Adam HAŁAT[1*], Renata KĘDZIOR[1],
Dawid GRZESIAK[1] and Józef GŁOWIŃSKI[1]

THERMAL STABILITY OF POLYPROPYLENE COMPOSITE REINFORCED WITH GLASS FIBRE IN THE OXIDISING ATMOSPHERE

STABILNOŚĆ TERMICZNA KOMPOZYTU POLIPROPYLENOWEGO WZMACNIANEGO WŁÓKNEM SZKLANYM W ATMOSFERZE UTLENIAJĄCEJ

Abstract: Stability of the polypropylene composite with fiber glass (45/55) in the form of low density mat was tested experimentally at increased temperature. It was examined by analyzing the influence of the atmosphere with various oxygen content on the decomposition rate of the polypropylene composite. It has been found that in the air atmosphere, the initial decomposition temperature is close to 200 $^{\circ}$C. Lowering the oxygen concentration in the atmosphere to 2 % results in increase of composite decomposition temperature to almost 240 $^{\circ}$C. Decomposition components were identified in the methylene chloride extract from composite and in the condensed reaction products. Rate of decomposition conversion at initial stage below 0.2 was estimated as a system of equations: zero order path $r = k_1$ for polypropylene degradation and first order path $r = k_2[O_2]$ for oxidative decomposition. A brief safety analysis is performed identifying the possibility of exceeding an explosion limit under certain conditions. The best way of mitigating the fire/explosion hazard is lowering the oxygen content below 2 % vol., especially for processing of recycled polypropylene.

Keywords: polymer composites, polypropylene composite, thermal stability, thermal decomposition, thermal-oxidising degradation, temperature of degradation

Introduction

Polypropylene is mainly used at the temperature below 100 $^{\circ}$C however its processing takes place at increased temperature. In this operation, temperature exceeding 200 $^{\circ}$C should be avoided as it triggers a slow process of slow polymer decomposition. It is noted that already at the temperature near 300 $^{\circ}$C quite rapid pyrolysis of polymer material occurs and volatile products are created, most of them

---

[1] Faculty of Chemistry, Wroclaw University of Technology, Wybrzeże Wyspianskiego 27, 50–370 Wrocław, Poland, phone: +48 71 320 38 65; fax: +48 71 328 04 25

* Corresponding author: adam.halat@pwr.wroc.pl

combustible. Oxygen has a large influence on the rate and mechanism of the polymer decomposition. The mixture of evolved flammable components with oxygen may be ignited, releasing energy that drives further pyrolysis, hence fire or explosion hazard appears. Decomposition and ignition of the polymer depends mainly on the form of material, for *eg* porous material are ignited easier and with smaller ignition energy.

The common feature of the majority of organic compounds is their little thermal stability. At increased temperature, they have tendency to decompose and small fragments may easily create gas phase. Additionally, nearly all organic compounds that contain C-H bond are subject to reaction with oxygen: slow – with atmospheric oxygen at ambient temperatures (degradation), faster – in the conditions of increased temperature or/and enhanced oxygen concentration (decomposition). The first stage of this autooxidation process is the formation of hydroperoxides, extremely reactive compounds that may start undesirable behaviour of organic substances, including in-depth decomposition or burning initiation [1, 2]. Similar oxidation paths occur also in the gaseous phase [3]. The complexity of this phenomenon is illustrated by huge spectrum of the oxidation products and spatial heterogeneity of the reaction, already at relatively low temperatures of 80–150 ^{o}C [4–6].

Material's susceptibility to ignition and burning is determined by oxygen index [7]. The higher oxygen index value the less flammable material: below 21 – is flammable, above 28 – non-flammable. Raw polypropylene usually has an oxygen index value varying between 17–29. The polypropylene examined in this study was reinforced by glass fibre filling and, most likely, its index was not modified.

