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EFFECT OF AGEING ON THE STRUCTURE AND THERMAL PROPERTIES OF POLYMER COMPOSITES WITH CARDBOARD FIBER

WPŁYW STARZENIA NA STRUKTURĘ I WŁAŚCIWOŚCI TERMICZNE KOMPOZYTÓW POLIMEROWYCH Z WŁÓKNEM TEKTUROWYM

Abstract: In this work the results of investigations of thermal properties and structure PE-HD with addition of cardboard fibre before and after UV radiation ageing were presented. In this work composites with content of 1, 3, 5% of cardboard fibre in relation to the polyethylene have been produced. The investigations for the influence of the fillers on the properties of prepared composites before and after ultraviolet radiation ageing have been conducted. Investigations of crystallinity degree by means of DSC method as well as investigations of the structure using optical microscope have been conducted. The DSC investigations prove the decrease in the crystallinity degree of PE-HD during addition of cardboard fibre and increase for the samples after ultraviolet radiation ageing. While increasing the amount of cardboard fibre in the composite the Vicat softening temperature and absorptivity of water decreases for the samples before ultraviolet radiation ageing.

Keywords: composites, thermal properties, cardboard fibre, structure, ultraviolet radiation ageing, recycling

In recent years, in various industries, polymer composites are in demand as a group of materials with interesting, sometimes very specific properties. Properties of polymer composites depend on structural factors of the polymer and the conditions of use. Structural factors include: molecular weight, chemical structure of the macromolecules chain constitution, crystallinity, molecular orientation, and the presence of additional components. However, among the conditions of utility it can be distinguished: temperature, time loading, pressure, type of deformation, etc. [1-9]. Modification of polymers is very important, as to obtain the best properties of the modified polymer. Polymers can be modified by introducing various kinds of polymer modifiers, fillers or stabilizers. There are three methods of modification: physical, chemical and physicochemical. Modification of natural polymers include changing their structure due to the forced orientation, mixing the polymer with modifiers, polymer complex formation, changing the degree of dispersion and the construction of supramolecular individual phases, changing the structure and nature of the interactions in the interfacial zones. The advantage of physical modification is a chance to fast implementation of research results and the ability to carry it as a part of the production process, which allows you to adjust - to some extent - their characteristics to the requirements of customers. To obtain composites with high homogeneity and necessary properties depends on the mixing conditions and physicochemical properties, thermodynamic and rheological characteristics of the starting polymer [4, 5]. The aim of the research was to determine the effect of UV aging on the thermal, utility properties and structure of the composite produced by using polyethylene (PE-HD) and fiber cardboard. The choice of fiber cardboard as a filler is justified by the possibility of changing specific

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properties of PE-HD for specific applications, for recycled paperboard and reduce the cost of developing a new polymer material.

Materials, apparatus and methods

Polyethylene PE-HD, produced by "CHEMO PETROL, a.s", cardboard and fiber with an irregular shape and length of 1-2 mm obtained from the packaging by mechanical fragmentation, have been used for study. The drying process of cardboard fibers has been carried in the dryer Zelmet with heat chamber KC-100/200 at 80ºC for 12 hours. In order to obtain composite, polymer was blended mechanically with fiber carton. Then plasticized and extruded in injection molding machine Krauss Maffei KM65 - 160C, using the following parameters: rotational speed of the screw 260 mm/s; each barrel zone temperature: T_1 = 180ºC, T_2 = 190ºC, T_3 = 200ºC, T_4 = 210ºC; die temperature T_5 = 220ºC. Follow this method, composites were prepared with the following composition: PE-HD + 1 wt.% fiber cardboard, PE-HD + 3 wt.% fiber cardboard, PE-HD + 5% by weight fiber cardboard. Samples for testing of PE-HD and composites made by injection molding were made on injection molding machine KRAUSS MAFFEI KM65 - 160C1. The parameters of the injection molding, which were obtained at the optimal values of the characteristics were as follows: maximum permissible pressure in the plasticizing 60 MPa, injection time 0.7 s, the contact pressure 30 MPa, holding time 30 s, cooling time 20 s, dosage time 6.8 s, mold closing force 650 kN, mold temperature 50ºC, barrel zone temperatures: t_1 = 160ºC, t_2 = 170ºC, t_3 = 180ºC, t_4 = 195ºC, die temperature t_5 = 205°C. Samples for testing of composites with different percentage compositions were prepared with the same parameters of the injection. Differential scanning calorimetry studies were performed using a scanning microcalorimeter type PC 200 NETZSCH 200. DSC curves were recorded during the heating rate of 10ºC/min in a temperature range from 20 to 190ºC. Preparations for DSC test were cut perpendicular to the direction of flow of the samples obtained by injection molding. To determine the degree of crystallinity, the software PC 200 NETZSCH was used. This program allows examination of the course of melting of the sample at a given temperature range and the designation of the area between the thermographic curve and the base line on the occurrence of reflexes endothermic. Indium was used as the pattern, sample weight was ranged from 7 to 10 mg.

