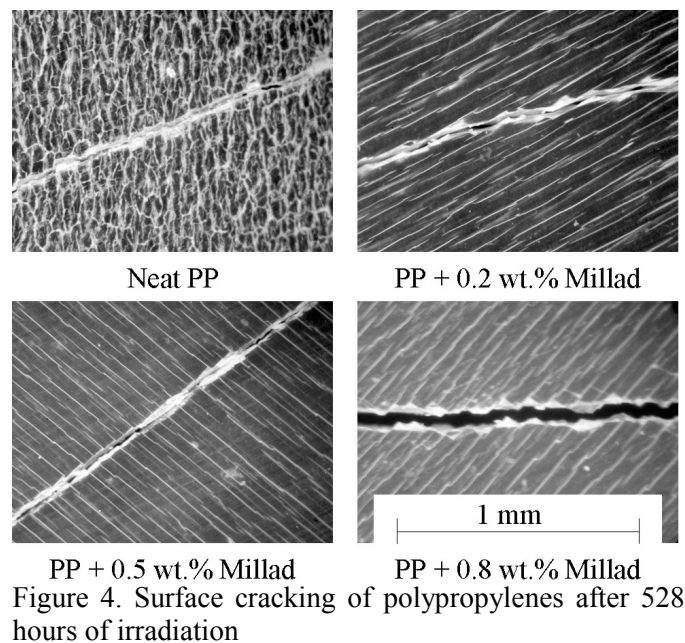PP + 0.5 wt.% Millad   PP + 0.8 wt.% Millad

Figure 4. Surface cracking of polypropylenes after 528 hours of irradiation

3.4 Recrystallization

The evolution of crystallization temperature (Tc) which is taken as a maximum of crystallization peak is shown in Figure 5.Recrystallization exotherms of all samples