Thermogravimetric analysis of non-stabilised powdered polypropylene heated at different rates in the argon atmosphere points that with increasing of the heating rate, the temperature of the beginning of decomposition shifts towards higher temperature [8]. This shift is caused by the shortening of reaction time at a given temperature and is clearly visible on all publicated thermogravimetric curves. Change of atmosphere from argon to air results in considerably lower degradation temperature, getting close to 235 ^{o}C [8].

A similar value is indicated in the study [9] where, the behaviour of polypropylene and the polypropylene composite with hemp fiber was tested in the air, with the heating rate of 10 K/min. It has been observed that the composite containing 30 % of hemp fiber is more thermally stable than the examined fibres, as well as the pure polypropylene. The temperature at the start of decomposition was nearly the same for all materials tested but the temperature of the highest rate of decomposition was 338 ^{o}C for polypropylene and 360–380 ^{o}C for the composite. Such surprising behaviour is intriguing and requires further understanding in order to specify safe processing conditions for composite materials [9].

An effect of injection temperature (170, 210 and 250 ^{o}C) as well as fibre content (20 and 30 % by mass) in the polypropylene composite with fiber glass was examined [10]. The thermal stability was also tested by heating samples in the nitrogen atmosphere. It has been stated that thermogravimetric curves of pure polypropylene previously processed at various temperatures and curves of the composites, overlapped up to the starting temperature of the decomposition close to 250 ^{o}C. Behaviour of the

samples tested at a higher temperature indicated marginal changes of their thermal stability and the composite was slightly more stable as compared with plain polymer.

The main aim of this paper was to propose a reaction model to describe the initial stage of polypropylene composite decomposition, useful to hazard analyses. In order to obtain a set of kinetic parameters for decomposition process, a range of thermogravimetric runs were performed. In addition, some decomposition products has been examined employing GC-MS.

Methodology of measurements

Composite material on the warp of recycled polypropylene (PP) contained ca. 55 % of mass. of glass fiber (GF). The analyzed samples relate to the material in the form of mats, used after the thermal treatment to design and soundproofing car interior. According to the literature information the composite reinforced with glass fiber (30 % of fibre) has similar temperature of melting to the temperature of pure polypropylene [2].

The samples of composite PP/GF (45/55) ca. 50 mg in the form of small chips were heated from the room temperature at the rate of 5 K/min in calorimeter NETZSCH STA 409C. Oxygen-free atmosphere (argon), mixtures of nitrogen with oxygen (with the oxygen content of 21, 11, 8 and 2 % vol.), as well as mixtures of nitrogen with carbon dioxide and oxygen (10 % vol. CO_2 and 2 % vol. O_2) were applied. TG and DTA measurements were conducted with the flow of gas approximately 50 cm^3 per minute

Subject to tests was also residue from the composite degradation collected from the industrial processing oven in which the composite was heated in the air, up to the temperature of 215 ^{o}C in 35 s of heating cycle, at no air exchange. The condensate has undergone GC-MS analysis and the same analysis was carried out for the methylene chloride extract obtained from the composite. The solvent extraction was made in the Soxhlet apparatus for the composite sample with dimensions 20 × 70 mm with 100 cm^3 of solvent for 24 hrs. Following this, the solvent was evaporated and residue was diluted with methylene chloride to the concentration of ca. 0.1 % of mass. similarly as the condensate sample.

The GC-MS analysis was done on Hewlett-Packard apparatus (gas chromatograph HP 6890 coupled with mass spectrometer MSD 5973) equipped with capillary column HP5MS.

Test results

TG/DTA analysis

During composite heating in the argon atmosphere an endothermic effect of transformation associated with polymer melting was observed at the temperature of 160 ^{o}C on the DTA curve (Fig. 1), similarly as in raw polypropylene [8]. At higher temperatures distinguished changes suggesting degradation of polymer were observed.