The samples were weighed by scale, produced by SARTORIUS company, with an accuracy of 0.01 mg, and internal calibration and measurement enclosed space. The structure was observed under an optical microscope Nikon Eclipse E 200. Test samples were applied to a thickness of 20 microns which were cut by microtome Thermo Electron Corporation of core samples used for DSC studies. Determination of Vicat softening temperature brought by a device HAAKE. The study of water absorption was carried out for samples weighing from 0.8 to 2.5 g in accordance with applicable standards. The ageing process was performed in a test chamber using a UV arc tube high-pressure mercury discharge lamp. Time of the ageing process in the chamber calculated assuming the literature data 1000 kWh/m^2 as the power of global solar radiation during the year and amounted to 223 hours, which using a discharge lamp with specified capacity equivalent to 4 years of solar radiation.

Results and discussion

In Figures 1-3 is shown a DSC thermogram of polyethylene and composites with cardboard fiber before and after UV ageing. Table 1 summarizes the sizes of determined on the basis registered thermography DSC curves. A polyethylene sample by subjecting the radiation, the energy absorbed by the polymer were decreased. The lowest values of the melting enthalpy obtained after the process of radiation.

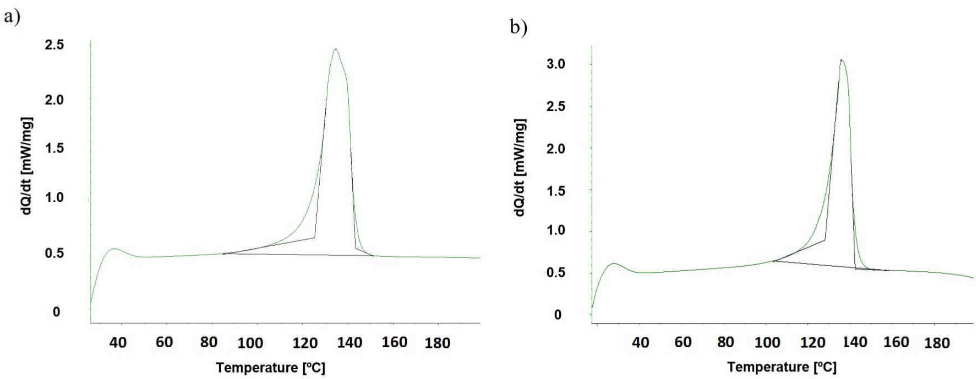

Fig. 1. DSC thermograms of polyethylene: a) before, b) after UV ageing

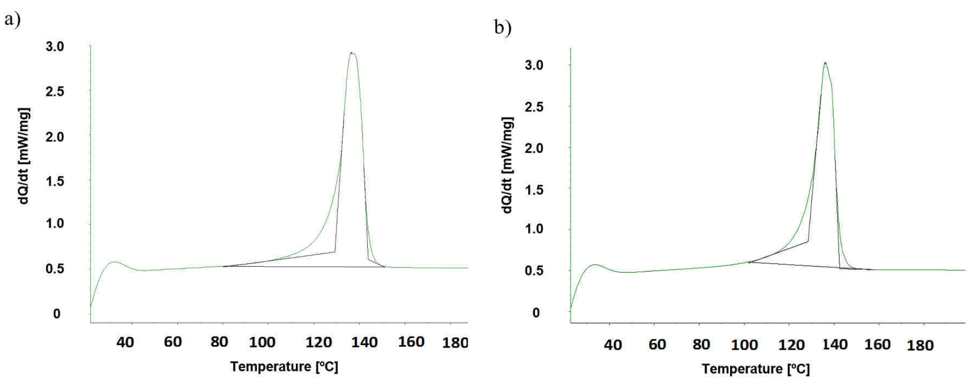

Fig. 2. DSC thermograms of polyethylene + 1% of cardboard fibers: a) before, b) after UV ageing

In proportion to changes in the enthalpy of fusion, start and stop temperature of convertion agent were changing. As a result of subjecting the reflexes of ageing has been narrowed and shifted to higher temperature range. As a result of subjecting the composite polyethylene of 1% cardboard fiber ageing, the energy absorbed by the sample is increasing. As a result of the ageing process reflexes has been narrowed and shifted to the higher temperature range, and the value of the degree of crystallinity increased (Fig. 2). For polyethylene with 3 and 5% of fiber carding after ageing showed an increase of enthalpy of fusion. The average value of the crystalline melting point has increased and reflexes has narrowed (Fig. 3). From the analysis of the study by DSC shows a significant effect of ageing UV rays on the thermal properties of polyethylene and cardboard fiber composites. In the case of test materials, the method of preparation and thermal history of the samples affect to the mobility of macromolecular segments, nucleation, growth and orientation of the crystallites.

