
P O L I M E R Y

Heterogeneous polymers degradation – microplastic

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Abstract: The process of semicrystalline polymers thermo-oxidative degradation was analyzed on the example of isotactic polypropylene (iPP). Oxygen degradation takes place mainly in the amorphous phase into which oxygen diffuses. This leads to oxidation (formation of hydroperoxides) and next the chains scission. The polymer becomes brittle and breaks down into small pieces (e.g. microplastics). The crystalline phase is more difficult to access for oxygen that initiates the thermo-oxidation process. An increase in the crystallinity degree and a decrease in the viscosity of the solutions diluted in p-xylene as a function of the degradation time were observed. The number of iPP chain scission (change in molecular weight) as a function of degradation time was also calculated. These values depend on the polymer initial crystallinity degree and its supermolecular structure.

Keywords: thermooxidation, semicrystalline polymers, chain scission, structure, viscosity.

Niejednorodna degradacja polimerów – mikroplastik

Streszczenie: Na przykładzie izotaktycznego polipropylenu (iPP) przeprowadzono analizę procesu termooksydacyjnej degradacji polimerów semikrystalicznych. Degradacja z udziałem tlenu odbywa się przede wszystkim w fazie amorficznej, do której dyfunduje tlen. Prowadzi to do utleniania (powstawania wodoronadtlenków), a następnie pęknięcia łańcucha polimerowego. Polimer staje się kruchy i rozpada na małe fragmenty (m.in. mikroplastik). Faza krystaliczna jest trudniej dostępna dla tlenu inicjującego proces termoutleniania. Stwierdzono wzrost stopnia krystaliczności i zmniejszenie lepkości roztworów rozcieńczonych w p-ksylenie w funkcji czasu degradacji. Obliczono również liczbę pęknięć łańcucha iPP (zmianę masy cząsteczkowej) w funkcji czasu degradacji. Wielkości te zależą od początkowego stopnia krystaliczności polimeru i jego struktury nadcząsteczkowej.

Słowa kluczowe: termooksydacja, polimery częściowo krystaliczne, pęknięcie łańcucha, struktura, lepkość.

The simplified name “plastics” most often means synthetic polymer materials. These materials are very diverse, from the simplest chemically polyethylene to polymer mixtures and composites. The development of the polymers production and application took place in the post-war years.

Their discovery is associated with wide use in various industries. It is difficult to imagine the lack of polymers in the household, packaging industry, construction and others.

Polymers have many useful properties, e.g. high durability, low density and easy processing. However, their

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use requires utilization of post-production and post-consumer waste, e.g. by recycling. Each year, millions tons of „plastic” waste are produced worldwide, and at least 30% of them ends up on landfill, as an economy does not use its potential ability in recycling.

Polymers as organic compounds are sensitive for different environmental factors e.g. physical, chemical, mechanical or biological, leading to their degradation. Degradation processes in high temperature, as well as in photooxidation under light and oxygen influence, lead first to decrease in polymers properties and then to cracking and forming of small pieces called „microplastic”. The presented study aims to explain, basing on our own research results, the polymer degradation process leading to formation of microparticles and their presence in an environment.

Supermolecular structure of polymers

Polyolefins i.e. polyethylene (PE) and polypropylene (PP) are most commonly used in packaging. Hence, the majority of post-consumer waste, mainly as a film made of this polymers, can be found in landfills. As these polymers are easily recyclable, they should not have been there. Polyolefins as lighter than water (their density is lower than 1) can float on surfaces of water reservoirs also in degraded form. Presented study is based on our knowledge concerning these polymers, mainly in terms of their structure and degradability [1–4].

