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Effect of Modification with a Biocide Containing Metal Nanoparticles on Selected LDPE Properties

Katarzyna Janczak , Daria Lisewska, Alicja Mazuryk and Rafał Malinowski *

Łukasiewicz Research Network—Institute for Engineering of Polymer Materials and Dyes, Marii Skłodowskiej-Curie 55, 87-100 Torun, Poland

* Correspondence: rafal.malinowski@impib.lukasiewicz.gov.pl

Abstract: In this work, the physicomechanical, chemical and thermal properties of low-density polyethylene (LDPE) modified with a biocide containing metal nanoparticles: nanoAg, nanoCu, and nanoFe_2O_3 were examined. The presented studies, apart from the previously proven antimicrobial effectiveness, have shown that the application of the biocide in concentrations of 0.5% and 1% has the least influence on the remaining properties. In the remaining concentrations (2–5%), despite the lack of significant influence on the chemical structure, the biocide primarily influenced the strength properties and melt flow rate (MFR). Previous research showed almost 100% antimicrobiological properties against bacteria and fungi of samples with the addition of 4% biocide. For such samples, the presented studies showed a decrease in MFR by approx. 17%, tensile strength at break by approx. 45%, an increase in elongation at breaking by approx. 25%, a decrease in density >2%, no increase in water absorption, and no significant changes in the chemical structure and in thermal properties in relation to LDPE without biocide.

Keywords: polyethylene; nanoparticles; MFR; physical and mechanical properties; DSC; FTIR

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1. Introduction

Since the start of the COVID-19 pandemic in 2020, many sectors of the economy have been striving to develop materials that protect us against the harmful effects of pathogenic microorganisms [1–4]. Companies and scientists related to polymer materials are focused on the development of materials with properties that limit the multiplication of microorganisms [5–7]. These are not only materials limiting the growth of fungi, which is justified especially in the construction sector for items such as window frames, ventilation ducts, plumbing installations, plasters, paints, and varnishes [8–10]. Currently, due both to the needs of consumers and the dynamic development of competition, producers have started to introduce more materials with bactericidal properties to the market [11–13]. Such materials are applicable to both sanitary products and everyday objects, as well as all surfaces exposed to the contact of a larger number of people or installations, ensuring the flow of drinking water or clean air in construction facilities and vehicles [14–17].

Unfortunately, additional components often introduced into the polymer material interfere with other properties of the material, e.g., changing their physicomechanical or chemical properties. Despite obtaining a material with strong antimicrobial activity, it is noticed, among others, a decrease in the strength of the material, change in color, increase in the absorbency of the material, or changes in rheological properties in relation to the material not exposed to the action of microbiologically active substances [18–21]. Apart from the high cost of many biocides, these are changes that are a major obstacle to commercial application [22].

The subject of our research is to examine the physicomechanical properties such as melt flow index, density, water absorption, strength tests, as well as thermal properties and changes in the chemical structure for low-density polyethylene (LDPE) modified with a biocide which showed bactericidal and fungistatic properties. LDPE is a material with a wide range of applications, among others, in the packaging industry, including food packaging, the construction industry, and medicine [23–25].

Among the various nanoparticles used in industry, the effectiveness of titanium dioxide (TiO_2), nanoAg and nanoCu has been particularly proven [26–28]. The effectiveness of two of these ingredients has been confirmed in previous studies [29]. It has been shown that the combined use of silver (nanoAg), copper (nanoCu) and iron oxide (nanoFe_2O_3) nanoparticles effectively reduce the number of model and pathogenic microorganisms. The very high anti-microbiological effectiveness of the applied biocide was found at a concentration of 4%, while partial growth inhibition (biostatic effect) was also observed at lower concentrations. Additionally, LDPE modified with biocide has successfully passed the tests of migration and modifier dispersion, which is also a common problem, especially for biocides containing nanoparticles [30,31].

In order to implement the material for mass production, it is necessary to examine the influence of the added biocide on the other parameters mentioned above. The aim of the presented research was to check whether the use of an effective antimicrobial biocide containing metal nanoparticles does not affect some properties of LDPE like physicomechanical, thermal, or rheological and does not exclude its use in industry.

2. Materials and Methods

2.1. Biocide

A biocide supplied by ZPTS Ingremio-Peszel (Bolesław, Poland) was used. According to the specification, a concentrate of nanomaterials in the odorless form of yellow-brown granules was prepared, containing nanoparticles with diameters of 5 nm–15 nm (for 95% of particles), containing approx. 150 ppm nanoAg, 100 ppm nanoCu, and 150 ppm nanoFe_2O_3.

2.2. Preparation of Samples

Samples of LDPE Malen E Fabs 23-D022 granules (LyondellBasell, Rotterdam, The Netherlands) and composites containing biocide at a concentration of 0.5%, 1%, 2%, 3%, 4%, and 5% by weight, respectively, were prepared. The granulates were extruded using a co-rotating twin screw extruder type Bühler BTSK with screws of 20-mm diameter and an L/D ratio of 40 (Bühler, Braunschweig, Germany). The extrudate was dried on a conveyor belt in a stream of dry air and then granulated.

