Changes in thermal properties of isotactic polypropylene with different additives during aging process

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Abstract: Polymer degradation is a change in the properties of a polymer under the influence of one or more environmental factors such as heat, light, humidity or chemicals. These changes may be undesirable, such as changes during use, or desirable, as in biodegradation or deliberately lowering the molecular weight of a polymer. A series of composites of isotactic polypropylene (iPP) has been obtained by the melt intercalation by introducing certain additive into the molten polymer matrix using a twin-screw extruder. The effect of additives (multi-wall carbon nanotubes as nanofiller, montmorillonites, pigments) on the process of isotactic polypropylene degradation, thermal stability, the characteristic temperatures (of melting and crystallization) during the aging process were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). A additives affect the degradation mechanism and consequently change thermal stability of iPP (the most stable are samples with addition of carbon nanotubes). The additives also affect the crystallization of polypropylene and thus the crystallization temperature and crystallinity index of the base material.

Keywords: composites, isotactic polypropylene, degradation, thermal stability.

Zmiany właściwości termicznych izotaktycznego polipropylenu z różnymi dodatkami poddanego procesowi starzenia

Streszczenie: Degradacja polimeru to proces prowadzący do zmian właściwości polimeru, następujących pod wpływem jednego lub kilku czynników takich, jak: ciepło, światło, wilgotność lub chemikalia. Zmiany takie mogą być niepożądane, np. w czasie użytkowania, lub pożądane — celowe zmniejszenie ciężaru cząsteczkowego polimeru podczas biodegradacji. Serię kompozytów polipropylenu izotaktycznego (iPP) otrzymano na drodze interkalacji w stopie, wprowadzając określone dodatki do matrycy roztopionego polimeru, przy użyciu wytłaczarki dwuślimakowej. Wpływ dodatków (wielościennych nanorurek węglowych, montmorylonitów, pigmentów) na proces degradacji, stabilność termiczną, charakterystyczne wartości temperatury (topnienia i krystalizacji) izotaktycznego polipropylenu badano metodami analizy termograwimetrycznej (TGA) i różnicowej kalorymetrii skaningowej (DSC). Dodane napełniacze wpływają na mechanizm degradacji, a tym samym na stabilność termiczną iPP (najbardziej stabilne są próbki z dodatkiem nanorurek węglowych), a także na proces krystalizacji polipropylenu, a zatem i temperaturę krystalizacji oraz stopień krystaliczności.

Słowa kluczowe: kompozyty, polipropylen izotaktyczny, degradacja, stabilność termiczna.

Polymer materials have unique material characteristics ensuring their universality for a wide scope of applications. Due to their considerably low density, plastics are very light and the presence of appropriate chemical groups and polymer crosslinking make them resistant to concentrated acids and alkali, while high decomposition temperatures allow easy processing. However, polymers in their pure form are often not suitable for many applications and require special additives. To modify physical properties of the final product, additives or modifiers and auxiliary additives are added during processing. These chemical compounds are generally divided into two groups: physical properties modifiers and aging and degradation protectors [1]. Currently it should be assumed that „additives" are understood as compounds added in the amount not exceeding 5 wt % and not causing significant changes to mechanical properties, while „modifiers" are compounds added in much larger amounts, modifying mechanical properties [2]. This approach makes difficult classification of, e.g. carbon nanotubes or layered silicates into any of these groups. Frequently the added component has more than one function, e.g., dyes can also act as heterogeneous crys-

