Inhibition of polymer photodegradation by incorporation of coffee silverskin

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INTRODUCTION

Over the last years, the trend associated with the incorporation of materials from renewable resources into polymer technology is getting significantly more vital. Researchers are trying to transfer the properties of natural raw materials into the polymer world. Therefore, different natural materials are more often investigated as potential additives for polymers. Such an effect is noted for the coffee industry by-products, such as coffee silverskin [1-3]. Because of the relatively high contents of compounds showing antioxidant activity, such as caffeine, polyphenols, tannins, or melanoidins, this by-product could be considered not only as a filler, but also as a potential modifier for polymer materials. Its antioxidant activity is comparable to commercially available antioxidants applied in polymer technology [4-7]. Therefore, in the presented paper, we examined the influence of the coffee silverskin (from 1 to 20 wt%) on the thermal and mechanical performance of polyethylene-based composites. Moreover, materials were subjected to accelerated aging tests in the UV chamber, which revealed that coffee silverskin could inhibit the photodegradation of the polymer matrix. Therefore, this by-product should be considered as an exciting alternative for the conventional lignocellulosic fillers, which could provide additional features to polymer composites.

EXPERIMENTAL

The composites were prepared by mixing high-density polyethylene with 1, 2, 5, 10, or 20 wt% of coffee silverskin using a ZAMAK EH16.2D co-rotating twin-screw extruder operating at 100 rpm with the maximum temperature of the process of 190 °C. The resulting composites were then compression molded at 170 °C and 4.9 MPa for 2 minutes and then kept under pressure at room temperature for another 5 min to enable solidification of the materialThe specimens were named in reference to their filler content, as PE and PE/XŁK, where X stands for the filler content.

The accelerated aging process was conducted under 0.55 W/m^2 irradiance at 340 nm UV light intensity, with constant max. temperature up to 63 °C during dry UV light exposure. The samples were subjected to UV light exposure in two time periods of 100 and 200 h. The tensile strength and elongation at break were estimated following ISO 527, while thermal properties were determined by the differential scanning calorimetry (DSC) analysis.