In case of isotactic polypropylene iPP (all CH₃ groups are on the same side of a chain), regular chemical structure enhances crystallization process. iPP degree of crystallinity can achieve even 70%. The polymers can cry-

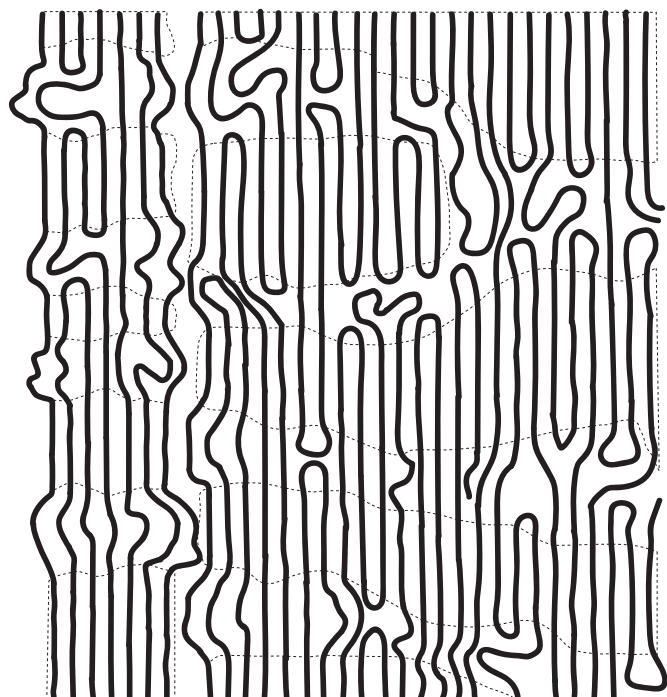


Fig. 1. Scheme of supermolecular structure of semicrystalline polymers (crystalline and amorphous) [7]

stallize from the melt or solution. Isotactic polypropylene is a partially crystalline polymer, i.e. a two-phase system in which the ordered crystalline phase is dispersed in the amorphous phase, forming a supermolecular structure.

The size of crystalline phase depends on nucleation kinetics and crystal growing. By controlling process of the film producing e.g. from the melt, we can control not only the degree of crystallinity but the polymer morphological-supermolecular structure and its properties as well [5–7]. Fig. 1 shows schematically the two-phase structure of the polymer.

The most important mechanism leading to the folding of the polymer chain in the crystallization process is related to the kinetics and thermodynamics of the nucleation processes and linear macromolecules crystallization from the random entanglement state. The lamellar shape of crystallite is typical for linear macromolecules, crystallizing by the chain folding from amorphous state (the melt or solution). Crystals sizes depend on crystallization conditions and a kind of polymer.

Thermo-oxidative degradation of polymers

From 1970s till today many studies were devoted to the question of thermodegradation as well as biodegradation of polymers [8–10]. The degradation process, but also the polyolefins biodegradation, is controlled by the rate of initiation of the sample oxidation process. Oxygen joining leads to forming of hydroperoxides, which disintegration causes cracking of polymer carbon chain and molecular weight reduction. Oxygen, high temperature and UV radiation are the factors that, by proceeding reactions, make the polymer degrade, which becomes brittle and disintegrates. The rates of this disintegration depend on the composition and structure of the polymer.

As polyolefins have partially crystalline structure, oxygen needed to start reaction cannot diffuse into the crystalline phase of the polymer easily (this is the orderly phase), hence, random chain cracking takes place mainly in the amorphous phase, which is placed between lamellas and inside the spherulite structures.

Thermooxidative degradation is a diffusion-controlled process. Oxygen molecules can diffuse into the film and be joined to the polymer (creating peroxides and hydroperoxides). If oxygen diffusion is accompanied by joining the oxygen in chemical first-order irreversible process, then one way diffusion can be described by the equation 1 [4, 9].

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} - kC \quad (1)$$

Where:

C – oxygen concentration,

D – diffusion coefficient,

k – first order oxygen uptake rate constant.

Hence, the oxygen absorption rate and chain cracking rate (scission) depend on parameters k and D [4].