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tallization nuclei and protect against fading or, on contrary, facilitate discoloring [2]. Polymers are affected by oxygen and ozone already during conversion into specific items, and also during their use. That action of oxygen, together with other weather conditions, promotes formation of free radicals which finally, through the degradation process, cause changes in the molecular structure and polymer crosslinking. To prevent the oxygen diffusion process and forming of free radicals, polymer oxidation processes are inhibited using barrier components, i.e. antioxidants or layered silicates, extensively studied in recent years. In the case of aluminosilicates the degree of additive dispersion in the polymer matrix is of importance. The following types of layered silicate dispersion in the polymer matrix are distinguished: conventional dispersion of non-intercalated clay particles with the dry matrix, an intercalated form and an exfoliated structure [3]. The most desired situation is found in exfoliated nanocomposites, where individual silicate layers are at some distance from each other, depending on the aluminosilicate charge. This structural situation results in advantageous changes in material physical and chemical properties. The montmorillonite dispersion rate can be significantly improved using an additional component acting as a compatibilizer between the polymer and the nanofiller. Aluminosilicate-based nanocomposites ensure significant improvement in parameters, i.e., increase in fire resistance, as well as polymer thermal resistance and stability, gas permeability reduction and increase in biodegradability in the case of biodegradable polymers [4, 5], when compared to polymer without a nanoadditive or a standard micro- and macrocomposite. During their use, polymer materials are exposed to light, oxygen, heat and water. The listed factors cause aging changes due to photodegradation (when degradation is caused by UV rays), photooxydation (when secondary reactions with oxygen occur in the air) and thermooxidation (resulting from exposure to oxygen at an increased temperature) [6—10]. Each new product should undergo aging tests in appropriately designed conditions, identical or similar to conditions of its use. The polymer destroying processes can be accelerated by exposure to contaminants of all types (catalyst residues, contamination with some metals present in mineral fillers, harsh environment during use, etc.) [11]. Textile products during their use are usually exposed to light, which contributes to their degradation, causing the „fading" effect. That effect is related to change in products' color and shine. Light absorption can be limited or onset of the degradation process can be delayed by applying components absorbing and suppressing UV radiation or by introducing small dispersed molecules, i.e., carbon black or some pigments. Radiation absorbers convert harmful ultraviolet radiation into harmless infrared radiation. The most effective and commonly used absorber is carbon black. Its effectiveness depends mainly on molecules size and structure. The polymer stability before degradation may also be modified by adding a dye or a pigment. Although the mechanism of polymer stabilization by some pigments has been studied and is well known, the chromatic dyes action, mainly concerning protection against degradation, remains unclear. The pigment used in the conducted studies — copper phthalocyanine — can have two effects: it can stabilize polymers before their degradation, while in other conditions it can accelerate their decomposition [12].

EXPERIMENTAL PART

Materials

— Polypropylene Moplen HP500 J, *MFR* = 3.2 g/10 min (230 °C/2.16 kg), was supplied by Basell Orlen Polyolefins (Płock, Poland).

— Montmorillonite NanoBent® ZR2 is aluminosilicate modified with a quaternary ammonium salt having two short-chain and two long-chain alkyl substituents. NanoBent ZR2 produced in cooperation with ZGM „ZĘBIEC" SA and Rzeszow University of Technology. The average size of aluminosilicate particles is 20—60 μm (56 %) B 20 (44 %) and the interlayer distance is 2.0— 2.4 nm.

— The compatibilizer Fusabond P613 from the company Du Pont was used as a coupling agent in a composition with montmorillonite, ensuring good mixing with the base polypropylene. It is polypropylene modified with functionalized maleic anhydride (PP-*g*-MA).

— To introduce carbon nanotubes into the polypropylene matrix, Plasticyl PP2001 masterbatch from Nanocyl was used. It belongs to a unique family of thermoplastic carbon nanotube concentrates, mainly for applications requiring electrical conductivity or electrostatic discharge (ESD) protection. The carbon nanotubes content in the concentrate is 20 %. Due to its low viscosity and high liquidity, Plasticyl PP2001 is an excellent material for injection molding and extrusion processes, and its great advantage is easiness of introducing nanotubes into the polymer matrix. Plasticyl PP2001 nanotubes are multi-wall, and their parameters are listed in Table 1.

Table 1. Characterization of multi-wall carbon nanotubes in Plasticyl PP2001

Carbon nanotubes loading, %	Real density g/dm^3	Melting temperature, °C	Average diameter nm	Average length microns	Surface area m^2/g
20 ± 1	872	165	9.5	1.5	250—300

— The third additive was a pigment belonging to the organic pigment family: Heliogen Blue K7090 from BASF Chemical Company. It is copper phthalocyanine (β form), a special type porphiryn, consisting of four indole rings connected with azomethine bridges.

