

Resistance of Polyethylene Terephthalate Foil to the Influence of Temperature and Humidity

Jovan Radulović, BSc (Eng)¹⁾

The resistance of polyethylene terephthalate foil against the influence of change of temperature and humidity was investigated. The physical, mechanical and optical properties of polyethylene terephthalate foils before and after exposure to the mentioned parameters are presented. The factors affecting the change of characteristics of this material were described.

It was concluded that decrease of tensile strength and tearing force had occurred, but material did not degrade in such manner that cracks, ie. cracking of polyethylene terephthalate foil, would appear.

Key words: polymers, thermoplastic polymers, polyethylene terephthalate, foils, temperature effect, humidity effect, material properties.

Introduction

POLYMERS represent materials acceptable in all areas of human activities in the whole world. It is considered that there are thousands of polymeric materials. Each polymer is characterised by a unique set of different properties [1].

Synthesis of polyethylene terephthalate

Polyethylene terephthalate is a thermoplastic polymeric material of the polyester family. The production of this material was patented in the middle of the previous century in England.

All methods of esterification known in organic chemistry have been applied for the preparation of polyesters, among which is polyethylene terephthalate.

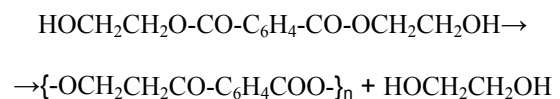
It is possible to obtain a monomer of polyethylene terephthalate by the esterification reaction between terephthalic acid and ethylene glycol with water as a byproduct, or the transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol as a byproduct. Polymerization is a polycondensation reaction of monomers with ethylene glycol as a byproduct, residual in the polymer.

Practically, polyethylene terephthalate is prepared by polycondensation process of dimethyl terephthalate and ethylene glycol in two steps [2]:

1. Firstly, an intermediate compound bis (hydroxy ethyl) terephthalate is obtained with elimination of methanol:



2. Secondly, the polyethylene terephthalate is obtained from the intermediate compound with the elimination of ethylene glycol:



A repeated unit of polyethylene terephthalate is shown in Fig.1.

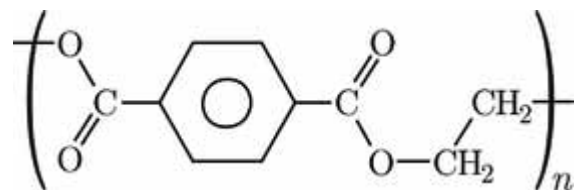


Figure 1. Repeated unit of polyethylene terephthalate

The polyester industry occupies the third place of the world polymer production (with about 18%), after polyethylene and polypropylene production industry. Polyethylene terephthalate is used in the production of fibers, bottles, foils, etc. There are types of this polymer reinforced with glass fibers [3].

In practice, polymeric materials are exposed to the influence of different factors which can lead to the change of physical, mechanical, optical, acoustic, thermal and other characteristics. Deterioration of polymeric characteristics, caused by chemical reactions, is called degradation. These reactions involve bond ruptures in the backbone of the macromolecule as well as weakening of the secondary intermolecular bonds. The degradation of linear polymers, polyethylene terephthalate being among them, is primarily caused by bond rupture in the backbone, while the chemical reactions in pendant groups and side chains have less influence [4,5].

The results of investigating the resistance of polyethylene terephthalate foil against the influence of the change in temperature and humidity, ie. which level of degradation of the mentioned polymer was provoked by

¹⁾ Military Technical Institute (VTI), Ratka Resanovića 1, 11132 Belgrade, SERBIA

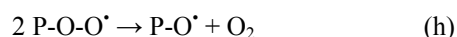
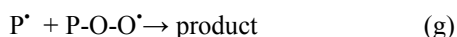
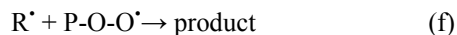
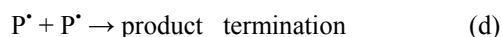
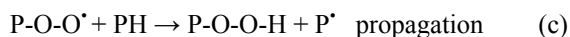
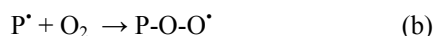
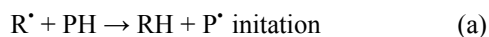
these factors, are presented in this paper.

Although there are more different modes of polymeric degradation, thermal degradation and influence of humidity will be discussed here.

Thermal degradation occurs when an elevated temperature causes chemical reactions in polymer, without the simultaneous involvement of other factors. It is often rather difficult to distinguish only thermal and thermo-chemical degradation. Polymeric materials are rarely chemically "pure". Impurities or additives might react with the polymeric matrix, if the temperature is high enough [4].