Samples for water absorption tests (60 mm × 60 mm × 1.5 mm) and for strength tests (dimensions 9.92 mm × 4.00 mm) were injected from the granules in accordance with ISO 527-2 [32] on an injection molding machine Battenfeld type Plus 35/75 (Wittmann Battenfeld GmbH, Kottingbrunn, Austria). The temperatures of the plasticizing zones of cylinders I and II were 200 °C and 190 °C, respectively, and the temperature of the injection die head was 200 °C. The temperature of the injection mold was 23 °C, and the injection pressure was 157–163 MPa, depending on the type of composite. The rotational speed of the screw was constant and amounted to 150 min^{-1}.

2.3. Physicomechanical Properties

2.3.1. Mass Flow Rate Index, MFR

The melt flow rate (MFR) test was performed according to standard ISO:1133-1 [33] using a load plastometer LMI 4003 (Dynisco, Franklin, MA, USA). The analyzes were carried out conducted at a temperature of 190 °C under a piston load of 21.6 kg. For each sample, 5 measurements were performed.

2.3.2. Density, *d*

The density (*d*) of the obtained materials was determined in accordance with ISO 1183-3 [34]. For each sample, 5 measurements were performed.

2.3.3. Water Absorption

The water absorption of the test samples was checked in accordance with ISO 62 [35]. Samples were previously dried at 80 °C, weighed with an accuracy of ±0.0001 g, and then immersed in distilled water for 72 h. The amount of water absorbed by the films was determined by measuring their mass changes, and the final result was expressed as a percentage of the initial mass of the sample according to the following equation:

$$C = \frac{m_2 - m_1}{m_1} \times 100\%$$

where C is water absorption, m_1 is the initial mass of the sample after drying (mg), and m_2 is the mass of the sample after immersion (mg).

2.3.4. Mechanical Properties

The static tensile mechanical properties of the film samples were determined according to ISO 527-1 and ISO 527-2 [32,36]. Five tests were performed for each sample at a tensile speed of 50.0 mm/min. The tests were conducted using TIRATest 27025 equipment (TIRA GmbH, Schalkau, Germany).

2.4. Fourier Transform Infrared Spectroscopy, FTIR

The method of infrared spectroscopy (FTIR) with the reflection technique (ATR) was used. FTIR spectra were recorded in the range 400—4000 cm^{-1} using a Cary 630 FTIR spectrometer (Agilent, Santa Clara, CA, USA) equipped with a diamond crystal (spectral resolution < 2 cm^{-1}).

2.5. Differential Scanning Calorimetry, DSC

A differential scanning calorimeter (DSC) was performed with a calorimeter DSC1 (Mettler Toledo, Greifensee, Switzerland) calibrated with pure indium and zinc standards. The standard ISO 11357 (Parts 1–3) [37–39] was followed. Each sample weighing from 4.5 mg to 5.5 mg was placed in an aluminum crucible and heated from 0 °C to 200 °C under a nitrogen atmosphere with a flow of 55 mL/min. The heating and cooling rate was 10 °C/min. Two heating scans were applied after the first sample was cooled to 0 °C and re-heated from 0 °C to 200 °C. Before cooling and the second scan, the sample was kept at a constant temperature for 3 min (before cooling at 200 °C, before heating at 0 °C). The crystallization and melting enthalpy were assessed from the integrated peaks. The following designations were adopted: T_m—melting temperature (°C), ΔH_m—melting enthalpy (J/g), T_c—crystallization temperature (°C), and ΔH_c—crystallization enthalpy (J/g).

2.6. Statistical Analysis

Figures are presented as mean ± standard deviation. For microbiological activity tests, the obtained results were analyzed using the Past 321 program (Softpedia, Past 321, Bucharest, Romania, 2018). Significant differences were determined based on a 1-way analysis of variance (ANOVA) using Tukey's test for $p < 0.05$.

3. Results

3.1. Physicomechanical Properties

The results of the tests of physical and mechanical properties for the samples with the biocide and for the samples without the biocide are summarized in Table 1.

Table 1. Results of physicomechanical tests of samples with biocide (from 0.5% to 5%) and control samples without biocide (Ctr); arithmetic means ± standard deviation.

	MFR (g/10 min.)	d (g/cm^3)	c (%)	σ_B (MPa)	ε_{tB} (%)
Ctr	41.38 ± 0.51	0.9483 ± 0.0005	0.0009 ± 0.0031	8.09 ± 0.23	30.56 ± 1.56
0.5%	41.03 ± 0.67	0.9479 ± 0.0004	0.0004 ± 0.0001	7.78 ± 0.13	31.01 ± 0.35
1%	40.38 ± 0.54	0.9473 ± 0.0003	0.0005 ± 0.0001	7.32 ± 0.05	31.97 ± 0.49
2%	39.57 ± 0.44	0.9470 ± 0.0002	0.0005 ± 0.0003	5.66 ± 0.13	35.12 ± 0.57
3%	36.60 ± 0.98	0.9438 ± 0.0004	0.0003 ± 0.0001	4.53 ± 0.09	37.02 ± 0.33
4%	34.54 ± 0.48	0.9328 ± 0.0007	0.0006 ± 0.0003	4.43 ± 0.21	38.09 ± 0.62
5%	31.79 ± 0.92	0.9303 ± 0.0004	0.0004 ± 0.0002	4.01 ± 0.47	40.32 ± 1.37

Abbreviations: MFR—mass melt flow rate, d—density, c—water absorption, σ_B—tensile strength at break, ε_{tB}—elongation at break.