Specimens preparation

Aluminosilicate-containing polypropylene samples were prepared using the twin screw extruder (compounder Maris TM 58 MW/40 D). Weighted amounts of individual composite components were mixed to obtain 2 wt % additive content. Composites with MMT were prepared with two methods. In the first method, pure polypropylene was extruded with organophilized aluminosilicate, without a compatibilizer (iPP MMT1). The second method consisted of two stages. First, a compatibilizer was extruded with organophilized aluminosilicate, and then the prepared concentrate was extruded with polypropylene (iPP MMT2). The pigment was mixed with polymer granulate (iPP Blue) in the amount of 0.15 % of polymer weight. Samples containing multi-wall carbon nanotubes (iPP MWCNT) were prepared with a twin screw extruder in accordance with manufacturer's recommendation, to obtain 2 wt % carbon nanotubes share in the composite. Using the injection mold technique, the above granulates were used to make plates ~1 mm thick, with injection molding machines: Battenfeld Plus 35/75 UNILOG B2 and ENGEL ES 200/40 HLS with a water thermostat BOE-THERM BT Temp. 14.62 CP. Profiles for tests were prepared in accordance with the standard PN-EN ISO 1873-1, -2. The cylinder temperature during manufacturing of polypropylene samples was 210 °C, and the mold temperature was 25 °C. All composites were made in Zakłady Azotowe in Tarnów-Mościce.

Aging process conditions and parameters

Tested materials were subjected to accelerated aging in the Atlas Xsenon Weather Ometer, Ci4000 series, with a water-cooled xenon lamp as a radiation source. The automatic control of radiation intensity together with temperature and relative humidity control allowed full monitoring and control of the aging process. Sample aging was conducted in accordance with the standard SAE J 1960:2003-08 in the following conditions: temperature in the chamber 60 ± 1 °C; black standard temperature 82 °C, radiation intensity at 340 nm wavelength 0.55 W/m^2, relative humidity ~50 %. The sample aging time ranged from 26 to 65 days, absorbed radiation doses during exposition: pure iPP, iPP with nanotubes and the phthalocyanine pigment (1560 h): 3.089 MJ/m^2, PP with aluminosilicate without the compatibilizer (696 h): 1.378 MJ/m^2, PP with aluminosilicate with the compatibilizer (624 h): 1.235 MJ/m^2. Consequences of the tested material exposure to UV radiation and temperature, as well as the effect of additives alone were assessed on the basis of changes in material thermal properties, using DSC and TGA.

Methods of testing

The crystallization and melting temperature of tested samples were examined using differential scanning calorimeter (DSC), Q2000-TA Instruments, under N_2 atmosphere, the flow rate of nitrogen was 50 cm^3/min and the temperature of DSC was calibrated with indium. Mass of the specimen was about 12 mg, condition of tests were consistent with standard ISO 11357-3:2013-06E. The measurements were started at 0 °C, then samples were heated to 210 °C with the heating rate of 20 °C/min. This temperature was maintained for 5 min. The next step was cooling to 0 °C — cooling rate 20 °C/min (maintained in this temperature 5 min). After erase of thermal history, the second scan of heating was performed to 210 °C with the heating rate of 20 °C/min. Thermal stability of the composites was determined by thermal gravimetric analysis (TGA) on TA Instruments Q500-thermobalance. The flowing atmosphere was nitrogen at the flow rate 50 cm^3/min and the heating rate of 20 °C/min, the measurement was performed according to ISO 11358:2004P. The temperature range was 25—800 °C.

