Evaluation of the protective PE foils properties after exposure in various environments

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Abstract: The subject of the research is testing of the polyethylene foils (PE) degradation exposed in various environments. The foils serve to protect transporting flasks and containers for the possible periodic repeated application. The experimental foils were exposed in three various aggressive environments (Coca-Cola, chloride cleaner and detergent) with different pH values. The time of exposure was 3 and 6 months. To study the changes of the PE foils properties, the rheological and tensile strength measurements were performed, as well as the microscopy of the surface. By the rheological measurements the changes of viscoelastic properties were determined. The rheological parameters (e.g. modulus of elasticity and viscosity, complex viscosity) react to the structural changes in the PE foils. The strength properties are also affected by the experimental environment. In this case the strength parameters were different in longitudinal and transversal directions.

1. Introduction

Polyethylene is a plastic material with long-term mechanical properties, easy treatability and weldability. Due to these properties, the light density polyethylene (LDPE) foils are convenient for protection of transit plastic containers. Application of the LDPE foils, as wrapping of plastic containers transported in multiplex media, makes possible their cyclic using. Nowadays, the containers are determined only for one usage and after it they are discarded. By application of the wrap foils the economical as well as environmental effect can be achieved. Decreasing of plastic waste is very urgent in this era. For eventuality of multiple times using of plastic container the LDPE foils must have optimal properties to be able protect the containers against contamination and after using to be safely removed.

Degradation of polymers according to affecting factors (temperature, mechanical loading, present microorganism, chemicals etc.) can be shown like thermo-degradation, biodegradation, oxidation, mechanical degradation and chemical degradation. Because physical and chemical activity of plastics they react with environment and degradation occurs. These processes in polymers can evoke the macromolecular splitting, crosslinking, monomer production, low molecular weight substances, transition of substituents etc. and thus change their useful properties [1, 2]. The chemically active substances can cause irreversible changes, which affect their chemical, physical and mechanical behavior [3–5]. The intention of this research is studying of the LDPE foils reaction to the chosen environments. Studying of various environmental effects on the LDPE foils structural changes was realized by rheological measurements evaluating the viscoelastic properties, tensile strength test and electron microscopy.
2. Experimental
The investigated foils are made of the light density polyethylene of thickness 50 μm ± 2 μm, welded in longitudinal direction. Low density is caused by high number of the side chain CH₃. Crystallinity is about 40–50%. Experiments are focused on investigation of viscoelastic and mechanical properties of the LDPE foils after their exposure in the coca cola marked C (acid environment, pH = 2.23), disinfectant marked S (the main component is the sodium hypochlorite, pH = 13.37) and tenside cleaner marked SR (pH = 3.35). Foil samples were exposed for 3 and 6 months in all the three media. After the exposure, all the evaluated parameters were compared with the unaffected foil.

Rheology is a very convenient research method of material changes activated by degradation. Measurements of the parameters representing the viscoelastic changes affected by structural modification after degradation are studied. This method is well understandable for technics, specimen preparation is easy and the measurement conditions can be exactly repeated.

Rheology is the science of flow behavior of liquids and the deformation behavior of solids, as well. Plastics are considered to be viscoelastic materials, exhibiting both viscous and elastic properties, which are changing with temperature and time. These changes can be measured as a response of the material to deformation by periodic forces (during the forced vibration or small-amplitude oscillatory shear). Stress and strain are not in phase, the strain delays behind the stress by a phase angle. If the oscillatory shear is sinusoidal, then the shear stress is equal to Eq. (1):

$$\tau(t) = \tau_0 \cdot e^{i\omega} = \tau_0 (\cos \omega t + i \cdot \sin \omega t)$$

where $\tau_0$ – stress amplitude, $\omega$ – angular frequency, $t$ – time and $i = \sqrt{-1}$.

The complex shear modulus $G^*$ is defined as:

$$G^* = \frac{\tau(t)}{\gamma(t)}$$

Equation (2) can be resolved into two parts:

$$G^* = G' + i G'' = \frac{\tau_0}{\gamma_0} (\cos \delta + i \cdot \sin \delta)$$

The first, $G'$ is in phase with strain and the second $G''$ is out of phase with strain for angle $\delta$. Therefore, the two dynamic moduli can be defined as:

$$G' = \frac{\tau_0}{\gamma_0} \cos \delta$$

$$G'' = \frac{\tau_0}{\gamma_0} \sin \delta$$

The $G'$ is called the storage modulus and $G''$ is called the loss modulus. The $G'$ value is a measure of the deformation energy stored by the sample during the shear process. Thus, it represents the elastic behavior. The $G''$ value is a measure of the deformation energy used up by the sample during the shear process and therefore it represents the viscous behavior of a material.

The complex viscosity $\eta^*$ is defined by the equation:

$$\eta^* = \frac{\tau(t)}{\dot{\gamma}(t)}$$

The described parameters very sensitively react on the structural changes evoked by reactions with environment [6–8]. By the Frequency Sweep test (FS) – Two-plates-Mode the viscoelastic properties were examined for the original LDPE foil and after 3 and 6 month of exposure in the mentioned media. The measured characteristics were: Complex viscosity $\eta^*$ (Pa s), storage modulus $G'$ (Pa) and the loss modulus $G''$ (Pa). The measurements were made by the Physica Rheometer MCR 301 with...
a convective thermal device CTD 450 by Frequency Sweep test to study changes of viscoelastic properties, changes of molecular mass and its distribution after various types and time of exposure. The principle of the mentioned evaluations is shown in figure 1, where, by drift of the intersection point of the modulus, a character of structural changes affected by environment exposure can be determined [8–10].