Mass Melt Flow Rate, MFR

For the obtained samples, MFR was appointed (g/10 min.). For the material without biocide, the MFR value was 41.38 g/10 min, while a decrease in the value of this parameter was observed depending on the amount of biocide used. The lowest MFR value was 31.79 g/10 min. (at 5% biocide content; Table 1). It was shown that the addition of 0.5% biocide did not statistically significantly affect the MFR value. The MFR for the samples containing 2% biocide was similar to the samples containing 1% biocide and was lower by approx. 2–4% compared to the control samples (without biocide). The increase in the biocide content (>2%) caused a significant decrease in the value of this parameter, compared to the control samples, approx. 12% (with 3% biocide), approx. 17% (with 4% biocide) and approx. 23% (with 5% biocide; Figure 1).

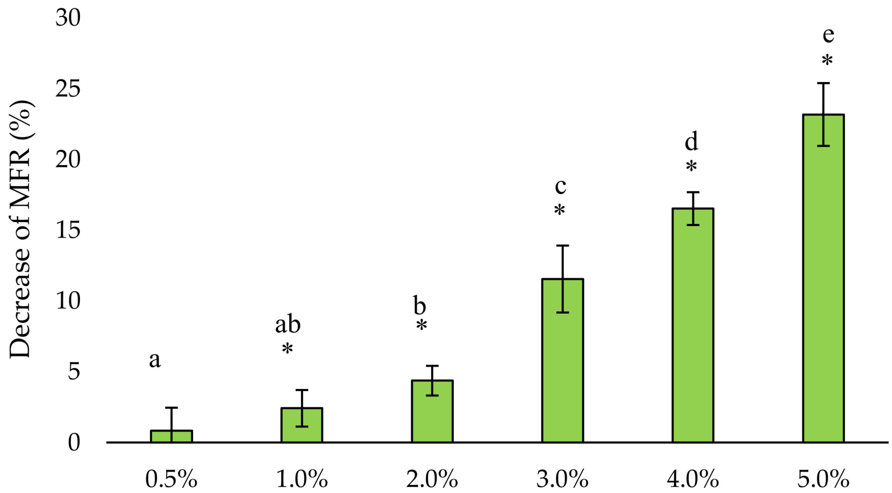

Figure 1. Mass melt flow rate (MFR) for samples containing 0.5% to 5% of the biocide (differences from control—samples without biocide). Statistically significant differences from the controls are marked with an asterisk. Statistically significant differences between the variants are marked with separate letters.

3.2. Density, d

The d value of the samples ranged from 0.9303 g/cm^3 (for samples with 5% biocide) to 0.9483 g/cm^3 (for samples without biocide; Table 1). Even the highest biocide content (5%) did not cause the parameter decrease >2% compared to the control samples (without biocide; Figure 2).

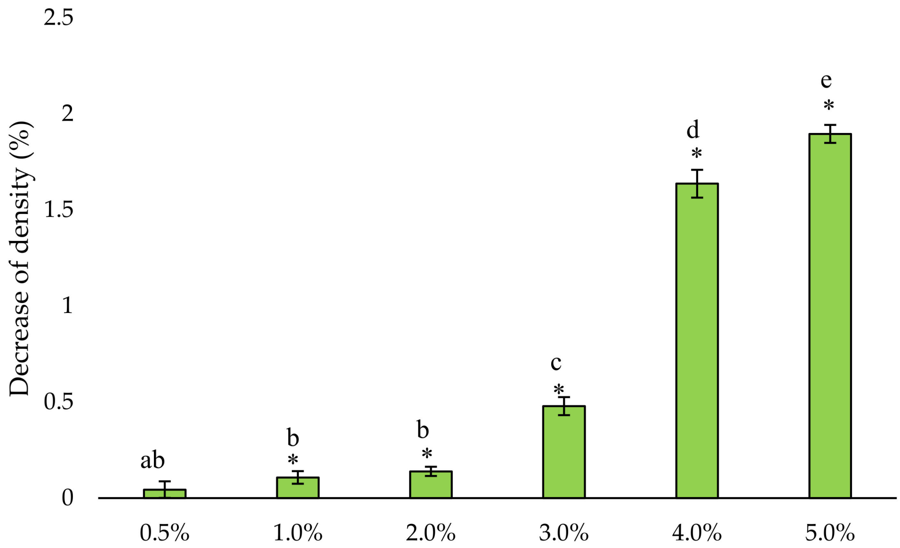

Figure 2. Density (*d*) for samples containing the biocide in a concentration from 0.5% to 5% (difference with the control—samples without biocide). Statistically significant differences from the controls are marked with an asterisk. Statistically significant differences between the variants are marked with separate letters.

3.3. Water Absorption, c

The *c* value for the control samples (without biocide) was 0.0009%, while for the samples with the biocide addition, the value ranged from 0.0003% to 0.0006%; this value did not change proportionally to the biocide content (Table 1). Also, the statistical analysis of the results showed that the *c* value for individual samples with the biocide did not differ significantly, despite the statistically significant difference compared to the control sample (without the biocide). The significant standard deviations visible in the graph were influenced by small numerical values in the order of hundred-thousandths of a percent (Figure 3). Therefore, it can be concluded that the addition of biocide slightly decreased the absorbency of the material, regardless of its percentage in the material.

