

EFFECT OF β -NUCLEATION ON CRYSTALLIZATION OF PHOTODEGRADED POLYPROPYLENE

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The work deals with crystallization of photodegraded polypropylene containing various amounts of β -nucleating agent based on N,N'-dicyclohexyl-naphthalene-2,6-dicarboxamide. Compression-moulded samples were irradiated by UV-light, melted and subsequently non-isothermally crystallized. The results showed that the crystallization temperature decreased with increasing irradiation time. The irradiation caused the splitting of crystallization exotherms into two peaks indicating two crystallization mechanisms. The presence of β -nucleating agent in the material suppressed the peak splitting; the higher was the amount of nucleating agent in the sample, the later was the splitting observed.

Keywords: crystallization, photooxidation, polymorphism

Introduction

Polymorphism of isotactic polypropylene (iPP) has been subjected to intensive investigations during last four decades. A part of these extensive scientific efforts has yielded thorough knowledge of structure, preparation and properties of less common trigonal β -phase. From a practical point of view, superior toughness and drawability belong to the main advantages of β -crystalline phase. As a consequence, isotactic polypropylene rich in β -phase (β -iPP) has been commercialized as an alternative to common polypropylene containing predominantly monoclinic α -phase.

Introduction of specific β -nucleating agents into iPP is merely reliable way of β -iPP preparation. A number of β -nucleating agents differing in both chemical nature and nucleating efficiency has been reported [1, 2]. A NJ Star NU 100 commercial-available β -nucleating agent based on N,N'-dicyclohexyl-naphthalene-2,6-dicarboxamide (NU 100) has attracted the attention of many papers [e.g. 3–6]. A concentration 0.03 mass% of NU 100 has been found to be critical; the content of β -phase within crystalline portion reaches saturation level and mechanical properties show maxima [3]. Recently, Varga and Menyhárd [7] have manifested a partial solubility of NU 100 in iPP melt consequently arising its nucleation duality (α - and β -phase). They thus suggested the critical concentration to be dependent on thermal history of the material.

Another important property has been latterly ascribed to β -iPP. As a consequence of intensive research efforts in degradation of polyolefins, the superior stability of β -iPP against UV-light has been revealed [8, 9]. Obadal *et al.* suggested that the high scattering of UV-light is the key factor for the UV-stability of β -iPP. Significantly higher haze of β -iPP compared to common iPP has been confirmed in our recent work [10]. In this paper, re-crystallization of UV-degraded iPP with 0.03 mass% of NU 100 has been also partly discussed. A gradual decrease of crystallization temperature followed by the splitting of the crystallization exotherm with UV-exposure time has been observed. Obviously, such behaviour reflects the change of nucleation mechanism; the photodegradation process strongly depends on the initial iPP morphology and phase composition, but, at the same time, polypropylene exposed to UV-irradiation shows distinct changes in morphology after re-crystallization. A remarkable effect is the formation of orthorhombic γ -crystalline phase originating from the presence of low molecular mass iPP fraction in the crystallizing polymer melt [11]. Several open questions, however, remains unanswered particularly in crystallization of degraded β -iPP as the competitive formation of all three polymorphs can be expected [9].

Present study directs attention to the thermal behaviour of UV-degraded β -iPP to contribute to this field interesting from both scientific and industrial (recy-

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cling) point of views. For these purposes, isotactic polypropylene with various amounts of NU 100 has been exposed to UV-light and studied systematically by differential scanning calorimetry (DSC) in individual stages of UV-degradation. This approach should facilitate the material recycling of β -iPP.