RESULTS AND DISCUSSION

DSC analysis

One of the most often used thermoanalytical methods for polymer material characterization is differential scanning calorimetry (DSC) allowing analysis of thermal effects and monitoring of various phenomena, including melting, crystallization, polymorphism, glass transition or specific heat. Thermal methods are used to determine some aspects of material aging in atmospheric or laboratory conditions or polymer degradation, however, they are conducted very rarely and the obtained results are used only as auxiliary data. Usually, combined techniques are used, e.g., TG-FT-IR for analyses of gases formed during the heating. This situation results from the fact that the thermal methods are affected by so many factors that they themselves can never provide quantitative data about the degradation process [8]. Scarce studies concern long-term polymer aging or its biodegradability, or thermal stability of polymers subjected to photo-oxidation [13, 14]. Composites containing various additives (pigment, montmorillonite or carbon nanotubes) were analyzed with DSC, determining the melting point, T_m, during the first and second heating cycle, as well as the crystallization point T_C. The studies aimed at determining the degradation effect of polymer materials containing various additives on the base line course in DSC thermograms and on the material crystallinity X_C (207 Jg^{-1} was used as melting enthalpy for 100 % crystalline iPP [15, 16]). Obtained results are shown in Table 2.

The data presented in the table show that no significant changes in the melting point (as in the standard ISO 11357-1:2009E, from the second heating cycle) were observed between the iPP sample without additives and samples with the pigment, montmorillonite or nanotubes, not subjected to the aging process in Weather-Ometer. The composite crystallinity also did not change significantly with the lowest value for pure iPP sample and the sample containing montmorillonite with the compatibilizer and the highest value for samples dyed with the phthalocyanine pigment and containing montmorillonite without the compatibilizer. The crystallization tempera-

Table 2. Degree of crystallinity X_C, melting temperature from I-st and II-nd cycle of heating T_m I, T_m II, crystallization temperature T_C, of composities before and after aging in Weather-Ometer

Composition	T_m I, °C	T_C, °C	T_m II, °C	X_C, %
Before aging				
iPP	163	113	161	50
iPP Blue	165	127	163	53
iPP MMT1	168	116	164	53
iPP MMT2	164	115	163	50
iPP MWCNT	162	124	162	51
After aging				
iPP	151	107	143	45
iPP Blue	151	116/121	144/153	47
iPP MMT1	149	108	140.2	45
iPP MMT2	150	110	143	45
iPP MWCNT	165	122	165	46

ture observed for iPP was 113 °C and it was 14 °C lower than for the sample with the phthalocyanine pigment, which was also observed in previous studies by J. Broda [17]. The similar increase in the crystallization temperature was observed for samples containing multiwall carbon nanotubes (T_C increase by 11 °C versus pure iPP). Results obtained after aging of composites proved to be more interesting. Practically all composites degraded, which was reflected in the lowered, already low, base line temperatures, proving the onset of melting of the low molecule degradation products. Melting temperature for all composites, except samples with carbon nanotubes, were decreased by ca. 20 °C. In the samples containing the pigment (see Fig. 2) two crystallization and melting peaks were visible, which may suggest forming of the less stable β form or melting of less stable crystallites formed during the exposure of dyed iPP to the set conditions. The aging process resulted in the reduction of samples crystallinity — the highest in the samples with mont-

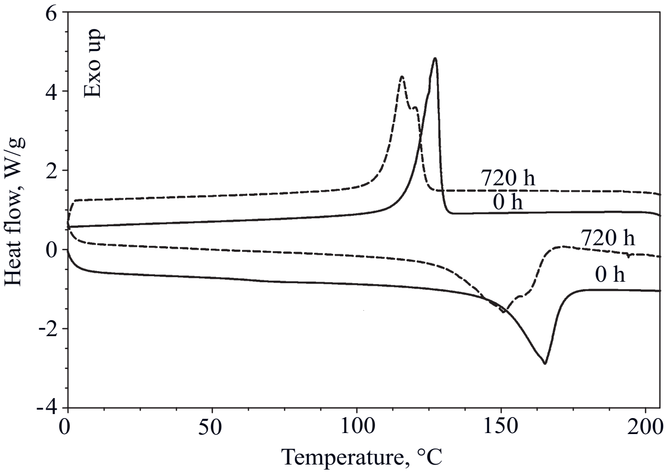

Fig. 2. iPP composite with phthalocyanine pigment before and after aging, at the first scan of heating and crystallization