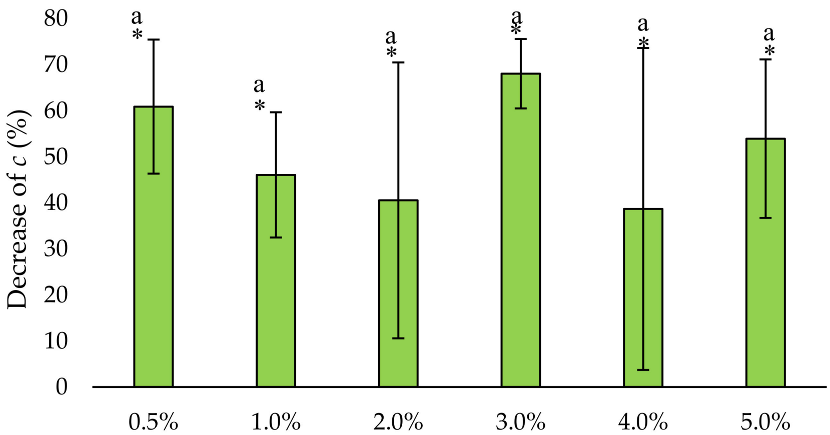

Figure 3. Water absorption (*c*) for samples containing the biocide in a concentration from 0.5% to 5% (differences to the control—samples without biocide). Statistically significant differences from the controls are marked with an asterisk. Statistically significant differences between the variants are marked with separate letters.

3.4. Mechanical Properties

Among the mechanical properties, the values of tensile strength at break (σ_B, MPa) and elongation at break (ε_{tB}, %) were analyzed. Tensile strength (σM, MPa) and elongation with tensile strength (ε_{tM}, %) were also checked, but these values did not change after adding the biocide in a concentration from 0.5% to 5%.

The values of σ_B ranged from 4.01 MPa (for the sample with 5% biocide) to 8.09 MPa (for the control sample without the biocide; Table 1). The addition of biocide at a concentration of ≥1% had a statistically significant effect on σ_B (Figure 4a), and the value of this parameter decreased with increasing biocide concentration (Table 1). The concentration of 0.5% of the biocide did not significantly affect σ_B. Increasing the concentration of the biocide caused a decrease in the σ_B value by approx. 10% (at a concentration of 1%), by approx. 30% (at a concentration of 2%), by approx. 44–45% (at a concentration of 3 or 4%) and by approx. 50% (at a concentration of 5%; Figure 4a).