Experimental

Materials and specimens

The common isotactic polypropylene produced under common Ziegler–Natta catalysis (complex of TiCl_4 with triethylaluminum on a MgCl_2 carrier) in a gas-phase reactor was used. This iPP is characterized by a melt flow index of $3 \text{ g } 10^{-1} \text{ min}^{-1}$ (2.16 kg, 230°C, ISO 1133), a mass-average molecular mass approx. $320\,000 \text{ g mol}^{-1}$ (GPC) and an isotacticity index of 98% (ISO 9113). The material contains a standard stabilization package based on phenol-phosphite stabilizers including Irganox 1010, Irganox 1076 and Irgafor 168 produced by Ciba Specialty Chemicals Inc., Basel, Switzerland. The virgin material was mechanically mixed with a commercial β -nucleating agent, NJ Star NU 100 (N,N'-dicyclohexylnaphthalene-2,6-dicarboxamide) supplied by Rika Int., Manchester, Great Britain, in several concentrations (0, 0.03, 0.05, 0.10 and 0.20 mass%) and subsequently processed in a Brabender twin-screw extruder. From the prepared blends, plates with dimension of $125 \times 60 \times 0.2 \text{ mm}$ were compression-moulded. Material was put into a preheated mould and after 1 min pressing at 210°C, the plates were cooled at 60°C for 10 min.

Methods

Optical properties

Haze of as-processed non-irradiated plates was measured using a Haze-Gard Plus instrument (BYK-GARDNER Co.) according to ASTM D1003. Haze is defined as a percentage of transmitted light being scattered in an angle higher than 2.5°.

UV-exposure

Rectangular specimens ($60 \times 10 \times 0.2 \text{ mm}$) cut from the plate were irradiated at 60°C in a SEPAP 12.24 irradiation device equipped with four medium-pressure mercury lamps. During irradiation the back of specimens was masked by black paper. The following exposure times were applied: 0, 24, 36, 48, 60, 72, 96, 120, 144, 192, 240 h.

Differential scanning calorimetry

A Mettler Toledo 822e differential scanning calorimeter was employed. Nitrogen was used as a purge gas constantly passing (50 mL s^{-1}) through the heat sink and over the cell. Irradiated samples of approx. 4 mg were loaded into standard aluminium pans. The thermal regime used was following: Heating to 220°C, annealing at 220°C for 5 min to erase thermal history, cooling to 100°C, annealing at 100°C for 10 min and heating to 190°C. The samples were not cooled below 100°C to prevent the $\beta \rightarrow \alpha$ re-crystallization during subsequent melting [1, 12, 13]. A rate of $\pm 10^\circ\text{C min}^{-1}$ was used for all thermal scans. Crystallization and melting temperatures hereafter reported refer to peak temperatures in the corresponding DSC curves.

Results and discussion

Melting

The melting endotherms of samples irradiated for 0, 48, 60, 96, 192 and 240 h are shown in Fig. 1. These irradiation times were chosen as representatives. The melting curves of non-nucleated material indicate only one melting peak associated with α -phase. On the other hand, the nucleated samples show two melting peaks corresponding to α - and β -phase at temperature approx. 170 and 150°C, respectively. Moreover, the curves are similar for all concentrations of the nucleating agent (NU 100); this excludes a significant effect of NU 100 presence itself on the material evolution upon UV-irradiation. What can be also observed is an undershoot of baseline of nucleated materials. This points to the $\beta \rightarrow \alpha$ re-crystallization occurring during melting. Indeed, if the β -iPP is cooled below the critical temperature 100°C the inter-phase transformation proceeds upon subsequent heating [1, 12–14]. Correspondingly, the melting peak of α -phase does not fully reflect the presence of α -phase in original material. The evolution of the curves shows that the $\beta \rightarrow \alpha$ re-crystallization is gradually suppressed upon the UV-exposure. This behaviour can be ascribed to chain scission and an introduction of defects into the polymer chains reducing their re-crystallizability [9]. The melting temperature (T_m) of β -phase does not significantly change with irradiation time, only a slight decrease at higher times can be observed. On the other hand, the significant decrease of T_m of neat polypropylene is evident: from approx. 165 to 150°C. This trend is observed also by White [15] and is ascribed to the oxidative reactions occurring at the lamellar fold surfaces. This causes an increase in the surface free energy of the crystals, resulting in a reduction of the melting temperature, as known from Thomson–Gibbs equation (i.e. melting

