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DSC investigations of the surface layer of an aged polypropylene/wood composite

RAPID COMMUNICATION

Summary — DSC investigations of composite material taken from the surface of the molded pieces formed with the injection molding method have been carried out in order to evaluate changes caused by ageing processes. Composites were prepared from polypropylene (PP) filled with wood flour in the amount of 50 wt. %. Moldings were aged for four years in atmospheric conditions or laboratory conditions under UV radiation for 100, 200 and 300 hours, respectively. Essential ageing changes have been noticed on the surface of the samples exposed to the atmospheric conditions on the basis of DSC curves recorded during the second heating. PP crystallites are much less organized and melt in temperature lower by over 25 °C than PP crystallites in the non-aged composite. On the other hand, the crystallites considerably different in terms of organization degree and melting temperature may occur side by side in composite aged with UV irradiation. There have been observed on the DSC endothermic curves of such samples even up to three melting areas of crystallites differing in macromolecules organization.
Keywords: polypropylene, wood flour, composite, natural ageing, accelerated ageing.

BADANIA DSC WARSTW POWIERZCHNIOWYCH STARZONEGO KOMPOZYTU POLIPROPYLEN/DREWNO

Streszczenie — W celu oceny zmian zachodzących na skutek procesów starzenia w polipropylenie (PP) napełnionym w 50 % mas. mączką drzewną przeprowadzono badania DSC materiału pobranego z powierzchni kształtek formowanych metodą wtrysku. Kształtki wykonane z kompozytu polipropylen/drewno starzono w warunkach naturalnych przez cztery lata lub w warunkach laboratoryjnych pod wpływem promieniowania UV odpowiednio przez 100, 200 i 300 h. Na podstawie przebiegu krzywych topnienia DSC zarejestrowanych podczas drugiego ogrzewania próbek zaobserwowano wyraźne zmiany starzeniowe, które zaszły na powierzchni kształtek wystawionych na działanie czynników atmosferycznych. Krystality polipropylenowe wykazywały znacznie mniejszy stopień uporządkowania i topiły się w temperaturze niższej o 25 °C niż krystality w osnowie kompozytu nie poddanego procesowi starzenia. Starzenie kompozytu w warunkach przyspieszonych tj. pod wpływem promieniowania UV powodowało utworzenie struktur krystalicznych w wyraźny sposób różniących się stopniem uporządkowania i temperaturą topnienia. Na krzywych DSC takich próbek można było zaobserwować nawet trzy obszary topnienia krystalitów różniących się uporządkowaniem makrocząsteczek.
Słowa kluczowe: polipropylen, mączka drzewna, kompozyt, starzenie naturalne, starzenie przyspieszone.

In recent years an increasing interest in polymer/wood composites as construction materials has been observed. This group includes the composites which have polypropylene (PP) as polymer matrix [1]. PP filled with wood flour has usually much better utility properties than wood, especially when exploited in atmospheric conditions for a long time. Such factors as light (UV radiation), humidity presence, temperature changes, chemical substances present in the atmosphere as well as microorganisms have major impact on ageing processes

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of these polymer materials in natural conditions [2]. It is difficult to determine which of them has decisive influence on the pace of weathering processes since all of these factors act simultaneously. In the research of accelerated ageing in laboratory conditions one should take into account such factors as UV radiation, temperature and humidity. Photo-oxidation plays a special role in weathering of PP stimulating creation of new functional groups, reactions of radicals and macroradicals recombination as well as decrease of polymer molecular weight [3]. The changes in the structure of PP chains worsen ability of the polymer to crystallize [4].

Similar processes occur in PP during ageing of PP/wood flour composites [5]. The structure of macromolecules becomes less regular. Crystallites formed as a result of melting and successive cooling will be less ordered. The effects of these changes should be visible on DSC curves.

The aim of this work were calorimetric investigations of an aged PP/wood composite in order to evaluate the changes occurring in the material caused by atmospheric conditions or UV irradiation.

EXPERIMENTAL

Materials

The polypropylene (PP, trade name, Moplen HP548R, Basell Orlen Polyolefins) have been used in these investigations. It is a homopolymer containing nucleating and antistatic agents, intended for processing with the injection molding method.

Wood flour Lignocel S 150tr (J. Rettenmaier & Söhne GmbH) has been used as a filler in the amount of 50 wt. %.

Preparation of composites

Polymer/wood composites have been obtained by mixing of PP granulate with dried wood flour and in the next stage by extrusion (temperatures of extruder areas: I — 90 °C, II — 160 °C, III — 180 °C, head — 175 °C). The material prepared in such a way has been ground and injected into double mould form at temperature of 20 °C. Temperature of cylinder heating areas were: I — 160 °C, II — 180 °C, nozzle — 180 °C. The times of injection stages were as follows: injection time 3.5 s, time of pressure holding 3.5 s, cooling time 1 min 40 s. Then normalized molded pieces with cross section 10 mm × 10 mm have been formed.