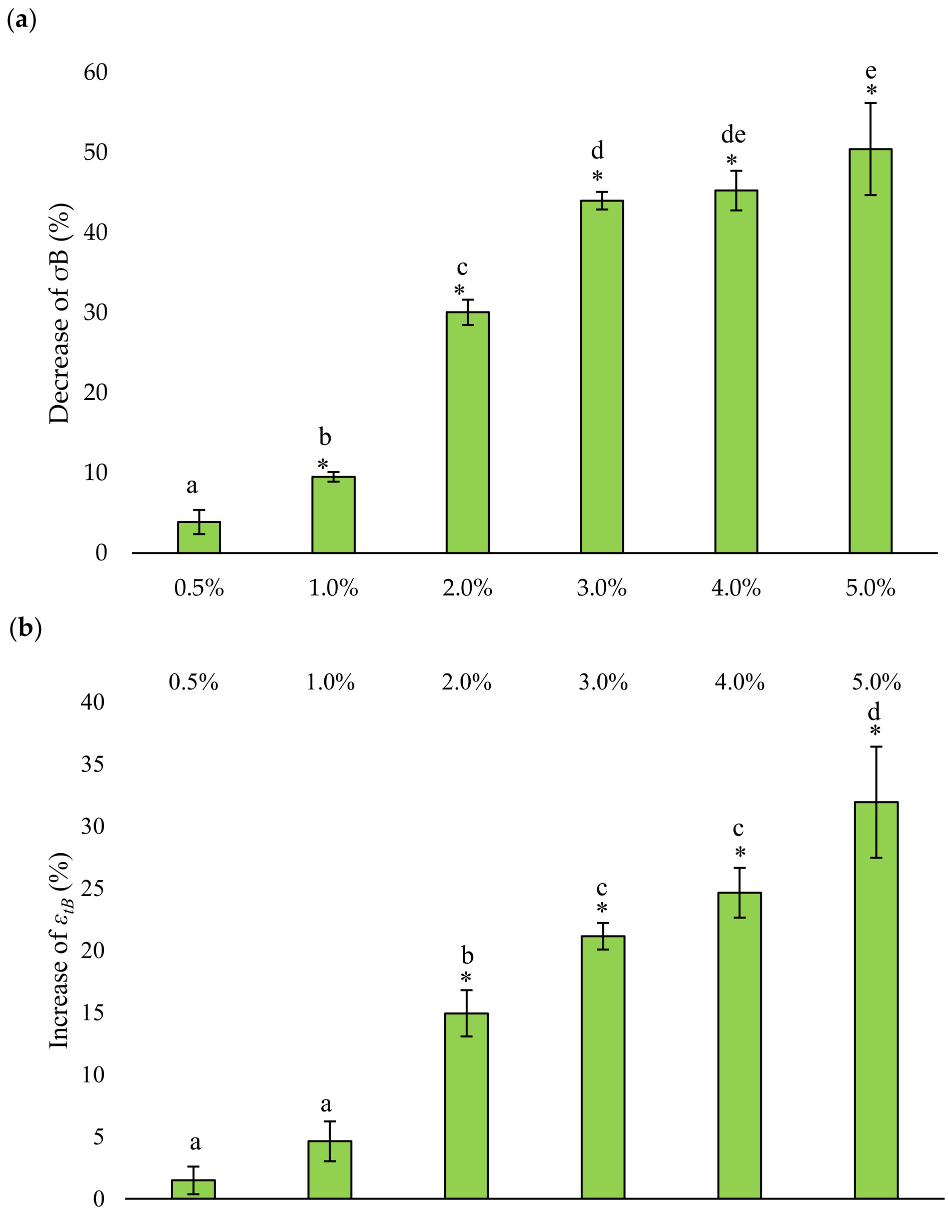

Figure 4. Strength properties for samples containing the biocide in a concentration from 0.5% to 5% (differences compared to the control samples without biocide): (**a**) tensile strength at break (σ_B); (**b**) elongation at break (ε_{tB}). Statistically significant differences from the controls are marked with an asterisk. Statistically significant differences between the variants are marked with separate letters.

The values of ε_{tB} ranged from 30.56% (for control samples without biocide) to 40.32% (for samples with a biocide concentration of 5%; Table 1). The addition of a biocide with a concentration of ≤1% did not significantly affect this parameter. On the other hand, in the remaining cases, an increase in ε_{tB} by approx. 15% (at 2% biocide concentration), by approx. 21–25% (at a biocide concentration of 3–4%) and by approx. 32% (at a biocide concentration of 5%) was observed (Figure 4b).

3.5. Fourier Transform Infrared Spectroscopy, FTIR

Analysis of the FTIR spectra revealed that there were no significant changes in the LDPE spectra with the biocide concentration of 0.5% to 5% compared to the control samples (LDPE without biocide). According to the literature, peaks were determined for CH_2 racking deformation at 718 cm^{-1}, for CH_2 bending at 1461 cm^{-1}, for CH_2 symmetric at 2846 cm^{-1}, and for CH_2 asymmetric at 2914 cm^{-1} [40,41]. The lack of significant changes in FTIR spectra between samples suggests that the addition of biocide did not affect the chemical structure of LDPE (Figure 5).

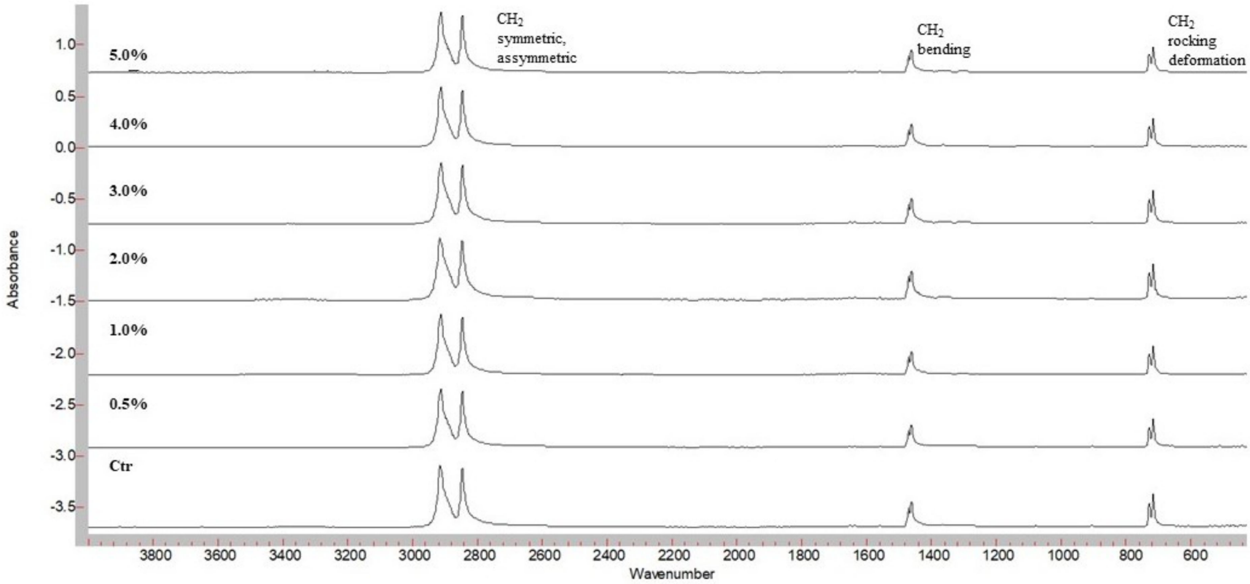

Figure 5. FTIR spectra for samples containing the biocide in a concentration from 0.5% to 5% and gfor the control sample - without biocide (Ctr).