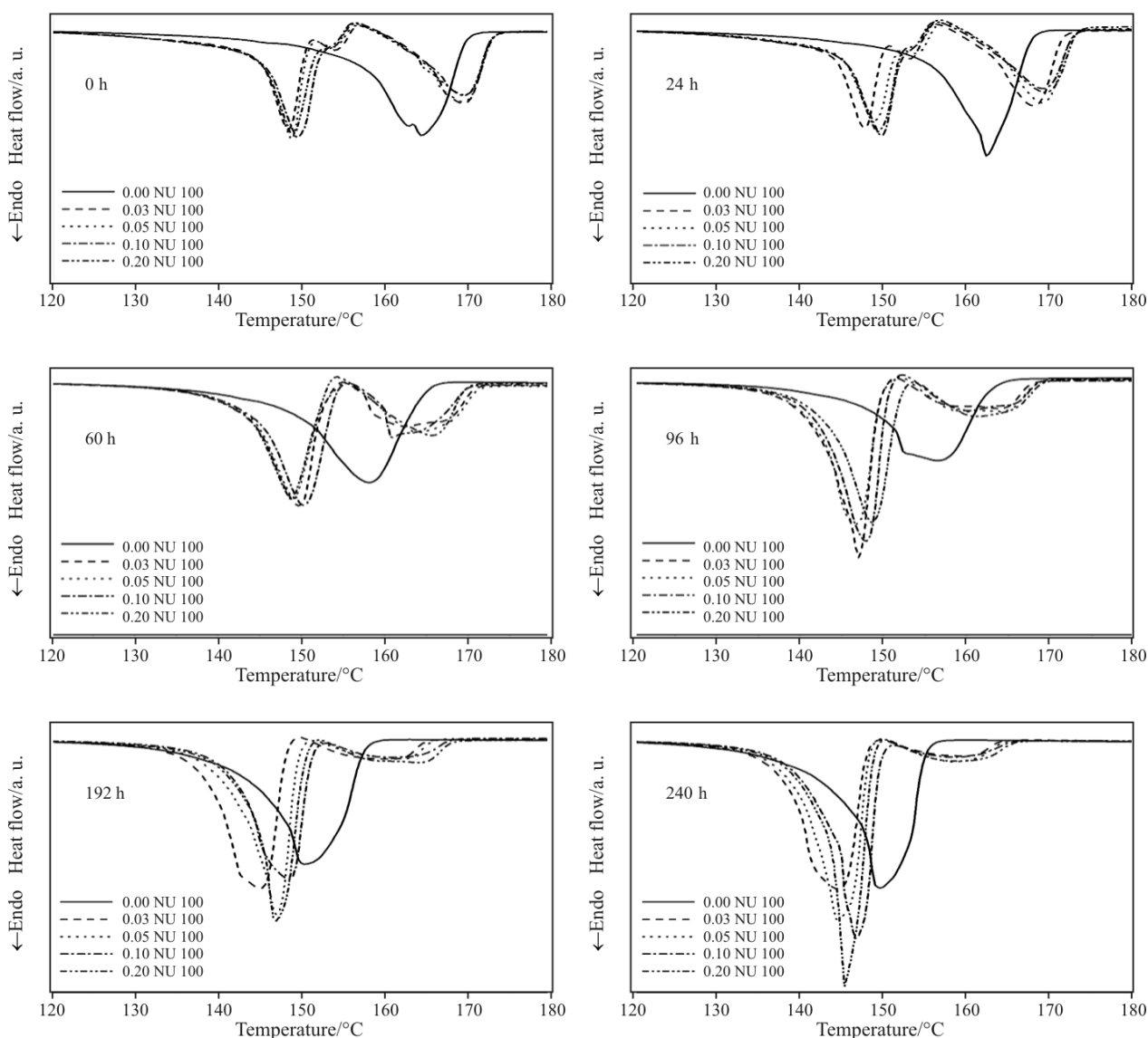


Fig. 1 Melting curves of the samples irradiated for 0, 48, 60, 96, 192 and 240 h

temperature decreases with rising surface free energy and decreasing lamellar thickness). Overall, the results presented above confirm an increasing UV-stability of β -iPP as compared to non-nucleated material.