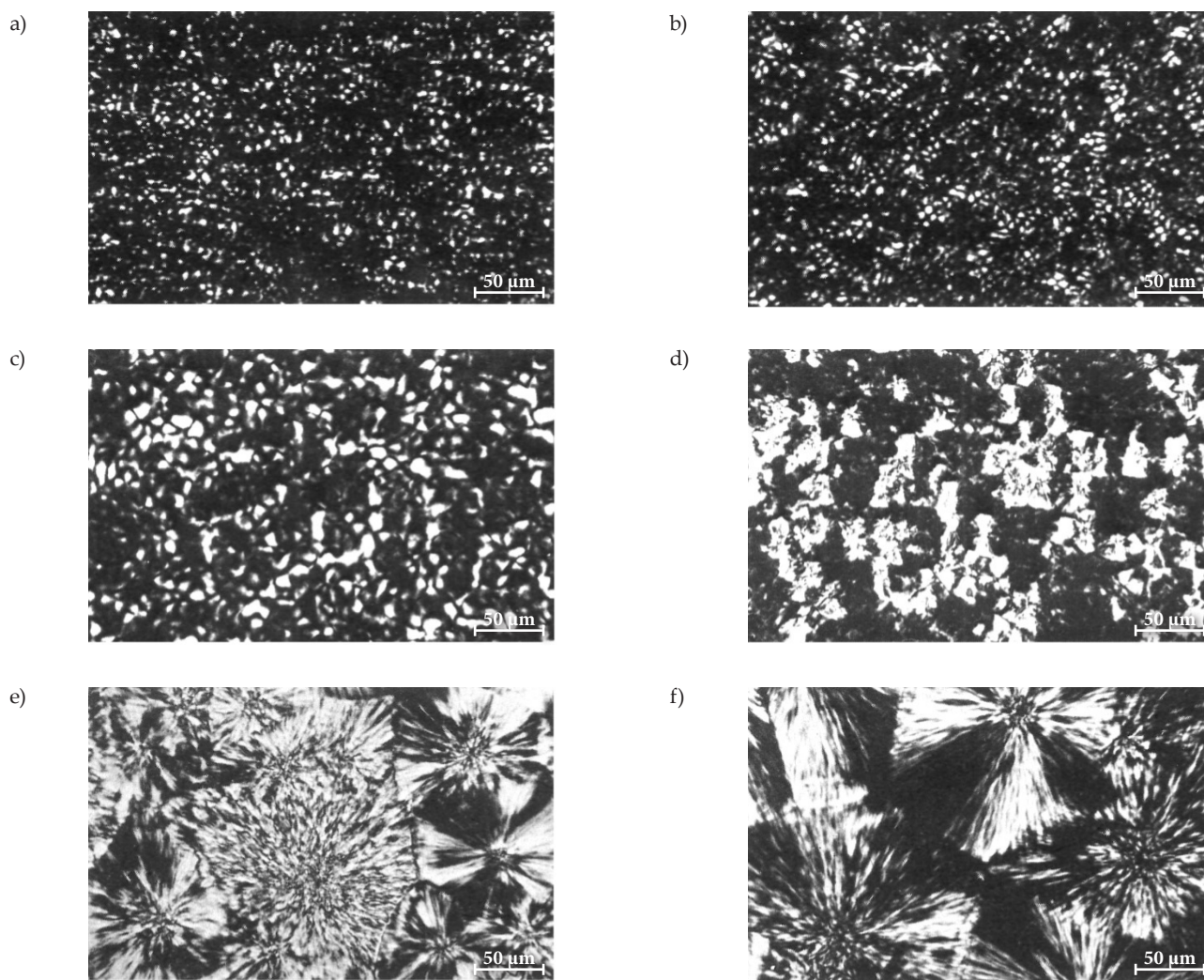


Fig. 2. Micrographs of iPP samples crystallized from melt in various temperatures: a) -75°C , b) 0°C , c) 60°C , d) 100°C , e) 130°C and d) 140°C