At the temperature of 200 ^{o}C the composite still did not show the signs of degradation. It is evident that very slow mass sample loss begins to be visible no sooner
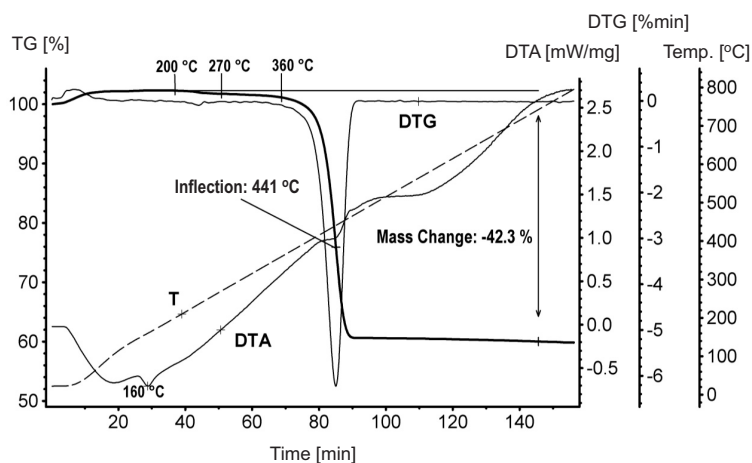
Fig. 1. TG, DTG and DTA curves of PP/GF (45/55) composite under argon atmosphere at 5 K/min

than at the temperature of 260–270 $^{\circ}$C. Significant acceleration of mass loss took place at temperature of ca. 360 $^{\circ}$C. At the temperature of ca. 440 $^{\circ}$C rapid degradation of polymer occured. The total loss of sample mass was ca. 42 % by mass.

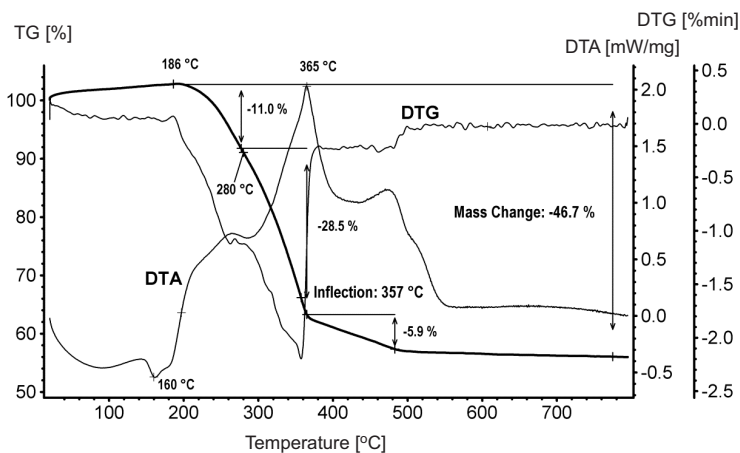   The composite behaviour in the presence of oxygen in the gas flowing around the sample was different.

Fig. 2. TG, DTG and DTA curves of PP/GF (45/55) composite under air atmosphere

    The following was observed for samples in air (Fig. 2):

    – endothermic effect at the temperature of ca. 160 $^{\circ}$C associated with the material melting,

    – above 186 $^{\circ}$C significant acceleration of mass loss occurs; at the temperature of ca. 280 $^{\circ}$C it is already close to 11 %,

– maximum rate of decomposition is achieved at the temperature of 357 ^{o}C,
– very clear exothermic effect at temperature of ca. 365 ^{o}C associated with the material incineration,
– at temperature of ca. 410 ^{o}C weight loss is ca. 42 %,
– total weight loss is ca. 46 %, what corresponds to the total content of polymer mass in the composite.