morillonite without the compatibilizer. The highest post-aging crystallinity was observed in samples dyed with the phthalocyanine pigment, however, in total, the composites containing carbon nanotubes were characterized by the weakest aging effect on the thermal properties of the studied samples, both during crystallization and melting of the crystalline phase. DSC curves for iPP with various additives, before and after aging process in the first heating cycle are shown in Fig. 1—5. After the materials were exposed to UV radiation, material crystallisation points decreased. Pure iPP crystallized at the lower temperature than composites with additives, while iPP containing the pigment or carbon nanotubes crystallized at the higher temperature than pure iPP and composite with MMT. Worth noting is the effect visible in DSC curves registered for plastics subjected to the aging process. That effect appears at the temperature above endothermic melting peak, as a characteristic sloping of the calorimetric signal line. A possible explanation is a

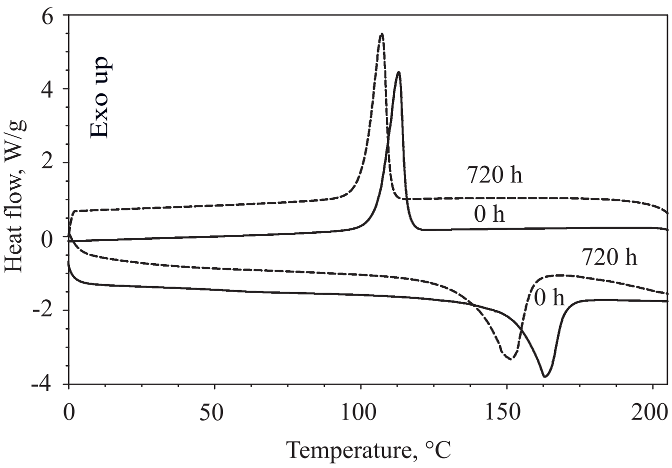

Fig. 1. Pure iPP before and after aging, at a first scan of heating and crystallization

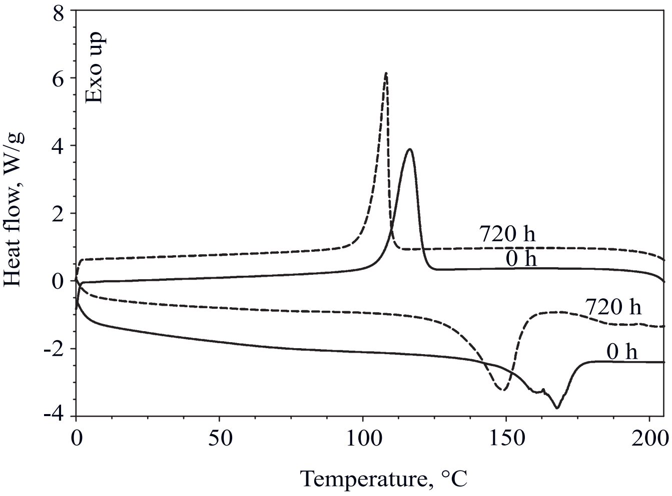

Fig. 3. iPP with aluminosilicate without compatibilizer before and after aging, at the first scan of heating and crystallization

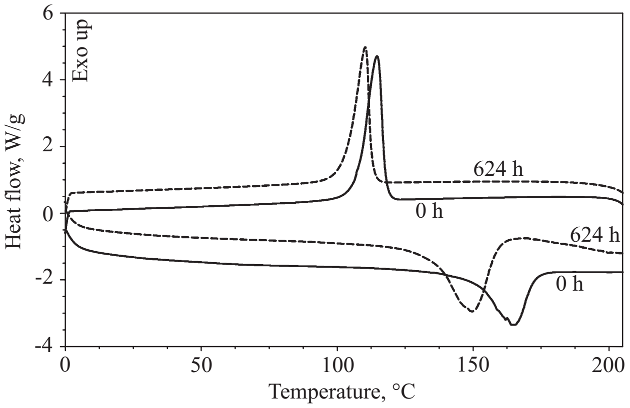

Fig. 4. iPP with aluminosilicate with compatibilizer before and after aging, at the first scan of heating and crystallization