EXPERIMENTAL PART

Materials and methods

Studies on thermooxidation in air were made with isotactic polypropylene from Montecatini (USA) of molecular weight 168 000 using thin films with thickness of $100\ \mu\text{m}$. The polymer was melted for 2 min in the temperature of 190°C between two metal plates under pressure of $2 \cdot 10^7\ \text{N/m}^2$. Afterward the samples were crystallized in isothermal conditions ($-75^{\circ}\text{C} \leq T_c \leq 140^{\circ}\text{C}$) in time dependent on crystallization temperature (about $2 \cdot t_{1/2}$). Half time crystallization ($t_{1/2}$) was taken from the literature [11]. The degree of crystallinity was calculated basing on samples density measurements (in liquid gradient pipes) methanol-water in the temperature of 25°C .

Thermooxidative degradation was made in the air in the temperature of $80\text{--}145^{\circ}\text{C}$. Polymer physical and chemical changes were determined basing on density changes, viscosity of diluted solutions (in p-xylene) and polarizing optical microscope.

RESULTS AND DISCUSSION

To obtain isotactic polypropylene films with approximate thickness of $100\ \mu\text{m}$ and various structure, crystallization of iPP from the melt state was made by quick cooling

Table 1. Effect of the crystallization temperature (T_c) on the initial crystallization degree (X_0) of iPP samples

Sample	$T_c, ^{\circ}\text{C}$	$X_0, \%$
1	-75	0,40
2	0	0,45
3	60	0,50
4	100	0,58
5	130	0,65
6	140	0,67

Where:

$$X_0 = \frac{\rho_c}{\rho_a} \cdot \frac{\rho - \rho_a}{\rho_c + \rho_a} \quad (2)$$

ρ, ρ_a, ρ_c – sample density,

ρ_a – amorphous phase density,

ρ_c – crystal phase density,

ρ – test sample density.

to the temperature from -75 to 140°C . Films that differs in degree of crystallinity (X_0) as well as in crystal structures size (morphology) were obtained (Table 1). Optical microscope micrographs of the samples obtained in various crystallization temperature are shown in Fig. 2. Afterward these samples were thermally degraded in the air in temperature from 80 to 145°C in different degradation time (under iPP melting temperature, which is about 170°C).

Fig. 3 shows dependence of viscosity number (η_t/η_0) on the degradation time for the samples. Decrease in

viscosity number indicates polymer chains thermooxidative degradation caused by molecular weight reduction (decrease of polymer diluted solutions viscosity). The decrease is the biggest for samples with low initial degree of crystallinity (large proportion of the amorphous phase).

Dependence of crystallinity degree on thermooxidation time in the temperature of 115°C is shown in Fig. 4. Increase in crystallinity degree as a function of degradation time is caused by the reorganization of sample struc-

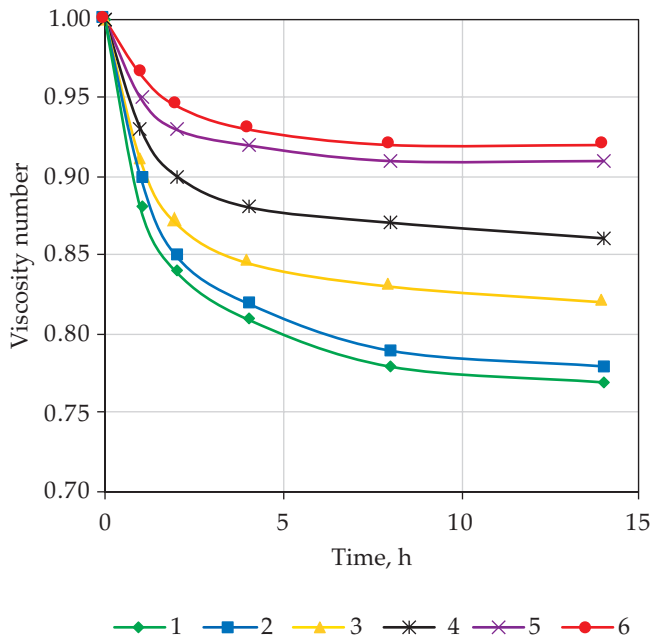


Fig. 3. Dependence of viscosity number (η_t/η_0) on degradation time for samples (degradation temperature 100°C)