3.6. Differential Scanning Calorimetry, DSC

By DSC, the values of T_m, ΔH_m, T_c, and ΔH_c were analyzed (Table 2). During the first heating, the T_m value for the samples was in the range of 129.26 °C–130.78 °C. Only for the sample with the 3% biocide concentration was the higher T_m of 134.18 °C recorded, while for the control sample, the value was 130.62 °C. The ΔH_m were similar; however, the greatest ΔH_m (190.69 J/g) was recorded for the control sample (Table 2, Figure 6a).

Table 2. DSC analysis results for samples containing biocide with a concentration of 0.5–5% and for control samples—without biocide (Ctr).

	Heating 1		**Heating 2**		**Crystallization**		**Peak on Second Heating (°C)**
	T_m (°C)	**ΔH_m (J/g)**	**T_m (°C)**	**ΔH_m (J/g)**	**T_c (°C)**	**ΔH_c (J/g)**	
Ctr	130.62	190.69	129.40	190.88	113.66	190.21	134.60
0.5%	130.35	180.84	129.03	187.12	114.71	182.62	-
1%	129.99	177.67	128.90	184.60	113.84	172.59	134.30
2%	130.78	184.15	128.62	183.97	115.13	166.19	-
3%	134.18	174.57	129.14	172.02	114.62	171.68	134.20
4%	129.26	173.88	128.85	180.36	114.70	179.15	134.24
5%	130.62	150.51	129.17	181.31	113.73	180.42	133.71

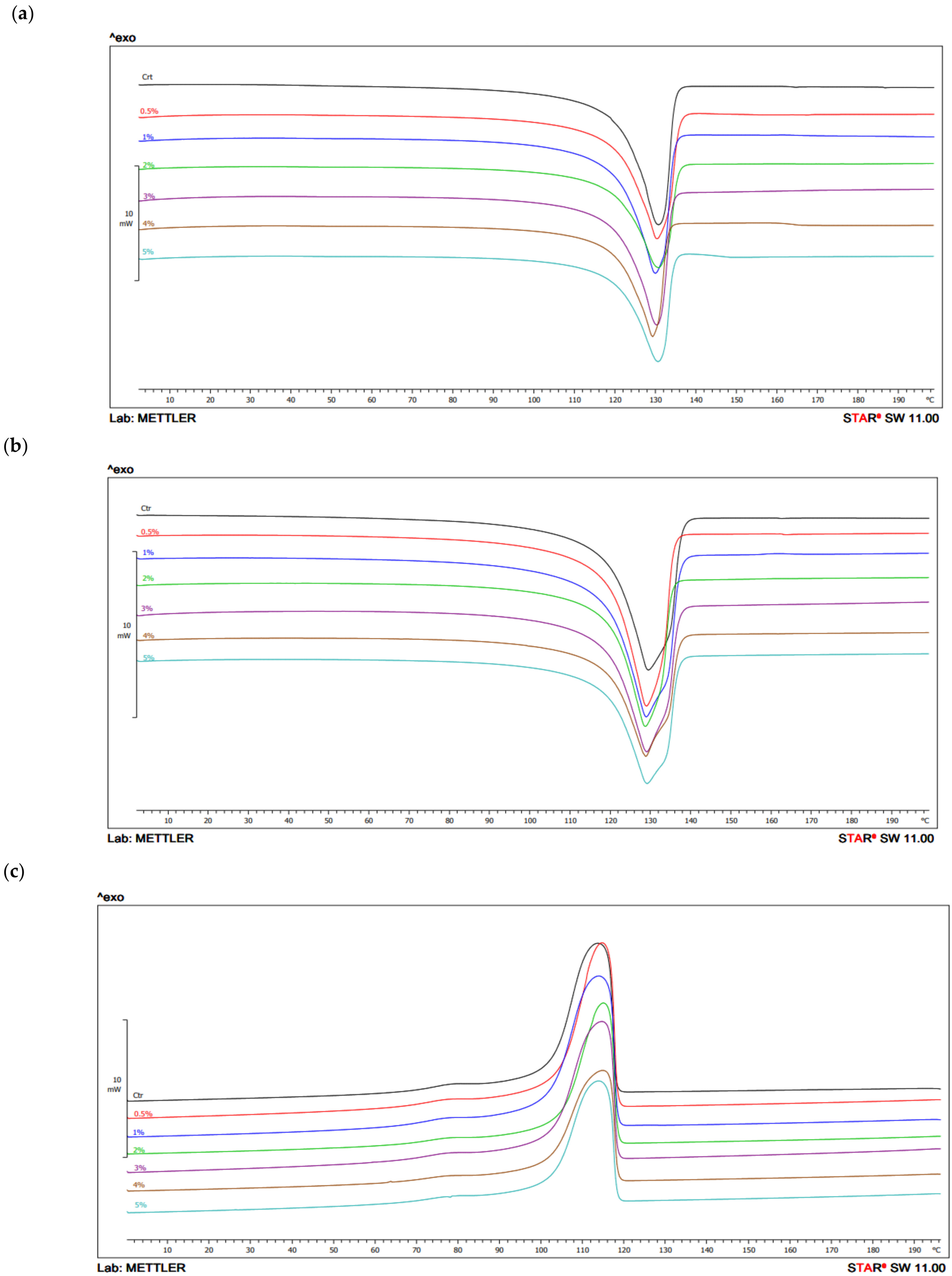

Figure 6. DSC thermogram: (**a**) first heating; (**b**) second heating; (**c**) crystallization.