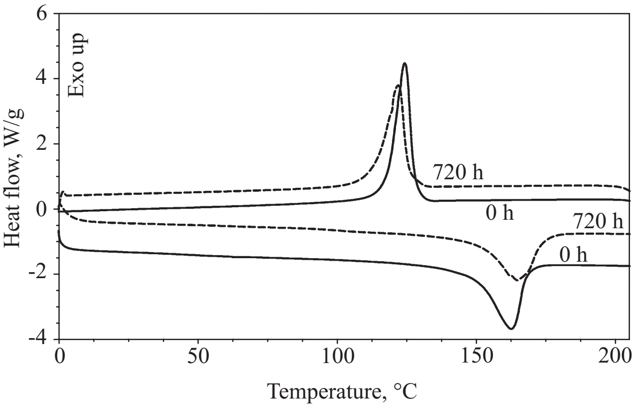

Fig. 5. iPP with multi-wall carbon nanotubes before and after aging, at the first scan of heating and crystallization

change in the character of the relationship between the aged samples specific heat and the temperature. That change is visible as the increase in dynamics of specific heat capacity as the function of temperature due to structural changes — polymer chains shortening in the aged plastic, with the linear character of C_p of T changes maintained. For plastic samples not subjected to the aging process the above effect does not occur.

Thermogravimetry (TGA)

Thermogravimetric measurements in polymer degradation studies mainly provide information on the thermal stability, composition, thermal decomposition process and its products. The polymer thermal stability is affected by factors including: presence of small molecule substances, crosslinking, presence of aromatic rings and decomposing functional groups. Polymers of both natural and synthetic origin decompose thermally at higher temperatures and when heated to high temperatures chemical bonds in their main and side chains are broken, low molecule gas products are emitted and often intramolecular cyclization and elimination reactions occur, while in the case of linear polymers depolymerization may take place. Due to this situation, the basic requirement for polymer materials is the specified thermal stability during their processing and use. The obtained thermogravimetric test results the temperature at the conversion start and end, the temperature, at which composite decomposition was the fastest, as well as the temperature at which 50 % of the material decomposed are provided in Table 3. Measurements were conducted both for samples not subjected to aging, as well as those exposed to the set conditions. Curves illustrating percentage weight reduction as the temperature function are showed in Fig. 6 and 7, for samples before and after aging, respectively.

Table 3. TG data for iPP and iPP composites before and after aging in Weather-Ometer: temperature at the maximum speed of decomposition T_{max}, temperature of the beginning T_{onset} and end T_{offset}, temperature at 50 % mass loss T_{50}

Composition	T_{max}, °C	T_{onset}, °C	T_{offset}, °C	T_{50}, °C
Before aging				
iPP	468	447	480	463
iPP Blue	471	450	484	467
iPP MMT1	458	449	462	455
iPP MMT2	456	449	460	454
iPP MWCNT	476	457	487	472
After aging				
iPP	455	408	464	439
iPP Blue	466	439	479	458
iPP MMT1	449	433	454	442
iPP MMT2	450	391	462	431
iPP MWCNT	473	454	482	468

The effect observed at TG curves concerns thermal stability of composites. The sample containing carbon nanotubes (curve „e" on Fig. 7) was characterized by the temperature of start of thermal decomposition higher that the rest of discussed materials. Generally, it can also be seen that aged materials decompose at much lower temperatures than samples before the aging process (except samples with carbon nanotubes). The iPP thermal