An effect of different content of oxygen in nitrogen was investigated. Figure 3 presents the weight loss of the composite samples.
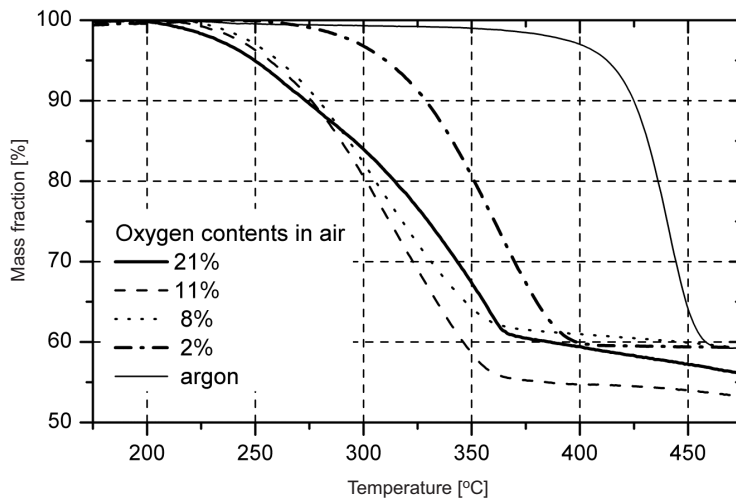

Fig. 3. TG, DTG and DTA curves of PP/GF (45/55) composite under air atmosphere

There is a clear dependence of the content of oxygen on the temperature of initiation of degradation; increase of oxygen content reduces the temperature. Differences in temperature values are small in the atmospheres containing sufficient amount of oxygen (over 10 %). Significant increase in temperature became evident at reduction of the content of oxygen below 2 % of vol. The following temperatures of thermal degradations can be: about 200 ^{o}C in the air, 240–250 ^{o}C at 2 % of O_2 in N_2 and CO_2, and 260–270 ^{o}C in pure argon.

Impact of carbon dioxide on decomposition of polymer is presented in Fig. 4 depicting the of weight loss curve of the composite heated in atmosphere of mixture of nitrogen-carbon dioxide and oxygen.

An attempt has been made to describe the observed changes of the composite mass during heating for small conversion of organic below 0.2. It has been assumed that the purely thermal decomposition can be described with the zero order reaction rate equation $r_1 = k_1$ and influence of oxygen follows first order path $r_2 = k_2[O_2]$. Concentration of oxygen refers to the oxygen concentration in the atmosphere surrounding the composite and $r = r_1 + r_2$ is an overall rate of mass change of
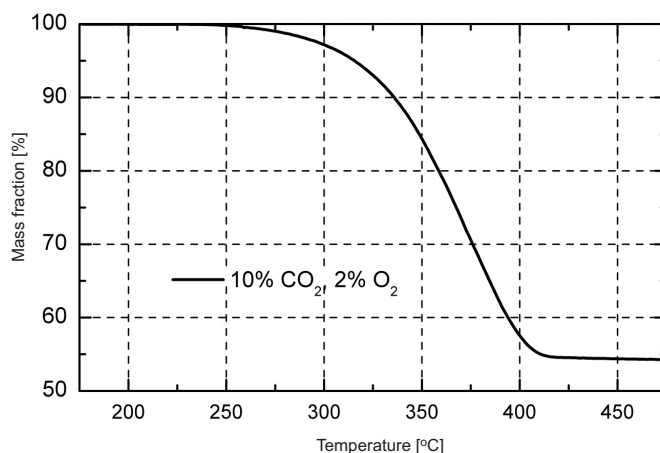
Fig. 4. Thermogravimetric profiles of PP/GF (45/55) in the atmosphere nitrogen – carbon dioxide – oxygen

polypropylene in composite. Coefficients of proportionality k_1 and k_2 have the following dimensions: k_1 [g of polypropylene in composite/s]; k_2 [g of polypropylene in composite/mole fraction of oxygen/s]. It has been assumed that they depend on the temperature and meet the Arrhenius equation: $k = A \exp(-E/(RT))$. Experimental results were used for evaluation of the A and E parameters

$$k_1 = 1.50 \ 10^{12} \exp(-204\ 000/(8.314/T)) \tag{1}$$

$$k_2 = 2.74 \ 10^{6} \exp(-92\ 000/(8.314/T)) \tag{2}$$

The resulting activation energies are similar to the value obtained for thermal decomposition of polypropylene in the works [5, 8, 11] and is lower than the activation energy given in the work [12]. Figure 5 presents reactivity of the composite considering the derived relations. A simple dependence used reproduces the results of the experiments reasonably well.