In the second heating, T_m was in the range of 128.62 °C–129.40 °C. For the control sample, the T_m was 129.4 °C. The intensity of the second heating was wider than that of the first heating. ΔH_m were similar for samples with different biocide concentrations. The ΔH_m for the second heat ranged from 172.02 J/g–187.12 J/g, and for the control was 190.88 J/g. Similarly to the first heating, the highest ΔH_m was observed for the control sample without the biocide. For some samples, bimodal thermal changes were recorded (two endothermic peaks). The value of the additional peak was approximately 134 °C. For samples with 0.5% and 2% biocide concentrations, no second peak was observed (Table 2, Figure 6b).

The T_c range was 113.73 °C–115.13 °C. For the control sample, the T_c was 113.66 °C; the lowest value was observed for the sample with 5% biocide and the highest for the sample with 2% addition. The ΔH_c was in the range 166.19 J/g (sample with 2% concentration biocide)–182.62 J/g (sample with 0.5% biocide concentration). For the control sample, ΔH_c was 190.21 J/g. Various intensities were noted in the crystallization. As the concentration of the biocide increased, the intensity of the peaks decreased. The highest peak was obtained for the sample with a biocide concentration of 0.5%, and the lowest was for the sample with a biocide concentration of 4%. The intensity of the control sample was average compared to the other sample variants (Table 2, Figure 6c).

4. Discussion

The subject of the research was LDPE modified with a biocide containing metal nanoparticles: nanoAg, nanoCu, and nanoFe_2O_3. The strong biocidal properties of this biocide against bacteria and fungi have been proven in previous studies. The effectiveness of the applied biocide against both model and pathogenic bacterial strains was tested (*Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Legionella pneumophila*, *Salmonella enterica* subsp. *enterica*) and fungi (*Aspergillus brasiliensis*, *Saccharomyces cerevisiae*, *Candida albicans*, and *Penicillium expansum*) [29]. A very strong antimicrobial effect, almost 100% limiting the growth of bacteria and fungi, was found for samples containing 4% of the biocide. The biocidal properties of LDPE were undoubtedly influenced by the very good dispersion of the biocide, which was confirmed by the microscopic analysis described in previous studies [29]. Thus, the material has a good chance of being implemented in industrial production. No other studies of polymeric materials modified with a biocide containing nanoparticles of three metals (nanoAg, nanoCu, and nanoFe_2O_3) have been found in the literature. There is a lot of research on the biocidal properties of materials containing nanoAg, the effectiveness of which has been confirmed mainly against bacteria, with very significant differences in antibacterial effectiveness depending on the strain [42,43]. In turn, Bazant et al. [44] found high antibacterial effectiveness of the Ag-ZnO combination in polypropylene (PP) at a concentration of up to 5% by weight. In the study by Li et al. [45], a concentration of 5% biocide containing nanoAg was also effective against yeasts *Candida albicans*. Our research confirming the biocidal activity against a wide spectrum of both bacteria and fungi allows us to assume high antimicrobial effectiveness in real conditions, not only during laboratory tests. The necessary next stage of the research was to check the influence of the biocide addition on the other LDPE properties. Therefore, in the presented research, the influence of the addition of a biocide in a concentration from 0.5% to 5% on rheological properties assessed by MFR, density, water absorption, strength properties, chemical structure assessed by FTIR, and thermal properties assessed by DSC were checked.

Research shows that often even the smallest interference in the composition of the material or even the next cycle during material recycling directly affects the MFR value [46,47]. Also, in the presented research, it was found that the modification of LDPE with a biocide with a concentration >0.5% causes a decrease in this parameter, the most significant at 5% concentration (a decrease by approx. 25% compared to unmodified LDPE). However, different conclusions were obtained by Janczak et al. [48], who, by modifying LDPE commercial additives used for food protection in the food industry, did not find their influence on the MFR value even at a concentration of 5%. In turn, Chylińska et al. [49] investigated the effect (0.5–2%) of the biocide in polyvinyl chloride and even found a two-fold decrease in the MFR value.

Contrary to MFR, even at a 5% biocide concentration, the differences in LDPE density were $\leq$2%. Presumably, these are not changes that could significantly affect the processing processes and properties of the material obtained. The decrease in material density is related to the decrease in the degree of crystallinity. The more so that the melting enthalpy of the crystalline phase in the first heating decreased from 190 J/g to 150 J/g (Table 2). With the decrease in crystallinity, the amount of the amorphous phase increases, which slightly affects the decrease in density.

Water absorption is also an important aspect of products made of polymeric materials. Water absorption is extremely important, especially in the construction and food industries [50]. Even with the highest biocide content, the developed LDPE showed a slight decrease in absorbency compared to the unmodified LDPE. Due to the low water absorption, the material can be used for the production of elements of plumbing and ventilation systems and in places where materials are often exposed to faster degradation caused by exposure to climatic conditions with high humidity [51]. As indicated by Domínguez et al., a valued effect is that the biocide increases the hydrophobicity of the material, as it prevents the formation of biofilm [52].