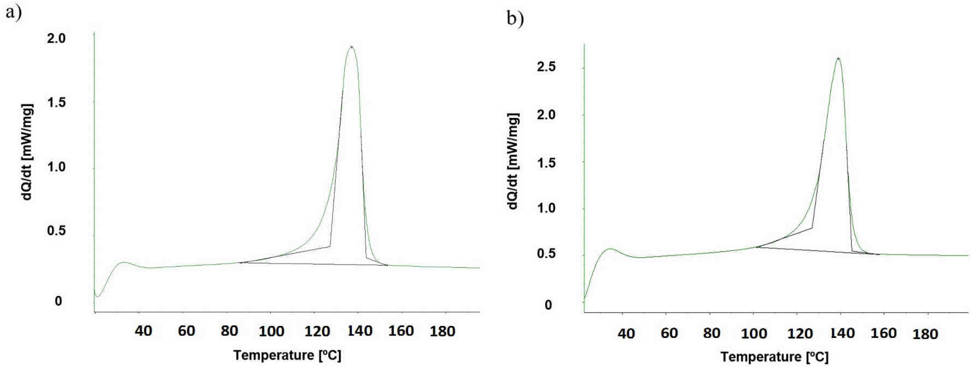

Fig. 3. DSC thermograms of polyethylene +5% of cardboard fibers: a) before, b) after UV ageing

Table 1

The results of DSC tests

Composition of the sample	The degree of crystallinity [%]	Melting range [°C]	The melting point of max. reflexes [°C]
PE	64.5	125.4-143.5	134.6
PE + 1% cardboard fibers	67.1	129.2-143.6	136.4
PE + 3% cardboard fibers	52.4	125.4-144.5	137.2
PE + 5% cardboard fibers	49.6	127.3-143.8	137
PE aged	61.9	128.2-142.4	135
PE + 1% cardboard fibers aged	61.1	128.6-142.6	136
PE + 3% cardboard fibers aged	60.4	128.3-145.2	134.8
PE + 5% cardboard fibers aged	58.8	127-145.2	138.8

In studies on the structure of the polyethylene on optical microscope after ageing the growth of crystalline structure was found. There are clearly visible shapes of spherulites with large dimensions. The structure is more visible and organized (Fig. 4).

Based on the analysis of the DSC thermograms revealed changes in the melting range of the crystalline phase, the temperature at which crystallization takes place at a maximum rate and the crystallization start temperature. This direction of changes reflects the capacity of the crystallization of polyethylene in the composite, which also affects to higher degree of crystallinity UV aged composite. A small amount of fiber carding, its specific shape and arrangement along the direction of flow may affect the increase in the degree of crystallinity (Table 1, Fig. 5). It follows to higher probability of intermolecular interactions in the polymer, leading to the creation of centers of crystallization upon cooling of the composite PE + 1% fiber.

a) b)

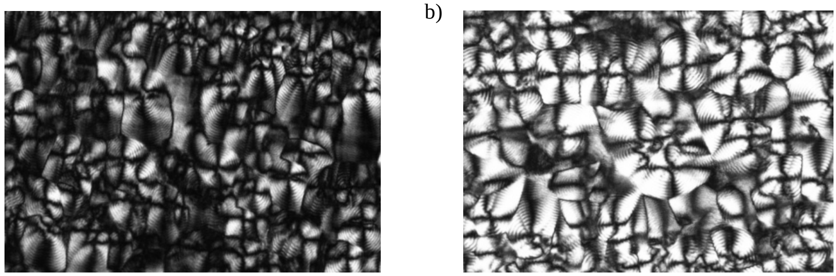

Fig. 4. Structure observed under an optical microscope at a magnification of 400x: a) PE, b) PE after UV ageing

a) b)

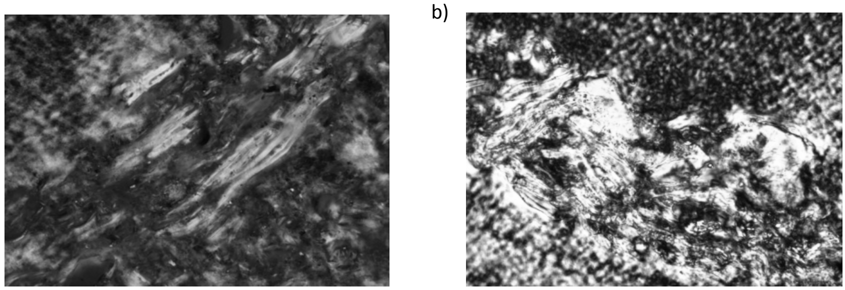

Fig. 5. Structure observed under an optical microscope at a magnification of 400x: a) PE/1% cardboard fiber, b) PE/1% cardboard fiber after UV ageing

a) b)

