RESEARCH ON INNOVATIVE FOILS
FOR AGRICULTURAL APPLICATIONS

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Abstract

The paper presents the results of a study investigating the impact of reduced graphene oxide (RGO) on selected mechanical and functional properties of LDPE foils. The foils were made by blow extrusion, with different amounts of RGO added to the granules prior to the extrusion process. The mechanical properties of foil samples were assessed in a static tensile test, and their bacterial resistance was tested. The impact of RGO on antibacterial interactions and the desirable mechanical properties of the foils was analyzed. The results of this study supported the selection of the most advantageous solution for industrial applications.
Introduction

Currently, due to EU requirements and the generally dynamic development of polymer processing, entrepreneurs producing plastic foils are looking for increasingly unusual and innovative solutions for these products (Siwek et al. 2010, Duda 2003). As an example, can be given materials with the content of additives that change their mechanical, physicochemical, structural properties, various types of blends with the addition of compatibilizers, polymers enriched with antimicrobial additives, or affecting their easier and faster degradation, and many others (Wenda et al. 2016, Wolska et al. 2017, Jalbrzykowski et al. 2018b, Liya et al. 2013, Łopacka 2013, Malinowska-Pańczyk et al. 2010).

One of the important activities in the field of packaging foils is the production of products with antimicrobial properties, while maintaining their maximally favorable mechanical characteristics (Falkiewicz-Dulik, Kowalczyk 2016, Juraszek, Grzesiak 2008, Zielecka et al. 2012, Gniazdowska et al. 2015). In order to obtain antimicrobial properties, the material is enriched with e.g. gold, silver or copper nanoparticles (Jalbrzykowski et al. 2018a, Liya et al. 2013, Łopacka 2013, Malinowska-Pańczyk et al. 2010, Malinowski 2015, Jalbrzykowski et al. 2018b, Jalbrzykowski 2019).

Currently, in the context of antimicrobial interactions, is observed a large interest of researchers in graphene oxide (Hebda, Łopata 2012, Xu et al. 2014, Yu et al. 2014, Yang et al. 2012, Kim et al. 2010). As it is commonly known today, graphene oxide is characterized by, among others extremely favorable mechanical (high mechanical resistance, tensile strength, considerable flexibility), electrical, conductive and bactericidal properties, biocompatibility etc. It is worth noting that this is a compound that combines many beneficial features and useful properties not found in such a rich combination, for any other substance. Certainly, this fact has contributed to many scientific works and a number of research and application experiments involving this substance (Li, Kaner 2008, Stankovich et al. 2006, Bai et al. 2010, Blake et al. 2007, Schwierz 2010).

Taking the above mentioned into consideration, this paper describes selected studies of polyethylene foils enriched with reduced graphene oxide (RGO). RGO was added to the polymer to check its effect on antimicrobial interactions and change of the mechanical properties of the foil produced.

Materials and research methodology

LDPE granules and reduced RGO graphene oxide were used for the tests (commercially available). Three-layered foils were produced by blow extrusion before testing. Due to the fact that the main purpose of the research was to assess the impact of RGO concentration on the analyzed characteristics, plastic
foils were made with the same parameters of the extrusion process, treating the values of these parameters as a constant quantity, having no impact on interesting issues. The following materials were prepared for testing: clean LDPE foil (without the addition of graphene oxide – Fig. 1a), foil with the addition of 2 g/l (Fig. 1b) and 3 g/l (g of graphene oxide / liter of granulate) (Fig. 1c). All foils were 40 µm thick (5 µm skin layers, 30 µm core, each layer was built the same).

The main purpose of the study was to evaluate the foils in terms of selected mechanical and microbiological properties. The assessment of mechanical properties was carried out using a Zwick/Roell testing machine in accordance with the methodology for testing tensile properties of plastic foils (ASTM D882). Escherichia coli (E. coli) was used to assess bactericidal properties. Before testing, the foil samples were sterilized, weighed and then exposed to Escherichia coli culture. It consisted of immersing them in BHI broth (from Oxoid) in which the E. coli bacterial strain with $10^5$ CFU/ml inoculum (CFU – bacterial colony forming unit) was suspended. Then they were placed in an incubator (temperature 37°C) under aerobic conditions. The samples were exposed for 72 hours to the bacterial strain. Bacteria were identified and propagated in accordance with applicable standards in microbiological diagnostics (Cryobank Mast Diagnostica). During the process, the number of bacterial cells was measured after 24, 48 and 72 hours. Tests were repeated three times.