The high stability of β -nucleated material has been ascribed to higher haze and light scattering of UV-light of β -phase [9]. Indeed, neat polypropylene manifests significantly lower haze as compared to nucleated sam-

ples, as presented in Table 1. The haze of nucleated samples does not markedly vary; only its slight increase with increasing β -nucleating agent content in the material is detected.

Re-crystallization

Figure 2 represents the re-crystallization exotherms of neat and nucleated PP irradiated for 0, 48, 60, 96, 192 and 240 h and Fig. 3 shows the dependence of crystallization temperature on exposure time of all samples under study. An interesting change in the shape of crystallization exotherms upon UV-irradiation is observed. At the first stage of the exposure, a symmetric peak occurs at a crystallization temperature (T_c) of approx. 125°C. At longer exposure, the peak splits into two peaks suggesting two crystallization mechanisms, as already discussed in our recent work [10].

Table 1 Optical properties of the samples

Material	Haze [%]
neat PP	43.7
PP+0.03 NU 100	97.5
PP+0.05 NU 100	98.7
PP+0.10 NU 100	98.7
PP+0.20 NU 100	99.2

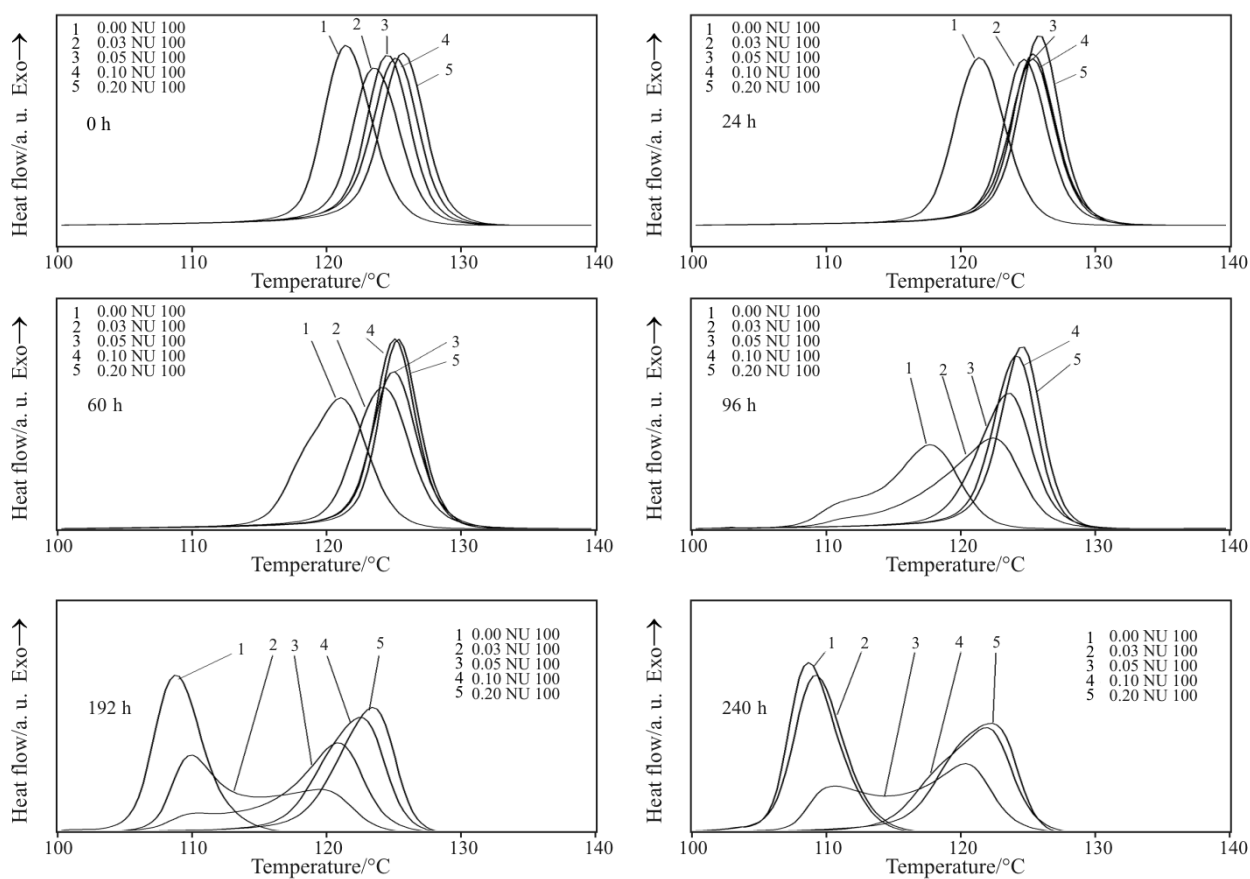


Fig. 2 Recrystallization exotherms the samples irradiated for 0, 48, 60, 96, 192 and 240 h

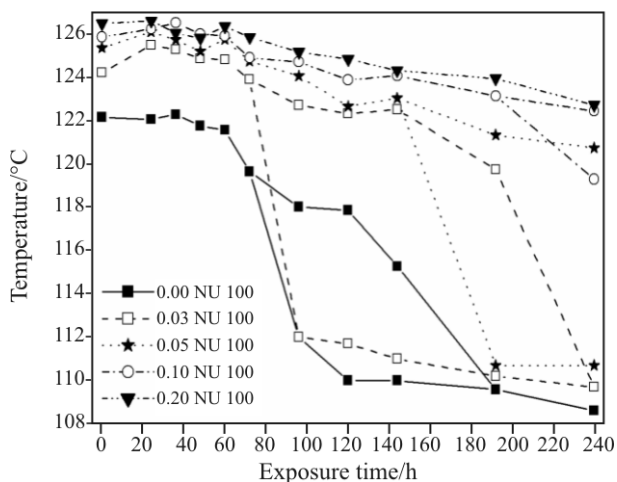


Fig. 3 The dependence of recrystallization temperature on exposure time. In the case of exotherm splitting, both T_c are drawn in the graph

The formation of other PP polymorph can be expected. Finally, at the longest irradiation times again a symmetric exotherm occurs, but shifted to lower T_c of approx. 110°C. The onset of the splitting of the crystallization peaks moves to longer irradiation times with increasing β -nucleating agent content. For the

highest concentration (0.20 mass%) and an exposure time of 240 h, only a weak tendency to a double exotherm occurs. It is well known that the increase of molecular degradation favours the formation of γ -phase. Indeed, in materials containing lower amount of NU 100 this effect will even become predominant being reflected by the observed doubling of crystallization exotherm.

Re-melting

Figure 4 represents the evolution of melting curves of re-crystallized samples in the whole range of UV-exposure. To precede the $\beta \rightarrow \alpha$ re-crystallization process which can take place during heating the samples were not cooled below 100°C [1, 12–14]. Indeed, no baseline undershoot is observed. It is well seen in the figure, that the irradiation of the samples causes broadening and lowering of the melting peaks. This is connected with incorporation of irregularities into the molecular chains and with significant decrease of their molecular mass. Such molecules form imperfect crystals with broad size distribution and lower thermodynamic stability based namely on lower broad-distributed lamellar thicknesses. Indeed, the