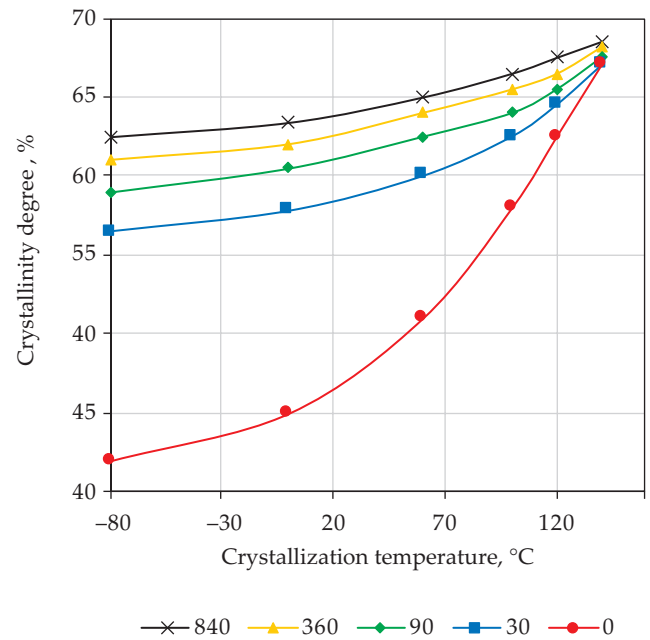


Fig. 4. Dependence of crystallinity degree on crystallization temperature for samples degraded at 115°C (in various degradation time: 0, 30, 90, 360 and 840 min)

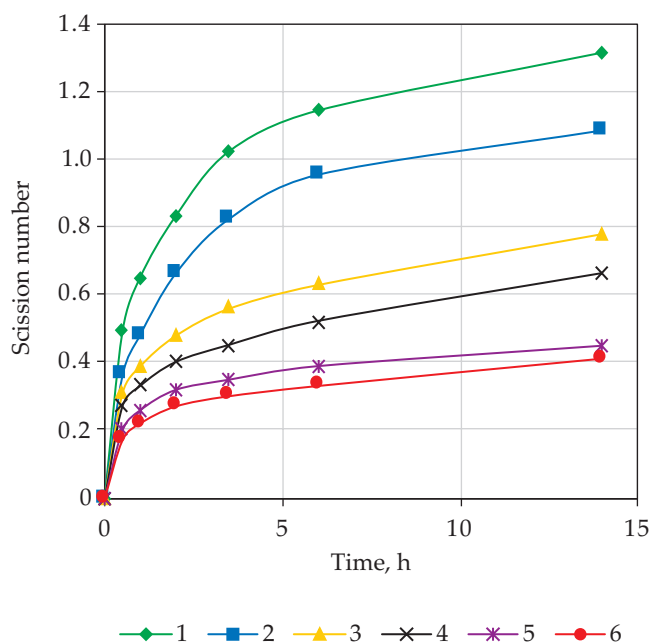


Fig. 5. Dependence of scission number on degradation time for samples (degradation temperature 100°C)