**Research results and discussion**

Figure 2 presents selected results of studies on the impact of incubation time and RGO concentration on bacterial colony development. The obtained results indicate that irrespective of the RGO concentration, a longer incubation time of the bacterial colony means its larger growth (Fig. 2a). At the same time,
Fig. 2. The number of bacterial cells depending on: 

a – colony incubation time (general trends for all samples), 
b – type of foil tested (incubation time 72 hours)
the higher the RGO concentration, the lower the bacterial colony growth for samples incubated for the same amount of time (Fig. 2b). Generally, the results obtained confirm the beneficial effect of graphene oxide on the antibacterial properties of LDPE. This is a very beneficial information, especially since this type of foil is a common material for packaging food products. It should also be remembered that despite the antimicrobial nature of such material, its beneficial effect is probably effective for a limited time. The point is that the longer the material is exposed to *E. coli* strains, the larger the clusters of these bacteria colonize on its surface. On the other hand, if *E. coli* settled on pure LDPE, the growth of bacterial colonies would be even greater. Generalizing this paragraph of the work, it can be stated that the addition of RGO to foil material certainly brings benefits in the form of increased resistance to bacterial effects, e.g. packaging for food products.

![Image](image_url)

Figure 3. Breaking force value depending on the type of foil tested:

1 – LDPE, 2 – LDPE + 2 g/l, 3 – LDPE + 3 g/l

Figure 3 shows the impact of RGO on the mechanical characteristics of LDPE. The graph presented illustrates the overall positive effect of graphene oxide on foil behavior during stretching. However, in the case of foils with RGO content of 2 g/l, a significant increase in relative elongation was obtained, while in the case of 3 g/l contents, a slightly smaller increase in elongation, but an increase in the value of the force causing the foil to break. This means that RGO generally improves the mechanical properties of the foil. In addition, it is likely possible to manipulate the ranges of individual features. This aspect also has its significance, because in addition to the fact that while maintaining the current thickness of the foil it is possible to get more durable packaging and also produce thinner foils basing on the fact that thanks to RGO it has better mechanical characteristics. This creates the possibility of more economical foil
production by producing thinner products. Economical production means higher sales profits. In addition, due to more economical use of the base material, we affect the environmental protection as a result of reduced exploitation of fossil sources being a raw material for production, among others technical plastics.

Conclusions

The paper presents selected results of testing the LDPE foils useful properties. The foils were enriched with reduced graphene oxide to improve its mechanical properties and assess the impact of RGO on the antibacterial properties of the foil. The research and analysis of the results obtained allowed to formulate the following general conclusions:

1. A favorable effect of RGO content on the examined features of LDPE foil was found. In general, it can be seen that the higher the RGO concentration, the better the antibacterial resistance and better mechanical characteristics of the foil.

2. In relation to studies on the impact of RGO on antibacterial interactions, it can be seen that the higher the RGO concentration, the smaller the bacterial (E. coli) colony growth, the longer the foil is exposed to bacterial interactions, the unfortunately the larger the bacterial colony growth. However, the presence of graphene in the film is no doubt a barrier for the bacteria.

3. In relation to testing the mechanical properties of the RGO enriched foil, it can be stated that the prepared samples have revealed the situation when it is possible to achieve either greater material elongation with slightly lower tensile strength and breaking strength, or less elongation with general improvement of the material’s mechanical properties. This means that with a properly prepared polymer composition, it is possible to control the ranges of selected mechanical properties of the foil.

4. By improving the mechanical properties of the foil, in this case, by enriching it with an RGO nanoadditive, the possibility of producing packaging materials with increased mechanical properties arises. At the same time, it is possible to produce foils with similar mechanical properties, but thinner (however, this has not been studied). The production of thinner films saves the polymer raw material, and thus the technology is more environmentally friendly, because it reduces the burden on natural deposits, which are the basis for the production of, among others technical polymers.
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