THERMAL AND MECHANICAL PERFORMANCE OF POLYETHYLENE/COFFEE SILVERSKIN COMPOSITES

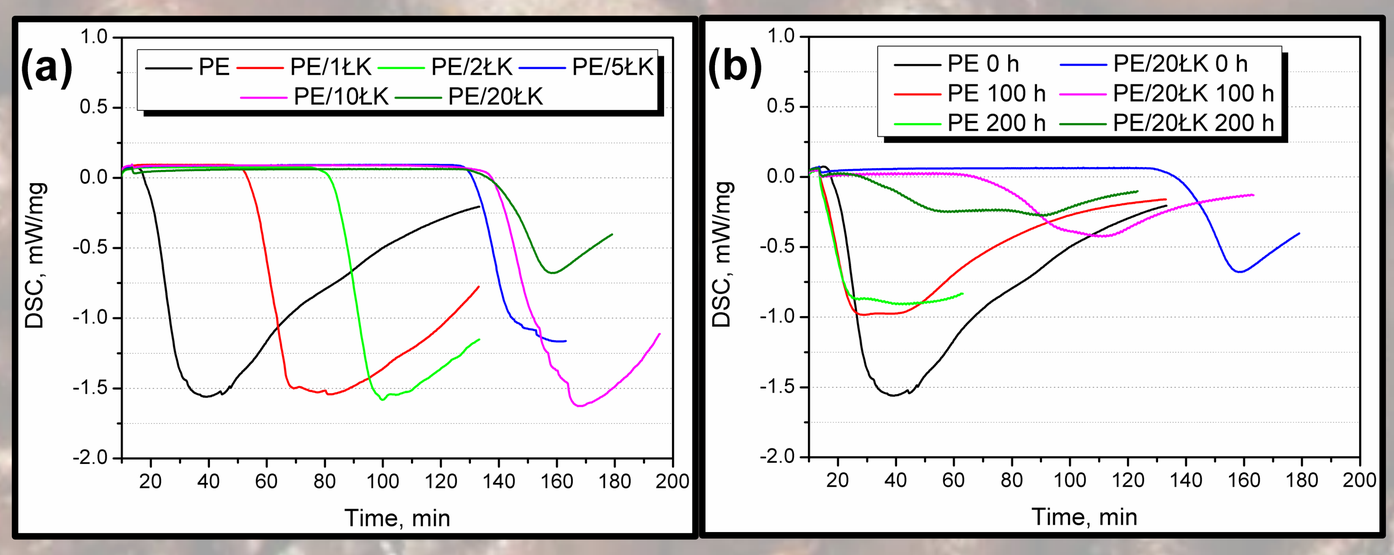

Figure 1. Thermograms of (a) unaged composite samples, and (b) PE and PE/20ŁK composites depending on aging time.

To determine the potential antioxidant activity of coffee silverskin, and its effect on the thermooxidative stability of prepared composites, the oxidation induction time was determined by DSC analysis. In Figure 1 there are presented thermograms for unaged samples, as well as for PE and PE/20ŁK depending on aging time. Moreover, in Table 1 there are presented values of oxidation induction time for all samples, along with the results of "conventional" DSC analysis. It can be seen that the introduction of coffee silverskin caused a significant delay in composites' oxidation process, confirming the antioxidant activity of this by-product. Values of OIT were over 2.5 times bigger even for 1 wt% content of filler, comparing to 20 minutes for neat polyethylene matrix. For higher contents OIT values reached even 130-140 minutes. Above 5 wt% the effect was not as distinct. Accelerated aging of samples significantly reduced the thermooxidative stability of analyzed composites. Nevertheless, sample PE/20ŁK still showed higher stability than neat PE, even after 200 hours of aging, which points to the very high activity of antioxidant compounds present in coffee silverskin. In Figure 1b it can also be seen that magnitude of signals was significantly reduced after aging, indicating partial oxidation of the material.

Incorporation of the coffee silverskin into the polyethylene matrix did not substantially affect the thermal properties PE. Temperatures of melting and crystallization were hardly affected by the filler incorporation. The decrease of the melting enthalpy (ΔHm) was noted, which was associated with the reduced share of the polymer matrix. Nevertheless, the degree of crystallinity was slightly increased from 63.8 to 66.6 %, which was related to the nucleating activity of filler. This phenomenon can be related to the previously described cases of the interaction of lignocellulosic fillers as heterogeneous nucleants of the PE [8].

Aging of samples did not cause noticeable changes in the T_m and T_{cr} values, but affected the melting enthalpy and degree of crystallinity, especially for unmodified polyethylene and sample PE/1ŁK. After 200 hours of aging, the degree of crystallinity for this samples was reduced, pointing to the partial decomposition of the material

Table 1. Results of DSC analysis for prepared composites.

Sample	Aging time, h	T_m, °C	T_{cr}, °C	ΔH_m, J/g	X_{cr},%	OIT, min
PE	0	134.1	112.8	187.4	63.8	20.0
	100	132.5	112.4	197.8	67.4	13.5
	200	133.2	110.6	146.6	49.9	13.5
PE/1ŁK	0	133.2	113.1	190.5	65.5	54.8
	100	132.7	112.3	189.1	65.1	13.5
	200	133.8	113.5	152.1	52.3	13.5
PE/2ŁK	0	134.1	113.0	188.9	65.7	83.9
	100	132.8	112.9	181.8	63.2	15.1
	200	132.7	112.8	182.1	63.3	13.5
PE/5ŁK	0	133.3	113.3	186.5	66.9	131.9
	100	133.6	113.1	174.8	62.7	15.8
	200	132.0	113.8	177.9	63.8	16.5
PE/10ŁK	0	133.0	113.4	174.5	66.0	139.5
	100	132.3	112.7	170.9	64.7	17.9
	200	132.4	112.9	170.7	64.6	16.7
PE/20ŁK	0	132.6	112.5	156.4	66.6	140.4
	100	133.6	112.2	148.5	63.2	76.8
	200	131.6	113.6	159.2	67.8	30.1