Organic macromolecules, as well as low molecular weight organic molecules are stable below a certain temperature level. Thus, at common temperatures bond scissions do not occur. However, in condensed systems, vibrational energy is rather rapidly dissipated among all molecules and all bonds. But, if the energy distribution is Maxwellian, a certain fraction of bonds in some molecules will be in the excited vibrational state corresponding to energies significantly higher than the average energy. The fraction of highly vibrationally excited bonds increases with temperature increase. It might, then, occasionally happen that a repulsive energy level of two parts of macromolecules i.e. bond breakage occurs. Slightly elevated temperatures can initiate chemical reactions (e.g. oxidations) which proceed more rapidly than at ambient temperature. Frequently, significant degradative conversion can be achieved at slightly elevated temperatures. This is, therefore, especially important if the chemical reactions are of chain type by free radicals mechanism. Scissions of chemical bonds under the influence of heat are a result of overcoming bond dissociation energies. The free radical mechanism of oxidative main-chain scission of linear polymers is shown at scheme 1[4].

Scheme 1: Oxidative main-chain scission of linear polymers



where are:

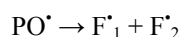
PH - macromolecule,

R[•] - high or low molecular weight free radical generated by decomposition of the polymer or an additive,

P-O-O[•]- peroxy radical,

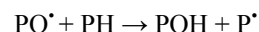
P-O[•] - oxyl radical.

Oxyl radical can play a deleterious role with a respect to physical-mechanical properties, when a main-chain rupture (so called β-scissions) occurs, what can be represented, in general form, by equation:



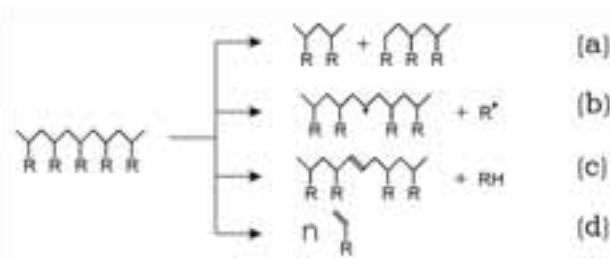
where F₁[•] and F₂[•] denote fragments.

The fragmentation process compete with the hydrogen abstraction process:



Chemical changes occurring during thermal degradation of polymers are scission of bonds in main chains, rupture of bonds in side chains and, at the end, evolution of gaseous products of low molecular weight. Linear polymers, for example, of polyolefin type decompose forming large amounts of monomers. This process, which is more significant at higher temperatures, is devoted as "depolymerisation". Strong temperature dependance of the rate of depolymerisation is due, mainly, to an increase of the rate of initiation.

Scheme 2 depicts main reactions occurring during thermal degradation of polymers [4].



Scheme 2: Main reactions during thermal degradation of polymers

The main reactions during thermal degradation of polymers are:

- reaction of bond scission in the main-chain of polymer (a),
- reaction of bond scission of side groups (b),
- reaction of elimination (c)
- reaction of depolymerization (d).

Most polymers contain "weak" bonds which are expected to break with higher probability than "strong" bonds. Compositions of synthetic polymers never correspond entirely to the molecular formula. Polymers, utilized for production of plastics goods, contain chemically incorporated "impurities" which very often function as "weak" links.

Ingredients found in commercial samples of polyethylene terephthalate are presented in Table 1 [5,6].

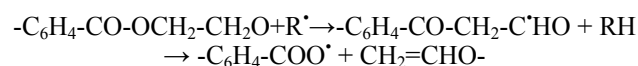
Table 1. Content of ingredients in commercial samples of polyethylene terephthalate

Ingredient	Content
Sb	from 20 ppm to 500 ppm
Zn	from 10 ppm to 250 ppm
Mn	from 10 ppm to 300 ppm
Ca	from 10 ppm to 250 ppm
P	from 10 ppm to 200 ppm
Ti	from 0,01 % to 0,1 %
SiO ₂	from 0,02 % to 0,5 %

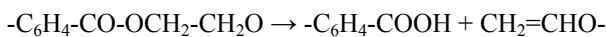
These elements can initiate forming of radicals in polymer and represent, in a way, a "weak bond" in materials.

Briefly, main products of thermal degradation of polyethylene terephthalate are carbondioxide, acet aldehyde and terephthalate acid.