exposed to UV-irradiation are shown in Figure 6. It can be seen that neat PP crystallizes at significantly lower temperature (approx. 120 °C before irradiation) than nucleated polypropylenes (approx. 130 °C). This is generally known fact; the presence of heterogeneous nuclei dramatically accelerates the crystallization. Crystallization temperature of nucleated samples varies only a little with concentration of nucleating agent. The evolution of Tc upon UV-exposure can be described as follows. At the beginning of irradiation (up to 100 hours) Tc remains stable. Than (up to 240 or 384 hours depending on the concentration of nucleating agent) it gradually decreases and subsequently the step change of Tc occurs; the temperature significantly drops. This sharp decrease is particularly evident in the case of nucleated samples. Finally (from 480 hours) it decreases gradually again. Such decrease of Tc upon UV-irradiation could be ascribed to the chain scission and an introduction of irregularities into crystallites as already suggested [11]. At the end of irradiation the difference between Tc of neat and nucleated samples is lower than that at the beginning of irradiation (approx. 10 °C versus 4 °C). What is interesting is that PP with 0.2 wt. % of nucleating agent possesses earlier step drop of Tc as compared with the others. (Figure 6). After 336 hours of UV-exposure this sample crystallizes at the same temperature as neat PP. Thus, it can be presumed that the nucleating agent present in the material looses its nucleating efficiency either by chemical transformation caused by UV-light or by the change of crystallization mechanism. Indeed, degraded macromolecules could prefer to crystallize into orthorhombic γ-phase after long term exposure [8]. This crystalline phase of iPP origins from low molecular weight fractions [1]. At even prolonged UV-irradiation the nucleation efficiency of nucleating agent in highly nucleated samples also ceases. Finally, at the end of UV-exposure Tc of nucleated samples is lower than that of neat PP before irradiation.
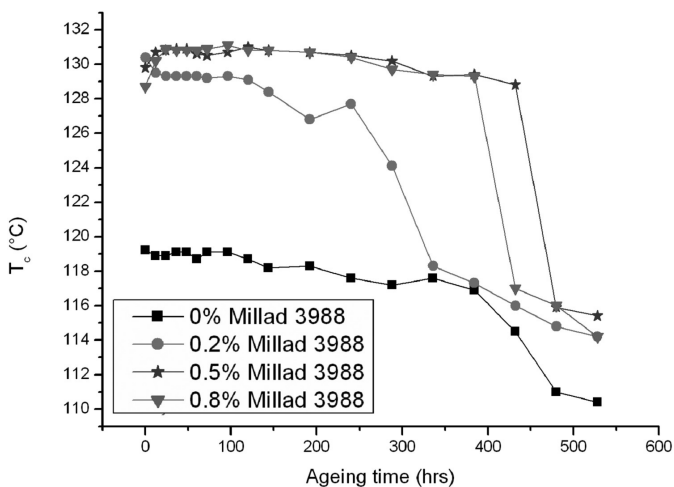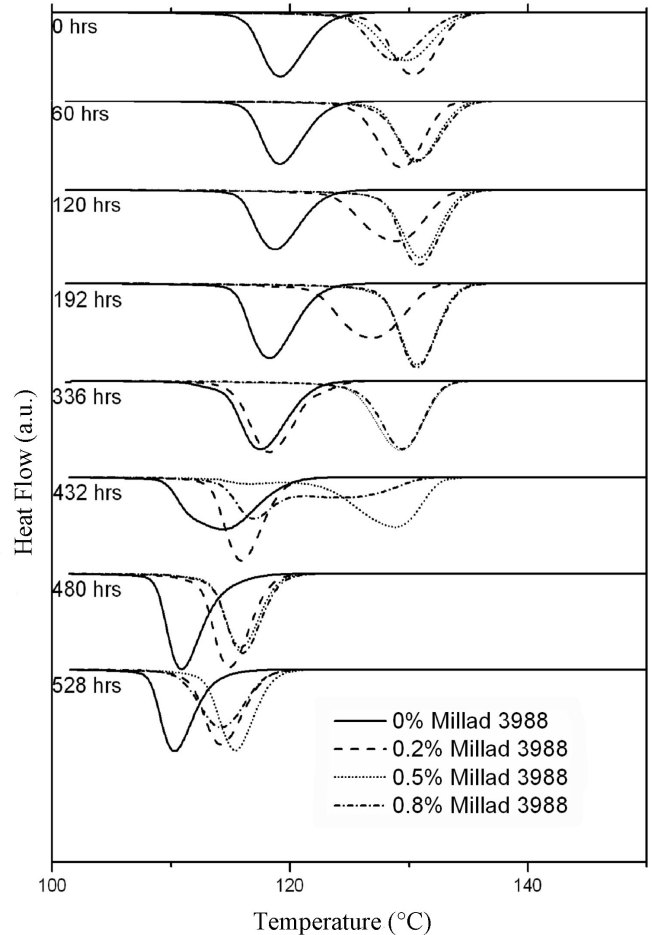

