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The changes of LD-PE films after exposure in different media

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1. Introduction

Nowadays non-metallic and metallic materials are very popular. Apart from these materials, plastic materials gain ground. Plastic materials have important properties which include low weight, high durability, corrosion resistance, and external coating. Plastic is easily treatable and it is the reason for the high production of plastic products (Hazlinger et al., 2010; Ovsik et al., 2019; Habrman et al., 2019; Vašina et al., 2018).

A large number of plastic products means a considerable problem with its recycling and accumulation of plastic waste. Accumulation of packing waste has an impact on the environment (Bulatovic et al., 2019; Raz et al., 2017; Pacana et al., 2016; Urban, 2019; Benaissa and Benabdelhafid, 2010).

Polymers are usually recycled only two or three times because of the mechanical properties of polymer material decrease in consequence of thermal degradation. Consequently, polymers cannot be recycled endlessly (Gaňa et al., 2019; Hazlinger et al., 2010).

This research dealing with degradation of LD-PE films is a part of the project Refillcase which offers the solution for LD-PE films recycling. The idea of this project is based on application of LD-PE films to the reversible bottles, which can be used 50 times. Moreover, the LD-PE films are recycled 2 or 3 times. This technological solution has its application in the pharmaceutical, agricultural, chemical and petrochemical industries. It is plastic packing with the possibility of packing and unpacking after use (Refillcase, 2018).

Polyethylene is a thermoplastic polymer which has a variable crystalline structure with the share of crystalline phase $50 \div 85$ %. Density of polyethylene ranges from 0.84 to 0.90 g.cm-3 . Polyethylene is a universal and stable material which absorbs a little amount of water. Mechanical and physical properties depend on the range and type of chain branching, crystalline structure and molecular weight (Noo-runnisa Khanam et. al., 2015).

The experimental material is made of low density polyethylene which is one of the ordinary polymers. LD-PE has universal application. It is able to apply in wrapping industry, agriculture, medicine, automobile industry, chemical industry. LD-PE is characterized by low density, which is caused by a high number of side-chain CH² (Liptáková et al., 2012).

Polyethylene is produced by polymerization. It is a process when a huge number of little molecules of monomers are connected into the high molecular chain. The secondary product is not formed during the chemical reaction (Katona, 2017).

2. Experimental

LD-PE film is a multi-layered material with high hot shrinkage and good tensile strength in both directions (longitudinal and transverse). The LD-PE film is a viscoelastic material whose properties mainly depend on the structure and chemical composition (Gaňa et al., 2019).

The material is dedicated for wrapping products of the consumer industry and for a collated package of goods like external protective packing. Tests were executed on original LD-PE films (original – O) and applied LD-PE films (applied – A).

Applied films have been affected by the selected media (Fig. 1). LD-PE films are applied by the medium of vacuum into polyethylene bottles in real operating conditions. Polyethylene bottles are produced through blowing. The goal of the research is to compare the properties of the original film and the applied film after exposure in three different media: Savo for the disinfection, Savo as a Saponate for dish washing and Coca-Cola which belongs to the most popular drinks in the world. The intensity of degradation influence of used media can be evaluated by water absorption, evaluation of melting temperature and the evaluation of the macrostructure. Experimental media have different pH. Coca-Cola has acid environment ($pH =$ 2.23), Savo disinfection has $pH = 13.37$ and pH of Savo Saponate is 3.35.

Fig. 1. Scheme of experimental material

Individual LD-PE film is colourless and plain. LD-PE films are biologically decomposable in compost. The investigated polyethylene films have a thickness of 50 ± 2 µm welded in a longitudinal direction (Refillcase, 2018).

Between used measurements of LD-PE film belong to water absorption and allocation of the temperature of the melting point.

Water absorption is the ability of plastic material or polymer to absorb humidity from the surrounding environment.

Factors of water absorption:

- morphology and type of plastic,
- properties and type of additives,
- fiber fraction and orientation (in composites),
- relative humidity and temperature,
- length of exposure (Vasile, 2005).

The presence of humidity in the material structure also influences dielectric properties and thermal insulation (Mleziava, 2000).

The water absorption of LD-PE films is measured in cold (method A) and boiling water (method C). The method is based on the weight increase measurement of the samples. At least three samples are immersed in rated time. They should have the same dimensions and shape.

Method A is characterized by the increase of weight in cold water of temperature 20 ± 2 °C for 24 hours. After this time samples were dried, cooled down in distilled water and weighed with an accuracy of 1 mg. Water absorption in mg is calculated (1) using method $A(X_1)$ and method $C(X_2)$ according to formula 1:

$$
X_{1,2} = m_2 - m_1, \tag{1}
$$

where m_1 is weight of the sample before immersion and m_2 is weight of the sample after water exposure.

Method C is characterized by the increase of weight in boiling water of temperature 100 °C for 30 ± 1 minutes. After this time samples have to be dried, cooled down in distilled water like for method A.