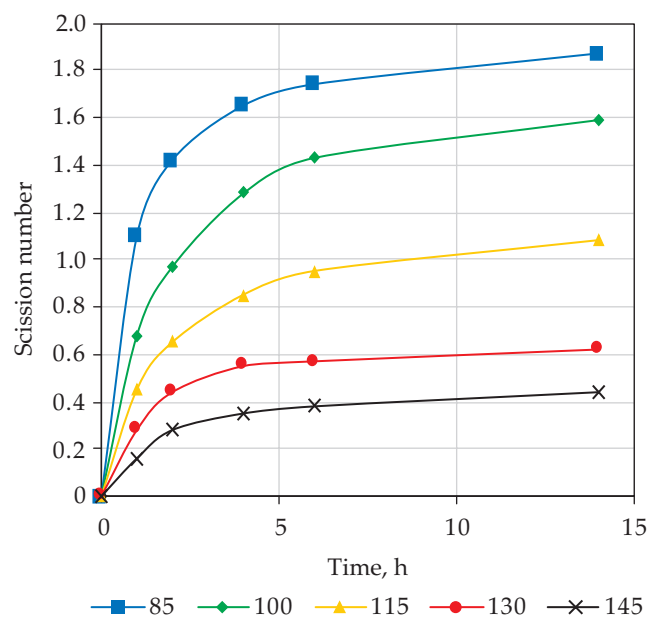


Fig. 6. Scission number versus degradation time (sample 2) in various degradation temperature (85 , 100 , 115 , 130 and 145°C)

ture as a result of chain cracking in amorphous phase, leading to their crystallization in both the amorphous and crystalline phases. Amorphous phase is partly removed as decomposition products.

In Fig. 5 and 6 the dependence of chain scission number (S) on degradation time (t) and polymer morphological structure is shown.

$$S = \left(\frac{\eta_t}{\eta_0} \right)^{\frac{1}{\alpha}} - 1 \quad (3)$$

where:

$\frac{\eta_t}{\eta_0}$ – the relative value of the viscosity index,

α – viscosity index,

The results show that polymer chain cracking rate (measured by decrease in viscosity of polymers diluted solutions after thermooxidative degradation) depends on initial participation of the amorphous phase. Nonlinear dependence means that the sample morphology has also influence on its oxidation initiation kinetics. Hence, the sample crumbles and breaks. These parts that make the crystalline phase are not easily accessible for oxygen and further development of oxidation process. This leads to creating of small pieces of the same polymer, inaccessible or not easily accessible for oxygen, that form “microplastic”.

CONCLUSIONS

Analysis of the partially crystalline polymers thermooxidative degradation indicates heterogeneity of this process. These polymers disintegrate into smaller pieces because of their heterogeneous reaction with factors that cause the degradation e.g. with oxygen. Oxygen has limited access to the crystalline phase due to its high ordering (lamella). Partially crystalline polymers structure, modified in processing, affects the rate of their degradation. The results indicate that the chain cracking process in amorphous phase decreases polymer molecular weight and depends on processing temperature and supermolecular structure. Creating smaller pieces of polymer after degradation results from polymer heterogeneity and “microplastic” consists of polymer small pieces, which can, in long time, degrade further in environment. Polyolefins are indifferent for environment and not biodegradable (just like “microplastic” – small pieces of the polymer). However, like dust, e.g. coal dust, microplastic is not indifferent to the lungs of organisms when inhaled. Its presence in environment is also no good for

underwater life, as floating on the surface it stops sunlight and oxygen from penetrating into the underwater environment. Therefore, uncontrolled storage of polyolefins in the environment should be avoided, especially as it is a material easy to recycle. When it becomes unfit for recycling, it should be taken to an appropriate incineration plant, adapted to the combustion of polymers. The polyolefins calorific value is higher than that of crude oil.

Uncontrolled littering of the environment with polymer waste should be severely punished. Reducing the amount of polymer waste in the natural environment should be achieved through proper management. Packaging producers should also be responsible for littering, perhaps the production of packaging should be linked to their subsequent recycling. Trade in waste, as it litters poorer countries, should be also prohibited.

Both the European Parliament and the European Commission have issued a number of directives on packaging and packaging waste that need to be complied with [12].

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