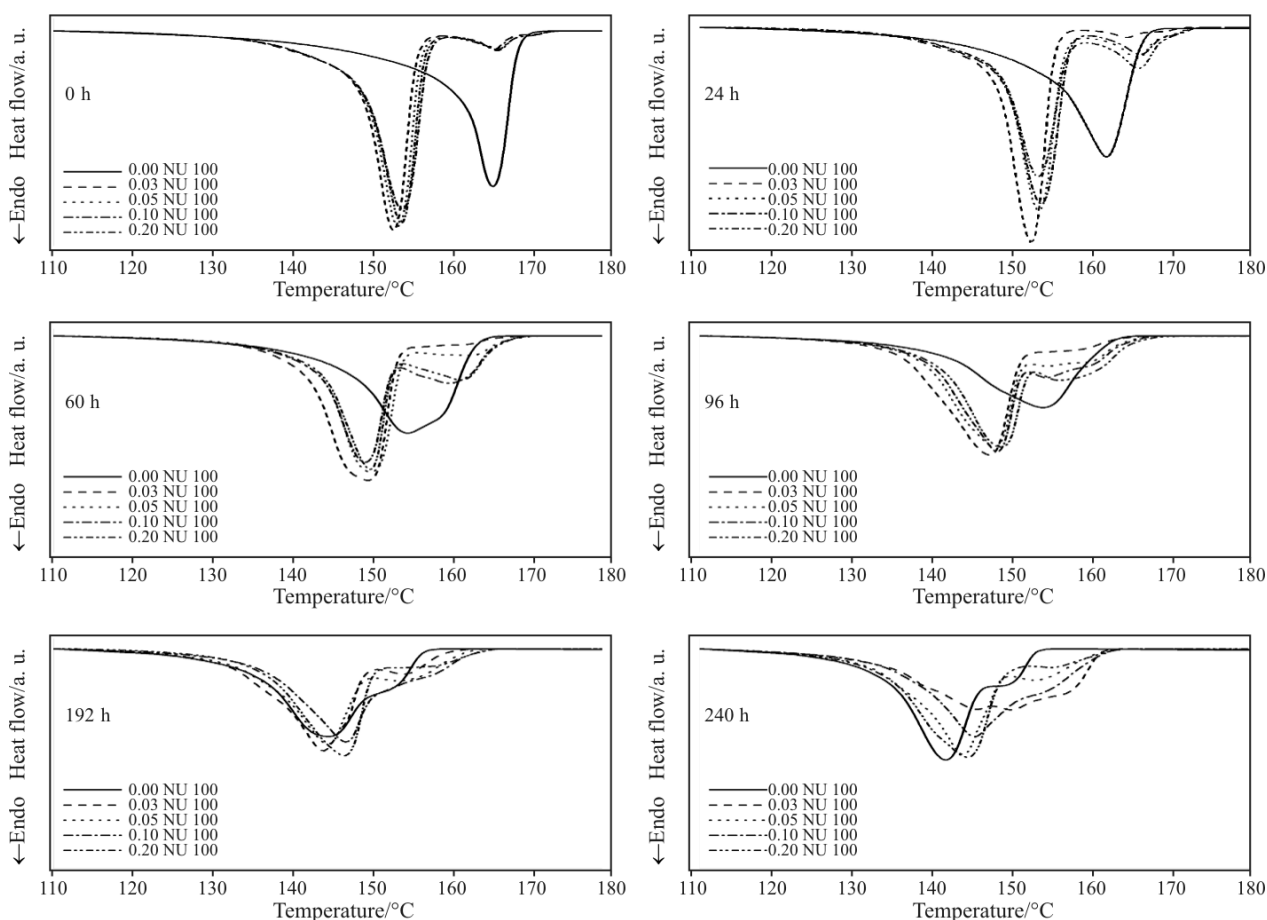


Fig. 4 Re-melting curves of the samples irradiated for 0, 48, 60, 96, 192 and 240 h

preferential growth of γ -phase is induced by the evolution of molecular degradation and irregularity introduction. The decrease in melting temperature is the most pronounced for neat polypropylene (from approx. 166°C before irradiation to approx. 142°C after 240 h UV-exposure). The evolution of the melting endotherm of neat iPP is following: *i*) an initial (individual) melting peak with maximum at approx. 166°C (α -phase), *ii*) a splitting of the endotherm starting after 60 h of UV-irradiation (in clear relation to the mentioned doubling of crystallization exotherm), *iii*) after long-term exposure the peak created during ageing process becomes predominant with maximum at 142°C (γ -phase [9]). Both peak maxima however decrease proportionally during photoageing, in the case of α -phase from 166°C to approx. 150°C after 240 h of UV-irradiation.