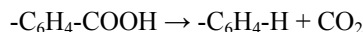
Degradation starts with the transfer of the proton from the β-C atom and continues by the elimination process:



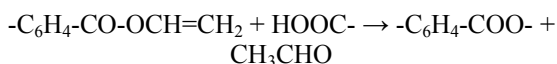
A following reaction is possible:



Carbon dioxide is produced by decarboxylation of carboxylic acid or carboxylic radicals:



Acetaldehyde is produced by acidolysis which leads to forming anhydride links:



Humidity i.e. water has important influence on polyethylene terephthalate properties.

Polyethylene terephthalate is, owing to its structure, hygroscopic material, meaning that it naturally absorbs water from its surroundings.

Changes on molecule i.e. macromolecule level can lead to macroscopic changes that can be registered by senses. Discoloration of color products and "fish-eye" formation can be observed visually. It is possible, in some cases, to detect smell of acetaldehyde, which is similar to fruity smell.

During an examination of polyethylene terephthalate it was concluded that hydrolysis process takes place much faster than oxidative and thermal degradation [7]. It is stated that there is a possibility of excitation of the carbonyl chromophore group, which then can react with water in the photohydrolytic process. Exsiccated groups can take place in the process, which leads to colored species formation i.e. a yellow colour appears. If there is a small quantity of water, then the predominant path of reaction would be color formation. If, however, there is much higher concentration of water, a photohydrolysis takes place and colorless products appear [8].

Recent investigations pointed out that in semicrystalline polyethylene terephthalate there are two amorphous phases: free amorphous phase and constrained amorphous phase [9].

Hydrolysis occurs only in the amorphous phase (i.e. phase permeable to water) and causes the cutoff of ester bridges, which leads to decline in both the degree of polydispersion and the average molar mass number [10].

It is noted that in polyethylene terephthalate, exposed to a relative humidity greater than 80 % at room temperature, a decrease of glass transition temperature occurred and imperfect crystals were formed [3].

It is considered that during simultaneous action of water and high temperature, besides a simple diffusion process, the following also occur:

1. hydrolysis of the macromolecular chains, which leads to the formation and migration of low-molecular-weight chains,
2. hydrophilisation, which tends to increase the equilibrium water uptake through the development of local or overall swelling and plasticisation (or softening) of the polymer, and
3. interfacial decohesion which induces a degradation of the material [11].

Experimental

Investigations and measurements in this paper are planned in a way to examine influence of changes in temperature and humidity on polyethylene terephthalate foil properties.

Material, external influences and methods of determination

Material used in this experiment is stabilized biaxially oriented polyethylene terephthalate foil, trade name YUBORLEN, produced by a polyester foil plant, Bor.

The term *external influences*, in this paper, refers to the overall influence of treatment which comprises influence of high temperature, influence of low temperature and, at the same time, influence of high temperature and humidity.

Comparison of the values of the examined properties of polyethylene terephthalate foils before and after exposure to the mentioned treatment pointed out the influence of temperature and humidity [12].

A polyethylene terephthalate foil was exposed to influence of temperature and humidity according to the following procedure:

1. a polyethylene terephthalate foil was placed in a chamber the temperature of which was +50°C and kept at this temperature for 14 days i.e. 336 hours,
 2. after the mentioned time, the chamber heating was switched off, the chamber door was opened and the polyethylene terephthalate foil was air-cooled to ambient temperature, which lasted for about 0.5 hours,
 3. after the ambient temperature was reached (in this case +18°C), the chamber door was closed and the polyethylene terephthalate foil was cooled to a temperature of -30°C which lasted for about 1 hour. From the moment when this temperature was reached, the polyethylene terephthalate foil was kept for 14 days i.e. 336 hours,
 4. after the mentioned time, the chamber heating was switched off, the chamber door was opened and the polyethylene terephthalate foil was naturally cooled to ambient temperature, which lasted for about 0.5 hours,
 5. the polyethylene terephthalate foil was placed in a climate device equipped with the system for controlling temperature and humidity and it was switched on. From the moment the temperature reached +46°C and a relative humidity of 95% (which occurred after about 1 hour), the polyethylene terephthalate foil is kept at these conditions for 3 days i.e. 72 hours,
 6. after the mentioned time, the system for controlling temperature and humidity was stopped by switching off the climate device, the door of the climate device was opened and the polyethylene terephthalate foil was air-cooled to ambient temperature during 1 day i.e. 24 hours,
 7. after this period of time, the system for controlling temperature and humidity was switched on again; after reaching a temperature of +46°C and a relative humidity of 95% (which occurred after about 1 hour), the polyethylene terephthalate foil was kept at these conditions for 1 day i.e. 24 hours,
 8. after the mentioned 24 hours, the parameters of the system for controlling temperature and humidity were changed so that the temperature was increased to +60°C and the relative humidity decreased to 60%. After reaching a temperature of +60°C and a relative humidity of 60% (which lasted for about 0.5 hours), the polyethylene terephthalate foil was kept at these conditions for 1 day i.e. 24 hours,
 9. after the mentioned time, the system for controlling temperature and humidity was stopped by switching off the climate device, the door of the climate device was opened and the polyethylene terephthalate foil was air-cooled to ambient temperature during 1 day i.e. 24 hours,
- In the described way, the treatment of exposure of the

polyethylene terephthalate foil to the change of temperature and humidity was over. The mentioned treatment lasts for about 852 hours ie. 35.5 days.