Figure 6. Crystallization thermograms of irradiated polypropylenes

3.5 Remelting

The evolution of remelting endotherms of samples upon UV-exposure is shown in Figure 7. The melting profiles of nucleated samples are similar with a little higher melting temperature as compared to neat PP (165 versus 163 °C). During UV-exposure the profiles do not significantly change up to 336 hours. After that the melting region gradually shifts to lower temperatures and the broadening and even splitting of melting endotherms occurs. The broadening and splitting of the individual melting endotherms with increasing time of irradiation reflect scission and introduction of irregularities into polymer chains. Consequently, the crystallites formed during recrystallization show lower thermodynamic stability. Finally, after the longest irradiation time (528 hours) the melting profile is similar for all the samples indicating resembling extent of photodegradation.
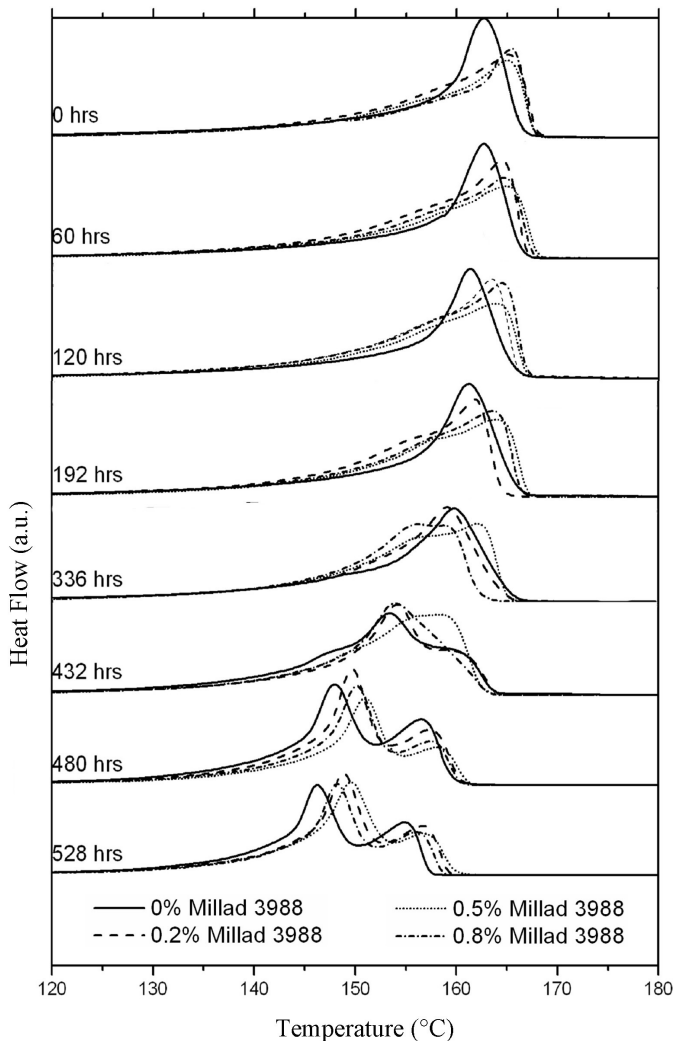

Figure 5. Evolution of crystallization temperature upon UV-irradiation

Figure 7. Remelting thermograms of UV-irradiated polypropylenes

4 Conclusions

The results show that the addition of α-nucleating agent 1,3:2,4-di(3,4- dimethylbenzylidene) sorbitol does not significantly influence the extent of photodegradation of PP. The recrystallization studies show that this nucleating agent looses its nucleation efficiency after long time irradiation; this lost is the fastest in PP with the lowest concentration of the nucleating agent. The presence of the nucleating agent influences the surface cracking of irradiated samples. In nucleated samples, the cracks are oriented in one direction and their network is significantly less dense as compared to neat PP.

4 Acknowledgements

References:
[1] J. Varga, Crystallization, melting and supermolecular structure of isotactic polypropylene. In: J. Karger-Kocsis, editor. Polypropylene: structure blends and composites, vol. 3, Chapman & Hall, London, pp. 56-115 (1995).
[2] C. Marco, G. Ellis, M. A. Gomez, J. M. Arribas, J. Appl. Polym. Sci., 84, 2440 (2002).
[3] T. A. Shepard, C. R. Delsorbo, R. M. Louth, J. L. Walborn, D. A. Norman, N. G. Harvey, R. J. Spontak, J. Polym. Sci. Pol. Phys., 35, 2617 (1997).
[4] M. Kristiansen, M. Werner, T. Tervoorth, R. Smith, M. Blomenhofer, H. W. Schmidt, Macromolecules, 36, 5150 (2003).
[5] M. Blomenhofer, S. Ganzleben, D. Hanft, H. W. Schmidt, M. Kristiansen, P. Smith, K. Stoll, D. Mäder, K. Hoffmann, Macromolecules, 38, 3688 (2005).
[6] M. S. Rabello and J. R. White, J. Appl. Polym. Sci., 64, 2505 (1997).
[7] A. V. Shyichuk, T. J. Turton, J. R. White and I. D. Syrotynska, Polym. Degrad. Stab. 86, 377 (2004).
[8] M. Obadal, R. Čermák, M. Raab, V. Verney, S. Commereuc and F. Fraïsse, Polym. Degrad. Stab., 88, 532 (2005).
[9] J. Výchopňová, R. Čermák, M. Obadal, M. Raab, V. Verney, S. Commereuc, Polym. Degrad. Stab., 92, 1763 (2007).
[10] M.S. Rabello and J.R. White, Polym Degrad Stab,, 56, 55 (1997).
[11] M.S. Rabello and J.R. White, Polymer, 38, 6379 (1997).