The non-irradiated β -nucleated materials possess nearly similar melting profile with predominant β -melting peak at approx. 154°C. The effect of UV-irradiation leads, as in the case of neat material, to decrease of the melting temperature to approx. 144°C (derived from endotherm of the sample containing 0.20 mass% of NU 100). An overlap of melting of β - and γ -phases can be thus expected. The UV-exposure

leads however also to the increase of α -melting peak indicating a decrease in β -specificity of heterogeneous nucleation in UV-degraded samples.

Conclusions

Differential scanning calorimetry measurements show that the addition of β -nucleating agent *N,N'*-dicyclohexyl-naphthalene-2,6-dicarboxamide lead to the predominant formation of β -phase within crystalline portion of the material. The amount of β -phase did not increase with concentration of β -nucleating agent as was reflected by nearly identical melting profile of all nucleated samples under study. The thermal behaviour of UV-irradiated samples can be summarized as follows:

- Decrease of melting temperature with increasing UV-exposure time was observed within all samples reflecting erosion of crystallite surfaces. This shift was the most pronounced for neat polypropylene showing its poorest stability against UV-light.
- The crystallization exotherms changed the shape with UV-exposure: the V-shaped exotherms split into W-shaped and finally merged into V-shaped

again but with significantly lower crystallization temperature. The formation of two crystallization peaks reflected gradual change of crystallization mechanisms. The onset of the splitting of the crystallization peaks moved to longer irradiation times with increasing β -nucleating agent content. For the highest nucleator concentration only a weak tendency to a splitting occurred.

- The broadening and splitting of the individual re-melting endotherms reflect the formation of crystallites with lower thermodynamic stability during re-crystallization. This is particularly pronounced for neat polypropylene.

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References

- 1 J. Varga, *J. Macromol. Sci. Phys.*, 41 (2002) 1121.
- 2 A. Menyhárđ, J. Varga and G. Molnár, *J. Therm. Anal. Cal.*, 83 (2006) 625.
- 3 J. Kotek, M. Raab, J. Baldrian and W. Grellmann, *J. Appl. Polym. Sci.*, 85 (2002) 1174.
- 4 M. Obadal, R. Čermák, N. Baran, K. Stoklasa and J. Šimoník, *Int. Polym. Proc.*, 19 (2004) 35.
- 5 J. Výchopňová, V. Habrová, M. Obadal, R. Čermák and R. Čabla, *J. Therm. Anal. Cal.*, 86 (2006) 687.
- 6 C. Marco, M. A. Gomez, G. Ellis and J. M. Arribas, *J. Appl. Polym. Sci.*, 86 (2002) 531.
- 7 J. Varga and A. Menyhárđ, *Macromolecules*, 40 (2007) 2422.
- 8 J. Kotek, I. Kelnar, J. Baldrian and M. Raab, *Eur. Polym. J.*, 40 (2004) 2731.
- 9 M. Obadal, R. Čermák, M. Raab, V. Verney, S. Commereuc and F. Fraïsse, *Polym. Degrad. Stab.*, 88 (2005) 532.
- 10 J. Výchopňová, R. Čermák, M. Obadal, M. Raab, V. Verney and S. Commereuc, *Polym. Degrad. Stab.*, 92 (2007) 1763.
- 11 S. Bruckner, V. S. Meille, V. Petraccone and B. Pirozzi, *Prog. Polym. Sci.*, 16 (1991) 361.
- 12 B. Lotz, *Polymer*, 39 (1998) 4561.
- 13 B. Lotz, *J. Macromol. Sci. Phys.*, 41 (2002) 685.
- 14 J. Varga, *J. Therm. Anal. Cal.*, 31 (1986) 165.
- 15 M. S. Rabello and J. R. White, *Polym. Degrad. Stab.*, 56 (1997) 55.

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