Methods of testing

Some of the prepared samples have been aged in atmospheric conditions while the rest of them have been aged in an accelerated way under irradiation with a xenon lamp. Moldings intended for ageing in natural conditions have been placed in open space facing south at the inclination angle 45° (according to standard PN-EN ISO 877:2001) for four years. Molded pieces aged in the accelerated way have been irradiated with a xenon lamp of power 450 W. The radiation source was placed at the distance of 20 cm from molded pieces. The first part of them were exposed to irradiation for 100 h, the second part for 200 h and third part for 300 h.

The dust of the composite aged in natural conditions, not attached to the moldings surface as well as the surface layer taken from the moldings with a scalpel to the depth of about 0.05 mm or 0.1 mm has been the object of investigation.

Thermal analysis of PP and its composite with wood flour has been performed using differential scanning calorimeter Netzsch DSC 204 F1 Phoenix. Samples 4—6 mg in weight were heated up to temperature of 220 °C in aluminum crucibles. This temperature was maintained for 5 min in order to erase the previous thermal history of polymer. Then samples were cooled down to 25 °C and heated again. Measurements have been carried out in the nitrogen atmosphere with heating and cooling rate V_h = V_c = 10 °C/min. DSC melting curves presented in this paper have been obtained during the second heating. The crystallinity degree of pure PP and composites was determined using DSC according to the method described in [6]. The value of PP melting enthalpy for polymer of 100 % crystallinity assumed in calculations was 148 J/g [7].

RESULTS AND DISSCUSION

All values of melting and crystallization temperature as well as melting enthalpy obtained during DSC investigations were presented in Table 1. The DSC curves for pure PP and non-aged composite are presented in Figure 1. It can be seen that the melting temperature of crystallites from non-processed pure PP equals to 164 °C. Similar melting temperature (162.9 °C) have PP crystallites in the non-aged composite. It means that operations of pro-

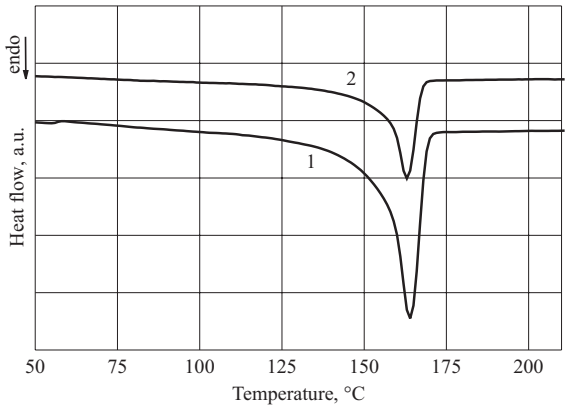

Fig. 1. DSC melting curves of: 1 — polypropylene Moplen HP548R, 2 — non-aged composite

T a b l e 1. Melting and crystallization temperatures together with corresponding melting enthalpy for all investigated samples

Sample	Melting temperature, °C			Crystallization temperature, °C	Melting enthalpy, J/g
	T_{m1}	T_{m2}	T_{m3}		
PP Moplen HP 548R	164	—	—	121.7	98.04
Non-aged composite	162.9	—	—	120.7	96.02
Composite aged in atmospheric conditions					
Material not attached to the molding surface	136.5	—	—	111.3	123.3
Layer up to 0,05 mm	146.4	—	—	117.6	114.42
Laver between 0.05 and 0.10 mm	156.7	—	—	121.1	97.34
Composite aged in the accelerated way					
100 h of irradiation	160.3	—	—	116.2	82.16
200 h of irradiation	159.6	152.3	137.7	115.5	62.32
300 h of irradiation	159.7	151.2	135.8	114.4	54.64

cessing by extrusion and injection molding methods do not apparently influence the crystallization capability of PP and do not significantly decrease the degree of crystallites organization. It is confirmed by the crystallinity degree of pure polypropylene and PP matrix in non-aged composite equaling to 66.22 % and 63.76 %, respectively.

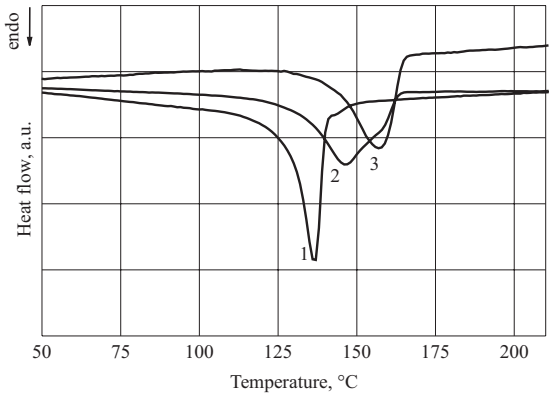

Fig. 2. DSC melting curves of the composite aged in atmosphere conditions: 1 — material not attached to the molding surface, 2 — material removed from the surface layer to the depth of about 0.05 mm, 3 — material removed from the deeper layer (from the depth between about 0.05 and 0.1 mm)