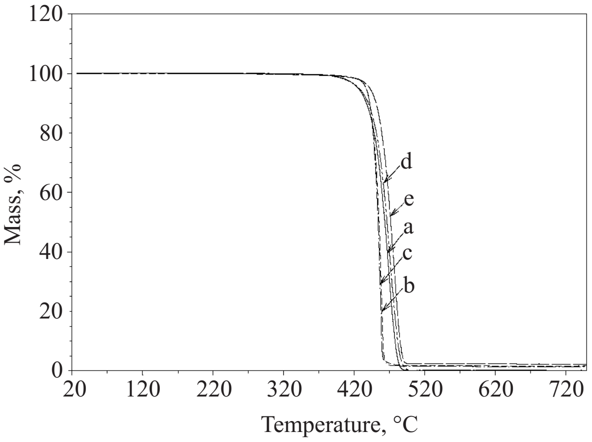

Fig. 6. TG curves of iPP with different additives: a) iPP, b) iPP MMT1, c) iPP MMT2, d) iPP Blue, e) iPP MWCNT before aging

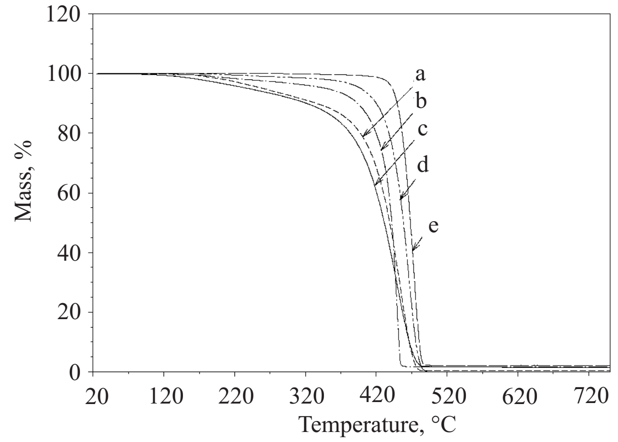

Fig. 7. TG curves of iPP with different additives: a) iPP, b) iPP MMT1, c) iPP MMT2, d) iPP Blue, e) iPP MWCNT after aging

stability was most unfavorably affected by addition of montmorillonite, and that was confirmed by thermal tests on samples before and after aging. The unaged samples subjected to thermogravimetric analysis are characterized by one-step decomposition, starting at similar temperature for all samples. That situation changed in the case of aged samples of pure iPP and with montmorillonite added. In these samples two very weakly separated decomposition stages were observed (in the case of iPP, at the first stage 10 % of polymer decomposes, for iPP with montmorillonite, with/without compatibilizer, the percentage weight reduction was 8 % and 4 %, respectively). In other aged samples decomposition was typical.

CONCLUSIONS

Conducted tests aimed at studying the effect of various additives on the iPP aging process and possibilities to verify its degradation with DSC and TG thermal methods.

The results show that the thermal analysis can be used as an important supplement in studies on effects of the aging factors on polymer materials. The paper presents changes in the melting temperature, crystallization temperature, start and end point of decomposition, as well as in crystallinity, depending on the plastic additive used and its effect on the degradation process. Results obtained in the DSC curves for unaged samples show that there are no significant changes in the melting point of the obtained composites, versus pure iPP. The crystallization temperature observed for iPP with phthalocyanine pigment and multiwall carbon nanotubes added is 10—12 °C higher than for pure iPP. The radical changes in thermal properties occurred in the aged samples, resulting in the composite melting temperature lower by ca. 20 °C for all samples except those with MWNT. Similarly, the T_C of pure iPP decreased, and T_C of iPP with MWCNT remained practically unchanged; in the thermograms of aged samples also a lowering of the basic line was noted and the samples crystallinity decreased. All above data show that aging was accompanied by material degradation together with forming of small molecule products, which melting begins earlier than melting of pure iPP. The data from thermogravimetric analysis showed that the samples with MWCNT had the best thermal stability, both before and after aging, while it was the worst for composites with montmorillonite. On the basis of the research it can be said that the best polypropylene additive, in terms of resistance to aging reflected in thermal properties is MWCNT, and the worst used is montmorillonite. The phthalocyanine pigment moderately increased the thermal stability and caused increase in the crystallization point of the base material.

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