![Figure 1](image1.png)

**Figure 1.** Determination of selected material characteristics from the curves obtained by the FS test.

3. Results

The results are shown in figures 2–4. The effect of Coca-Cola on the measured viscoelastic properties was not very strong. The shift of the $G'$ and $G''$intersection point after 3 month exposure is practically in the same position as in the original foils. The small structural changes are observed after 6 month exposure. The shift to the left signalized increasing of the average molar mass. It is confirmed by the advanced complex viscosity.

![Figure 2](image2.png)

**Figure 2.** Changes of viscoelastic properties of the LDPE after 3 and 6 months in the coca cola (C).
Entirely different reaction of the LDPE foils to the disinfectant is visible in figure 3. Already after 3 months the evident fall of the average molar mass, as well as fall of the complex viscosity were observed. After 6 months, the changes were of the same character but of higher intensity. For three months the LDPEs were resistant in the tenside cleaner. After 6 months the shift of complex viscosity to lower values is visible and the decreasing of the average molar mass, as well (figure 3).

Figure 3. Changes of viscoelastic properties of the LDPE after 3 and 6 months in the disinfectant (S).

Figure 4. Changes of viscoelastic properties of the LDPE after 3 and 6 months in the tenside cleaner (SR).

The attack on the LDPE foils was observed on the surface by SEM (figure 5) already after the 3 month long exposure. It is evident that character of reaction in all the testing environments is different. The LDPE foils exposed in Coca-Ccoca and tenside cleaner are attacked very unevenly but by the disificant the attack is distributed quite uniformly over the whole surface.
The tensile strength characteristics of the PE are sensitive to structural changes. This is because the crystalline regions significantly affect the modulus. The other effect observed is that of strengthening due to the molecular orientation imparted during the film blowing. This is because of the molecular grade tensile properties are higher in the direction of the covalently bonded carbon–carbon chain than in the transverse direction, which is dominated by the much weaker van der Waals bonds [11–13]. The effect of various exposure environment and exposure time on the LDPE mechanical properties foils in the longitudinal and transverse directions were examined. The tensile strength at break was determined according to STN EN ISO 527, with a jaw speed of 50 mm min⁻¹. In each direction (longitudinal – L, transverse – T) 5 samples were tested, the results being the average of 5 measurements. The tensile strength after 3 months of exposure increased in all the environments compared to the tensile strength of the original sample (figure 6). A slight decrease of tensile strength at break in the samples exposed in Coca-Cola and detergent after a 6-months exposure was observed. On the contrary, the disinfectant caused the tensile strength increase approximately 2.5 times compared to the original foil. Figure 7 shows the change in tensile strength at break depending on the environment and exposure time. These statements are supported by results of the tensile strain at break measurements (tables 1 and 2).
Figure 6. Dependence of the breaking strength of the LDPE film on exposure environment and exposure time in longitudinal direction.

Table 1. Change in tensile strain at break in longitudinal direction depending on the exposure environment and exposure time.

|       | C – L $\varepsilon_B$ (%) | S – L $\varepsilon_B$ (%) | SR – L $\varepsilon_B$ (%) |
|-------|---------------------------|---------------------------|---------------------------|
| Original - L | 276.02                   | 276.02                   | 276.02                   |
| 3 months     | 360.99                   | 562.44                   | 496.39                   |
| 6 months     | 705.86                   | 460.20                   | 715.05                   |

Figure 7. Dependence of the breaking strength of LDPE film from exposure environment and exposure time in transverse direction.

Table 2. Change in the tensile strain at break in transverse direction depending on the exposure environment and exposure time.

|       | C – T $\varepsilon_B$ (%) | S – T $\varepsilon_B$ (%) | SR – T $\varepsilon_B$ (%) |
|-------|---------------------------|---------------------------|---------------------------|
| Original - T | 164.82                   | 164.82                   | 164.82                   |
| 3 months     | 149.50                   | 215.93                   | 301.12                   |
| 6 months     | 494.58                   | 256.14                   | 543.83                   |
4. Conclusions
According to results of rheological measurements in the whole volume of the molten tested samples after 3 months the negligible structural changes were observed in environments with the low value pH (Coca-Cola, tenside cleaner). The disinfectant with the pH 13.37 evidently affected the viscoelastic properties. After the 6 month exposure the changes of viscoelastic properties were determined in all the testing media. The clear decreasing of the complex viscosity is caused by the disinfectant and the tenside cleaner media. The growth of their plasticity supports the position of the intersection point of the moduli ($G'$, $G''$).

Non-uniformity of the surface attack by the testing media can be caused by the different sensitivity of amorphous and crystalline phases in the LDPE foils.

Evaluation of the tensile strength test results are more complicated because they are influenced by the loading direction (longitudinal, transversal), as well as by regularity of the surface attack of media.

The tensile strength of the LDPE foils increased in all the media already after 3 month exposure in both tested directions. It can be caused by physical effect of the liquid media which penetrate to intermolecular area.

The physical and chemical attack of the LDPE foils by the testing media did not disturb their compatibility after 6 months exposure.

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Acknowledgements
This work was supported under the project of Operational Programme Research and Innovation: Research and development activities of the University of Zilina in the Industry of 21st century in the field of materials and nanotechnologies, No. 313011T426. The project is co-funding by European Regional Development Fund.