The results of four year ageing of the composite in atmosphere conditions can be easily noticed on the surface exposed to sun irradiation. It is decolored and covered with dust of the composite which is not attached to the molding surface. The melting DSC curves obtained for the composite aged in atmosphere condition are presented in Figure 2. The comparison of DSC curves of the non-aged composite (Fig. 1, curve 2) with the aged one in atmosphere conditions (with the dust cleared away) (Fig. 2, curve 1) indicates that T_{m1} of the crystallites of the aged sample is significantly different from non-aged one. Crystallites in the aged sample melt at the temperature lower by more than 25 °C (T_{m1} = 136.5 °C). After the dust has been cleared away from the surface of the aged composite in natural conditions and the material from the surface layer has been removed to the depth of about 0.05 mm, then T_{m1} of the crystallites equals to 146.4 °C (Fig. 2, curve 2).

T_{m1} of the material removed from the layer to the depth between about 0.05 mm and 0.1 mm equals to 156.7 °C (Fig. 2, curve 3). When the aged material is removed from the layer deeper than 0.1 mm the DSC curve becomes similar to the non-aged composite curve. The curves presented in Fig. 2 prove that weathering process of polymer PP matrix of composite occurs in natural conditions mainly on the moldings surface.

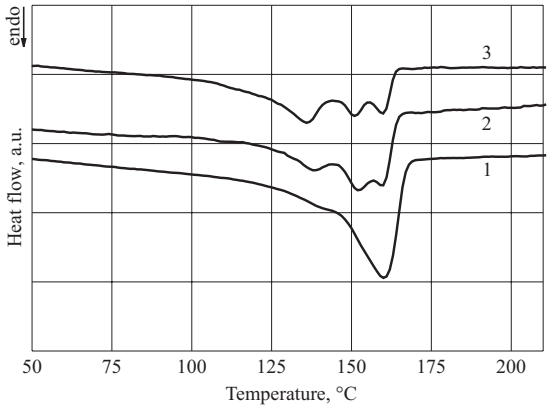

Fig. 3. DSC melting curves of composites aged in the accelerated way by xenon lamp irradiation for: 1 — 100 h, 2 — 200 h, 3 — 300 h; depth of removed sample 0.05 mm

In Figure 3 DSC melting curves of composite which has been exposed to the xenon lamp irradiation are presented. The shape of DSC curves of the samples taken from the surface of molded pieces change depending on the time of irradiation. Several tests for the irradiation periods shorter than 100 h showed that only one minimum is observed on the endothermic curve and melting tem-

perature of crystallites equals to about 160 °C and is not substantially different from the non-aged material. Irradiation for 100 h results in the curve being slightly rounded at the temperature of about 140 °C (Fig. 3, curve 1). This phenomenon is more visible in the samples exposed to irradiation for longer time. Three minima corresponding to the melting temperatures of three kinds of crystallites (T_{m1}, T_{m2} and T_{m3}) significantly different in terms of organization degree can be observed on both curves 2 and 3.

When the irradiation time is extended for 200 h and 300 h the minima of more organized crystallites melting are decreasing. At the same time the amount of less organized crystallites melting at the temperature lower than 140 °C is increasing. However, irradiation of the composite for 300 h has not caused considerable ageing effects as ageing in natural conditions for four years.

In Table 1 it is particularly worth to focus on values of crystallites melting enthalpy of the composite aged in atmospheric conditions concerning the dust not attached to the molding surface and the material removed from the molding surface layer to the depth of about 0.05 mm. In both cases the melting enthalpy values are higher than the value of the melting enthalpy of crystallites in unfilled PP. These do not result from incorrect calculations but from so called skin effect, which may occur in the filled polymer samples formed with the injection molding method. In the outer layer of the composite material, which touches the mold, the concentration of filler is usually lower than the average in the whole material. In this paper melting enthalpy of samples was calculated assuming that the ratio of PP and wood flour included in the composite is 1:1. When the material was taken from the molding surface layer to the depth between 0.05 mm and 0.1 mm, then the results of the DSC analysis were similar to those for the non-aged composite.

CONCLUSIONS

Significant ageing changes occur in the material non-attached to the surface of moldings samples exposed to the natural conditions for four years. Crystallites of PP matrix are much less organized and melt in the temperature lower than non-aged composites by more than 25 °C. In the composite aged long enough in the accelerated way, under the influence of a xenon lamp, crystallites with notably different organization degree and melting temperature may occur side by side. Three areas correspond to crystallites, different in terms of macromolecules organizations, have been observed on the DSC melting curves of such samples. When the time of irradiation is extended the melting areas of more organized crystallites are smaller.

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