Obtained dependence forms the basis for risk analysis during the thermal or thermal-oxidative composite processing. The estimated increase per every hour in the concentration of the reaction products in the oven of volume of 10 m³, which processes in the air the composite with content of 100 kg/h of pure polypropylene, is close to 0.44 % vol. at a temperature of 200 °C, assuming the average molecular weight of 60 g/mol. For temperature 220 °C it is almost 1.13 % vol. and for 240 °C it comes to 2.72 % vol. Such quantity of volatile substances makes it possible to achieve a lower explosion limit (approx. 2 % vol.), especially when periodic overheating of handled material is possible, *eg* in the emergency state of the device. Therefore, thermal processing of the composite material must take place in an environment of reduced oxygen content or oxygen-free atmosphere.

In order to obtain better understanding of stable decomposition products several analytical methods were applied.
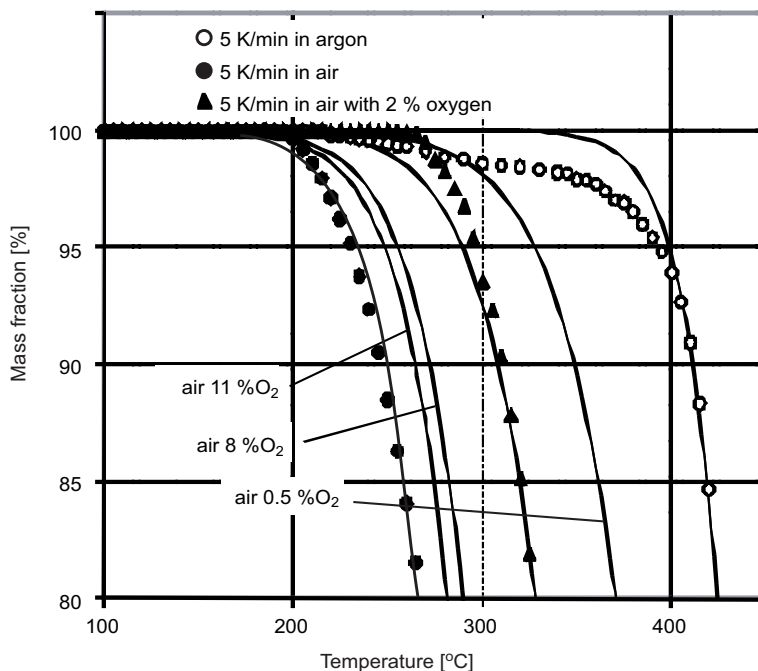
Fig. 5. Calculated and experimental mass change of the polypropylene composite in various atmospheres

GC-MS analysis

In the extract sample, saturated chain hydrocarbons with a wide range of molecular masses were observed. The majority constitute hydrocarbons with the number of carbon atoms from 15 to 24. There are also hydrocarbons C12–C14 as well as hydrocarbons with the number of carbon atoms higher than 25 (Fig. 6).

In the condensate distillation, it was diagnosed that this is a mixture of compounds with high boiling temperature above 325 $^{\circ}$C and the temperature of ignition 228 $^{\circ}$C (open crucible method). This mixture was subjected to analysis to compare with the results obtained during the extract analysis and standard (hexadecane, docosane, octacosane).

The following was established (Fig. 6):

– presence of saturated chain hydrocarbons,

– as opposed to the result with the composite extract, there were not observed hydrocarbons with molecular masses lower than C17 were observed,

– hydrocarbons with boiling temperature above 350 $^{\circ}$C dominated.