A proportional decrease in tensile strength at break and an increase in elongation at break were observed with the increase in biocide concentration. Such an effect was not noted for lower concentrations (tensile strength at breaking at 0.5% of biocide and elongation at breaking at 0.5% and 1% of biocide). There was no difference in tensile strength at breaking between the 3% and 4% biocide concentrations. In our study, at 5% biocide concentration, the tensile strength at break decreased from 8.09 MPa to 4.01 MPa. A Similar result was found by Mousavian et al. [53] when examining the properties of LDPE foil with antibacterial thymol; they observed a decrease in tensile strength at breaking by approx. 5 MPa. The same research also noted an increase in elongation at breaking by approx. 20% [53]. In our research, an increase at a comparable level was noticeable at 3% biocide concentration, and at 5%, it was approx. 40%. Also, Rogalsky et al. [54] noticed changes in elongation at break at a similar level of 20–30% after adding the biocide in the form of polyhexamethylene guanidine hydrochloride. Some researchers, at lower concentrations of biocides, especially those containing metal nanoparticles, did not find a decrease in the strength of the polymer material or even find their improvement. This is undoubtedly dependent on the type of biocide. Jo et al. [55] showed an improvement in the mechanical properties of nanoAg-modified polypropylene film compared to commercial polypropylene, but the very high concentration of silver nanoparticles (290 mg/kg) resulted in their weakening. As pointed out by Mousavian et al. [53], active antimicrobial compounds can act as a plasticizer in biocomposites after placing them in the amorphous area of the polymer. Plasticizers tend to reduce the intermolecular strength of the polymer chain, which has a direct impact on the arrangement of the polymer chains and improves the flexibility of the material, which is manifested in increased values elongation at break [56].

The addition of a biocide has not been shown to affect the chemical structure of LDPE assessed by FTIR. Therefore, it is difficult with this method to clearly determine the presence of the biocide used. Similarly, Feng et al. [57] observed no significant changes in FTIR spectra between biocide-containing LDPE samples and controls. Meanwhile, among others, Calero et al. [58] used the FTIR method to characterize the functional groups and bond types present in chitosan film enriched with antibacterial titanium dioxide in order to finally confirm the presence of the biocide. The phenomenon we observed was explained by Mousavian et al. [53]. Antimicrobial agents are initially located in areas of lower density in the polymer structure and are not involved in the polymer-polymer chain. It has been proven that the crystal structure becomes weaker, and the tensile strength at the breaking of the film decreases.

In our study, no major changes in thermal properties were found, but a decrease in the enthalpy of crystallization and enthalpy of melting was observed in the presence of the biocide. The change in ΔH_m is related to the degree of crystallinity. This can be seen especially in the case of the first heating, where the melting enthalpy of the crystalline phase decreases by 27%. As a consequence, a greater share of the amorphous phase of the material may lead to a slight decrease in its density, which would be consistent with the density tests described by us earlier. A similar result was obtained by Siddiqui et al. [59]. Meanwhile, the addition of a biocide may reduce the melting point of the material [54,60]. No changes in thermal properties in relation to the additive were also observed by Zapata et al. [61], Abareshi et al. [62] and Jouni et al. [63]. Also, Li et al. [64] did not observe any significant changes in thermal properties after modifying the polymer material with an additive containing Ag. In some embodiments, including the control sample, two peaks of crystallization were observed. According to the literature, they indicate the existence of crystallites of different thicknesses, as well as a high degree of branching occurring in LDPE [59–65].

Summing up, the tested physicomechanical, chemical and thermal properties showed that the application of the biocide in concentrations of 0.5% and 1% has the least influence on the initial properties. In the remaining concentrations (2–5%), despite the lack of significant influence on the chemical structure, the biocide primarily influenced the strength properties and MFR. Previous research showed almost 100% antimicrobiological properties against bacteria and fungi of samples with the addition of 4% biocide. For such samples, the presented studies showed a decrease in MFR by approx. 17%, tensile strength at breaking by approx. 45%, an increase in elongation at breaking by approx. 25%, a decrease in density >2%, no increase in water absorption, and no significant changes in the chemical structure and in thermal properties in relation to LDPE without biocide. As shown in previous studies, partial inhibition of the growth of microorganisms was also observed at lower biocide concentrations in LDPE. Depending on the level of antimicrobial activity that we want to impart to the final material, the above results should also be taken into account.

5. Conclusions

Both the current and previous studies indicate that it is possible to develop an LDPE composite, for which the addition of a biocide containing metal nanoparticles, in addition to imparting properties limiting the growth of bacteria and fungi, will not significantly affect other properties such as rheological, strength, thermal and water absorption parameters. The 0.5% and 1% biocide content had the least influence on the tested parameters. Previous studies have shown that 4% of this biocide is the most appropriate for complete inhibition of bacterial and fungal growth. The lower concentration of the biocide also had a biostatic or biocidal effect against selected strains of microorganisms. Therefore, in order to reduce production costs or depending on the application, it is also worth considering a lower dosage of biocide. The presented research has shown that such content significantly influences, first of all, the decrease in MFR, tensile strength at break and increase in elongation at break. The knowledge about the antimicrobial effectiveness of individual biocide concentrations and their influence on other properties is undoubtedly useful in the development of new types of polymer materials.

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