In Figure 2 there are presented tensile properties of the analyzed PE/ŁK composites before and after the accelerated aging. The initial values of tensile strength were at a similar level for neat polyethylene matrix and composites containing up to 5 wt% of coffee silverskin. For higher loadings of filler, drop of the tensile strength was noted. Similar effects were observed in our other work [9]. Such a phenomenon is associated with the insufficient interfacial adhesion between filler and matrix, which was especially pronounced for the elongation at break. This parameter was drastically decreased when solid particles were introduced into the polymer matrix.

The aging of composite samples resulted in noticeable changes in their mechanical performance. Nevertheless, a very beneficial influence of coffee silverskin can be noted. For the neat polyethylene matrix, a drop of tensile strength, and especially elongation at break was very significant after aging. Similar effects were noted by other researchers [10]. It can be seen that the incorporation of even 1 wt% of coffee silverskin caused a noticeable improvement of the mechanical performance. The share of the initial values of mechanical properties was increasing with the loading of coffee silverskin. It confirms the results of the thermal properties analysis indicating the elongation of oxidation induction time with the addition of applied coffee industry by-product

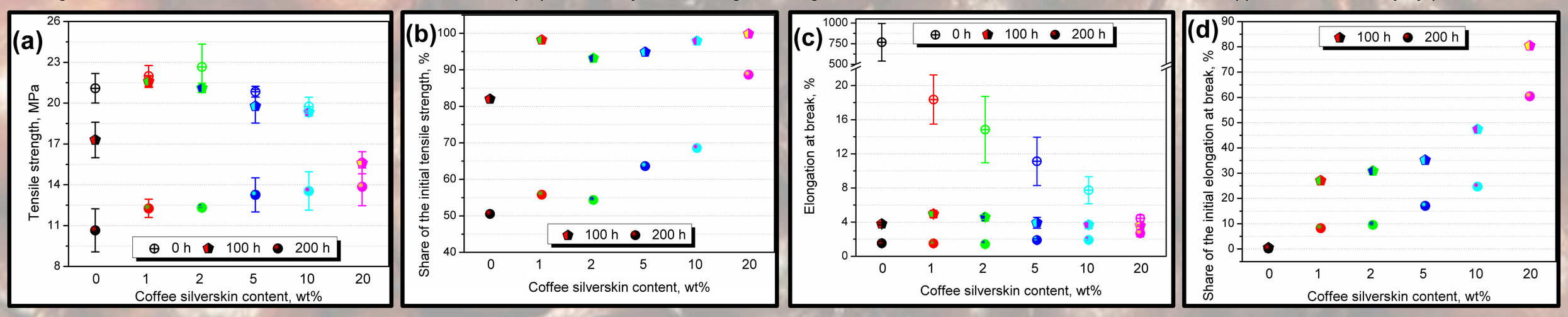

Figure 2. Plots showing (a) tensile strength, (b) share of the initial tensile strength, (c) elongation at break, and (d) share of the initial elongation at break for PE/ŁK composites depending on the filler content.

CONCLUSIONS

In the presented work, the polyethylene-based composites modified with natural waste filler in the form of coffee silverskin were produced and tested. It has been shown that incorporated filler shows novel functionality, in the form of an antioxidant effect, resulting from the active compounds it contains. The introduction of a lignocellulosic filler with a complex structure and chemical composition made it possible to suppress the aging effects caused by exposure to UV radiation in controlled conditions. Thermal analysis, performed by differential scanning calorimetry, was correlated to and remained in agreement with the results of mechanical studies performed using tensile test evaluation. Based on the obtained results, it can be concluded that coffee silverskin can be used as a low-cost filler for the production of highly-filled composites with additional functionality in comparison to different lignocellulosic waste fillers, as well as an effective additive which influences negative effects of oxidation induced by aging processes.

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