The results suggest that the condensate is already free of substances with relatively low boiling point or higher partial vapour pressure. The remaining substances undergo subsequent oxidation yielding small compounds in the gaseous phase.
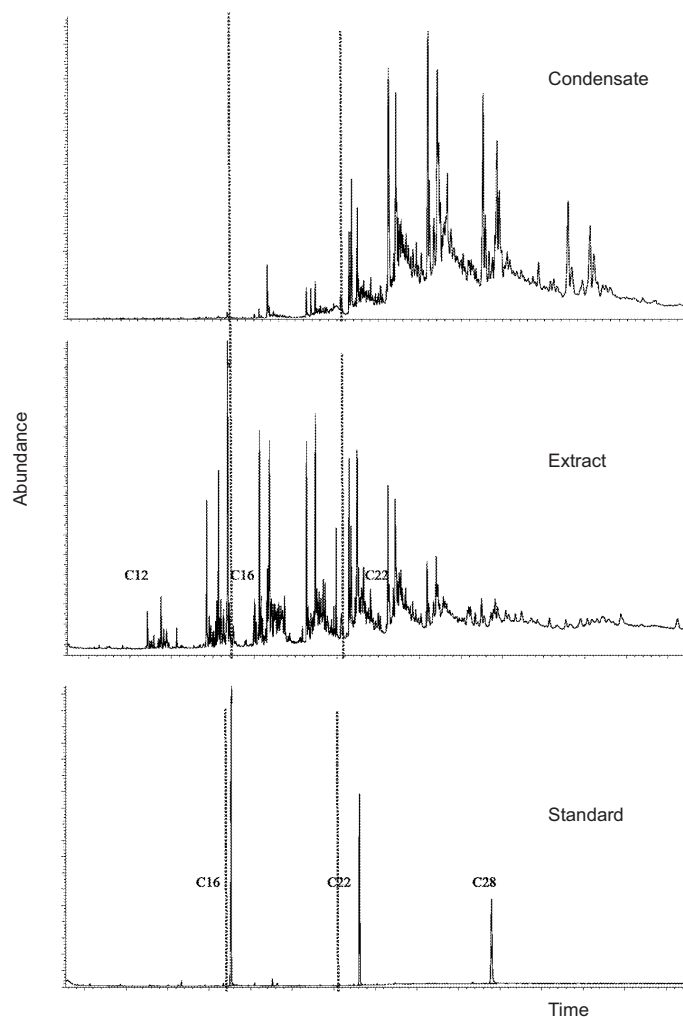
Fig. 6. Chromatograms of the condensate and the composite extract of the polypropylene mat degradation

Summary of results and conclusions

Polyolefines are thermally less stable than their relevant monomers. In the neutral atmosphere, the networking breakdown of the polypropylene commences at the temperature of approximately 160 ^{o}C, while decomposition resulting in mass reduction, at the temperature of 260–270 ^{o}C. In the examined composite, both C-C bonds and C-H bonds are relatively easily subject to break since every second carbon atom is a quaternary atom. The mechanism of destruction includes cracking of C-C bonds in random places of the chain, leading to disintegration of macromolecules into fragments

of different lengths [7]. It is fully confirmed by the results of GC-MS analyse; in the composite extract hydrocarbons from C12 to C26 were found. In the condensate, the mixture of hydrocarbons is already deprived of C12–C22 hydrocarbons.

The oxygen contained in the gas flowing round the composite has an adverse effect on the durability of the examined composite. It enhances destruction of organic substances of the composite, it oxidizes them and at the same time is a key component of the produced post-decomposition flammable mix creating fire/explosive hazard.

Reduction of oxygen concentration in the atmosphere increases the initial degradation temperature. In the air atmosphere this temperature is ca. 200 ^{o}C. Reduction in the content of oxygen in the atmosphere to ca. 2 % causes the shift of degradation temperature to ca. 240 ^{o}C.

The obtained thermal stability dependencies constitute the basis for safety analysis (thermal stability) of the composite after thermal or thermal-oxidizing treatment in a plant. The data can be further applied for calculation of weight loss for a given industrial process, for the formation of flammable atmospheres in order to define minimum ventilation requirements to avoid accumulation of explosive atmosphere.