The melting temperature is the temperature at which the solid and liquid phases of a given substance are in equilibrium. In laboratory practice, the melting point is determined by directly observing the phase transformations as the amount of the test substance is heated gradually. To determine the melting point a capillary or microscope may be used. When determining the melting point under a microscope, the temperature at which the crystals placed between thin glass slides begins to melt on an electrically heated metal plate. The instrument is called the Kofler block. The Kofler block consists of the around electrically heated plate - a heating table with a sliding device and a special microscope. By heating, sharp edges of samples are rounded. Temperature changes and edge rounding are observed simultaneously in the field of view of the microscope.

3. Results and discussion

The test of water absorption was carried out by method A and C. Measurement shows that the weight of the original LD-PE film was increased by the selected media after 3 months. Averaged values for method A are in Table 1 and averaged values for method C are in Table 2.

Table 1. Values of water absorption (WA) in cold water of LD-PE influenced by the medium

Sample	Surface (cm ²)	Sample weight (mg)		
		Before (WA) m ₁	After (WA) m ₂	$X_{1,2}$ (mg)
Cold water				
O LD-PE	2.83	12.60	12.67	0.07
Savo disin- fection	1.43	7.62	7.66	0.04
Savo Saponate	1.52	8.22	8.29	0.07
Coca-Cola	1.87	8.72	8.74	0.02

Table 2. Values of water absorption (WA) in boiling water of LD-PE influenced by the medium

LD-PE film absorbed some part of the fluid and, therefore, film was increasing its original weight in cold water. In cold water came to an increase in weight in all samples. It represents water absorption from 0.2 to 1%.

In the boiling water the LD-PE film affected by Savo disinfection had reduction of own weight. Water absorption in boiling water was from 0.4 to 1 % for other samples.

Water absorption of LD-PE in cold and boiling water in mg is shown in Fig. 2. It is valued after 3 months of exposure. Lower water absorption in boiling water compared to cold water had an LD-PE film affected by Savo disinfection and Savo Saponate. LD-PE film affected by Coca-Cola has the highest water absorption in boiling water.

Fig. 2. Water absorption of LD-PE film influenced by medium in units of mg after 3 months

Determination of temperature of melting point by Kofler block did not show any significant differences of melting temperature of LD-PE films after 3 months of exposure. The arithmetic values of temperature (Table. 3) for individual LD-PE films differ only minimally from the tabulated values. The tabulated values of LD-PE films are in the range of $100 \div 115$ °C.

The macrostructure of LD-PE films was documented using the ZEISS optical microscope. The measured area of the samples was of 1 cm². The evaluation of macrostructure was realized in a program AxioVision LE64.

Fig. 3. Macrostructure of LD-PE films before (a) and after exposure (b, c)

Based on the experiment is able to observe the influence of media. On the surface of original LD-PE film (Fig. 3a) some straps as a result technological process can be seen. Savo disinfection (Fig. 3b) causes formation of pores, because Savo contains small amount of chlorine. The influence of Savo Saponate on the structure of LD-PE film is documented in Fig. 3c. The most destroyed LD-PE film after exposure is LD-PE, which has been affected by Coca-Cola (Fig. 4).

Fig. 4. Macrostructure of LD-PE film after exposure in Coca-Cola

4. Summary and conclusion

Degradation of polymers depends on mechanical loading, temperature, chemistry and present microorganism. The experiment shows the following conclusions:

- Polyethylene has good resistance to low and elevated temperatures.
- At higher temperatures, it is more sensitive to attack by aromatic and chlorinated hydrocarbons.
- The water absorption of the LD-PE film in the water is up to 1 %.
- The chlorine in Savo disinfection caused a reduction in the film weight in the boiling water.
- The melting point of the material is in the range of 100 to 115 ° C, which corresponds to the tabulated melting temperature values of LD-PE.
- Macrostructure affected by Savo Saponate is the most unchanged compared to the original LD-PE film.
- It is possible to use LD-PE film for the transport of Savo Saponate after exposure, but it is necessary to practice the long term tests on LD-PE films.
- For further research, it is recommended to study effect of chosen media a longer time of exposure.

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不同介质曝光后 LD-PE 膜的变化

關鍵詞 聚乙烯 回收利用 LD-PE 膜 吸水率 熔点温度 摘要 这项工作涉及聚合物,尤其是聚乙烯的研究。 其生产,类型,属性和用途。 实验部分评估了 在各种暴露条件下可重复使用的聚乙烯薄膜的性能变化,并选择了最适合其应用的介质。 由 低密度聚乙烯(LD-PE)制成的薄膜受到具有不同 pH 值的侵蚀性介质的影响,特别是 Savo, Saponate 和可口可乐。 在 LD-PE 膜上进行了以下测试:吸水率和熔融温度评估。 进行的测试 表明,用过的介质中用于 LD-PE 膜的最具腐蚀性的介质是可口可乐。 LD-PE 薄膜如包装在运输 的容器上的最有效应用是洗碗液,即皂苷。