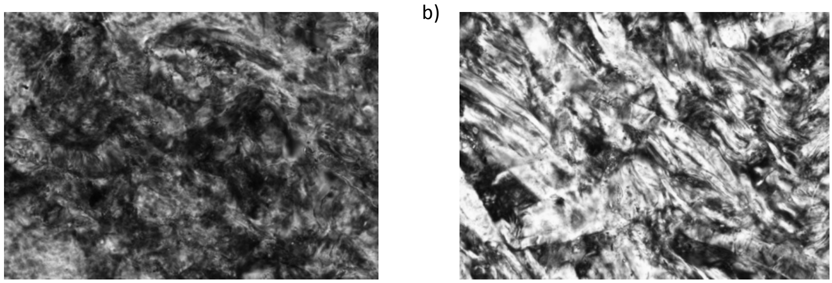

Fig. 6. Structure observed under an optical microscope at a magnification of 400x: a) PE/5% cardboard fiber, b) PE/5% cardboard fiber after UV ageing

The results of DSC tests show a decrease in the degree of crystallinity for composites with fiber 3 and 5%, which alters the performance of composites. The reason for the decrease in the degree of crystallinity may be changing the structure system: the fiber orientation along the direction of the polymer flow in the injection mold cavity, however, small disturbances at 3% of the fiber board and then the entanglement of fibers together in the fiber content of 5% (Fig. 6).

The study shows that with increasing filler content in the composite increases the value of Vicat softening temperature. The same increase in temperature followed by a sample after ageing. In the case of samples with the same content of the filler, the softening point was lower after aging. The higher the filler content is in the composite, the greater is the water absorption (Table 2).

Table 2

The results of Vicat softening temperature and water absorption tests

Composition of the sample	Vicat softening temperature [ºC]	Water absorption [%]
PE	115	0.01
PE + 1% cardboard fibers	116	0.02
PE + 3% cardboard fibers	117	0.11
PE + 5% cardboard fibers	118	0.13
PE aged	113	0.01
PE + 1% cardboard fibers aged	114	0.01
PE + 3% cardboard fibers aged	115	0.17
PE + 5% cardboard fibers aged	115	0.25

Conclusions

On the basis of DSC tests, it was found that the content of filler fibers in the form of a cardboard a composite of polyethylene influences the crystalline melting point. The influence of the degree of crystallinity of the filler whose value decreases with the increase of its content in the composite. The properties of the polyethylene as well as a test of the composite are significantly affected by UV ageing. After UV ageing decreases the degree of crystallinity, however, an increased with increased fiber content compared to the paperboard samples instead of the aged. There were significant changes in the structure during the test composites under an optical microscope. At higher fiber content in the composite cardboard are arranged in clusters, and there is no visible direction along the direction of the flow lines. With an increase in the filler content, the softening temperature increases. In the case of samples with the same content of the filler, the softening point was lower after ageing.

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WPŁYW STARZENIA NA STRUKTURĘ I WŁAŚCIWOŚCI TERMICZNE KOMPOZYTÓW POLIMEROWYCH Z WŁÓKNEM TEKTUROWYM

Politechnika Częstochowska

Abstrakt: W pracy przedstawiono wyniki badań właściwości termicznych oraz struktury polietylenu o dużej gęstości i kompozytów polietylenu z włóknem tekturowym przed i po procesie starzenia promieniami UV. Zbadano stopień krystaliczności metodą DSC oraz strukturę za pomocą mikroskopu optycznego w świetle przechodzącym. Określono również temperaturę mięknienia wg Vicata oraz chłonność wody. Badaniom poddano kompozyty polietylenu o zawartości włókna: 1, 3 i 5%. Stwierdzono wpływ napełniacza na stopień krystaliczności, którego wartość maleje ze wzrostem zawartości włókna tekturowego zarówno przed, jak i po starzeniu promieniami UV. W przeprowadzonych badaniach zarejestrowano niższe wartości temperatury mięknienia wg Vicata i większą chłonność wody dla kompozytów polietylenu z włóknem tekturowym po starzeniu promieniami UV.

Słowa kluczowe: kompozyty, właściwości cieplne, włókno tekturowe, struktura, starzenie promieniami UV, recykling