A simple correlation was suggested to describe the observed mass changes of the composite during heating in an atmosphere of varying oxygen content. The overall rate of mass change is the sum of polypropylene thermal degradation rate with a constant k_1 and the rate associated with the presence of oxygen (constant k_2). Temperature dependences of both constants were determined. Developed correlations fairly well reproduce the results of the experiments.

Knowledge of the decomposition curves in various atmospheres and at various heating rates enables not only qualitative but also quantitative determination of the safety critical process parameters for the plant, like product throughput, maximal allowed heating rate, residence time, minimal addition of inert gas.

Acknowledgements

References

[1] McMurry JE. Organic Chemistry 8th Edition. Cengage Learning; 2011.

[2] Sobczak R, Nitkiewicz Z, Koszkul J. J Composites. 2002;3(8):343-349.

[3] Pekalski A, Zevenbergen J, Pasman H, Lemkowitz S, Dahoe A., Scarlett B. J Hazard Mater. 2002;93(1):93-105, DOI: 10.1016/S0304-3894(02)00041-9.

[4] Verdu S, Verdu J. Macromolecules. 1997;30:2262-2267, DOI:10.1021/ma960627v.

[5] Achimsky L, Audouin L, Verdu J. Polym Degrad Stabil. 1997;57:231-240, DOI: 10.1016/S0141-3910(96)00167-X.

[6] Rychly J, Matisova-Rychla L, Csmorova K, Achimsky L, Audouin L, Tcharkhtchi A, Verdu J. Polym Degrad Stabil. 1997;58:269-274, DOI: 10.1016/S0141-3910(97)00057-8.

[7] Janowska G, Przygocki W, Włochowicz A. Flammability of polymer and polymer materials. Warszawa: Scientific and Technical Publishing House; 2007.

[8] Chan J, Balke S. Polym Degrad Stabil. 1997;57:135-149, DOI: 10.1016/S0141-3910(96)00160-7.

 [9] Pengfei N, Baoying L, Xiaoming W, Xiaojun W, Jie Y. J Reinf Plast Comp. 2011;30(1):36-44.
     DOI: 10.1177/0731684410383067.
[10] Ota WN, Amico SC, Satyanarayana KG. Compos Sci. 2005;65:873-881,
     DOI: 10.1016/j.compscitech.2004.10.025.
[11] Chrissafis K, Paraskevopoulos K, Stavrev S, Docoslis A, Vassiliou A, Bikiaris D. Thermochim Acta.
     2007;465:6-17, DOI: 10.1016/j.tca.2007.08.007.
[12] Zhiming G, Tsuyoshi K, Iwao A, Masahiro N. Polym Degrad Stabil. 2003;80:269-274,
     DOI: 10.1016/S0141-3910(02)00407-X.

STABILNOŚĆ TERMICZNA POLIPROPYLENU WZMACNIANEGO WŁÓKNEM SZKLANYM W ATMOSFERZE UTLENIAJĄCEJ

Wydział Chemiczny, Politechnika Wrocławska

Abstrakt: Sprawdzano doświadczalnie wrażliwość kompozytu polipropylenu, w postaci maty o niskiej gęstości upakowania, na działanie podwyższonej temperatury. Wrażliwość oceniano, analizując wpływ atmosfery o różnej zawartości tlenu na temperaturę początku rozkładu kompozytu polipropylenu z włóknem szklanym o składzie zbliżonym do 45/55. Stwierdzono, że w atmosferze powietrza, początkowa temperatura rozkładu wynosi ok. 200 $^{\circ}$C. Obniżenie stężenia tlenu w atmosferze do ok. 2 % powoduje wzrost temperatury rozkładu kompozytu do ok. 240 $^{\circ}$C. Produkty rozkładu zidentyfikowano w kondensacie oraz ekstrakcie kompozytu w chlorku metylenu.

Słowa kluczowe: kompozyt polipropylenowy, stabilność termiczna, rozkład termiczno-oksydacyjny, temperatura rozkładu