Before and after the exposure to temperature and humidity change effects, specimens for determining characteristics have been cut from the samples of the polyethylene terephthalate foil.

The following characteristics have been determined: color, thickness, tensile strength in extrusion direction (further: longitudinal tensile strength), tensile strength perpendicular to extrusion direction (further: perpendicular tensile strength), tensile strain at break in extrusion direction (further: longitudinal tensile strain), tensile strain at break perpendicular to extrusion direction (further: perpendicular tensile strain), tear resistance in extrusion direction (further: longitudinal tear resistance), tear resistance perpendicular to extrusion direction (further: perpendicular tear resistance), flexibility at low temperature (-30°C) and integral light transparency.

Color was determined visually. Thickness was determined by the CARL FRANK thickness meter using an 100 mm x 100 mm specimen and the procedure described in standard SRPS G.S2.733, method A [13]. Tensile strength and tensile strain were examined on the ZWICK dynamometer at 100 mm/min crosshead speed using a 200 mm long and 25 mm wide specimen with 50 mm gauge lengths, in accordance with standard SRPS G.S2.734 [14]. Tearing force was determined on the ZWICK dynamometer at 500 mm/min crosshead speed using a specimen and the procedure described in standard SRPS G.S2.735, method A [15] Flexibility at low temperature was examined on an 100 mm x 10 mm specimen in the VOETSCH chamber by the MEHNERT method. Integral light transparency was determined on an 100 mm x 100 mm specimen on the BECKMAN UV 5240 spectrophotometer by the optical method.

Results and discussion

The results of determining tensile strength, tensile strain and tearing force (for all three characteristics in longitudinal and perpendicular direction), as well as thickness, color, flexibility at low temperature and integral light transparency of polyethylene terephthalate foils, before and after exposure to temperature and humidity change effects, are shown in the Table 2.

Table 2. Results of determining tensile strength, tensile strain and tearing force (in both directions), thickness, color, flexibility at low temperature and clarity of polyethylene terephthalate foils, before and after exposure to temperature and humidity change effects

CHARACTERISTICS	BEFORE EXPOSURE	AFTER EXPOSURE
Tensile strength, MPa		
- longitudinal	177	162
- perpendicular	149	133
Tensile elongation, %		
- longitudinal	16	15,5
- perpendicular	15	14,5
Tearing force, N		
- longitudinal	360	321
- perpendicular	307	278
Thickness, mm	0,03	0,03
Color	Colorless	Colorless
Flexibility at low temperature (-30°C)	No break	No break
Integral light transparency (%)	89	89

The results of investigation of physical, mechanical and optical characteristics of the polyethylene terephthalate foil before and after exposure to influence of change of

temperature and humidity pointed out the drop of tensile strength and tearing force, a slight change of tensile strain and no change in thickness, color, flexibility at low temperature and integral light transparency.

The tensile strength of the polyethylene terephthalate foil, in longitudinal and perpendicular direction, after exposure is lower for about 10% than before exposure.

The values of tearing force of the polyethylene terephthalate foil, in both directions, before exposure to influence of change of temperature and humidity, are for about 10% higher than the values of this characteristic after the influence of the mentioned factors.

The decrease of tensile elongation of the polyethylene terephthalate foil, in longitudinal and perpendicular directions, for about 3%, is not significant regarding the values of this characteristic before exposure to influence of change of temperature and humidity.

There are no changes in color, thickness, flexibility at low temperature and integral light transparency of the polyethylene terephthalate foil after exposure to the mentioned influences, regarding the initial quality.

The decrease of the initial values of tensile strength and tearing force of the polyethylene terephthalate foil, regarding the initial values, indicated that the change of temperature and humidity led to the hydrolysis process, which causes bond scission of the macromolecular chains, and to the interfacial decohesion process, which leads to decline of mechanical characteristics.

In the polyethylene terephthalate foil tested after exposure to influence of the mentioned parameters, the change of color was not detected ie. yellowness did not appear, which pointed out that the specimens were in high humidity environment.

Based on the fact that there were no crackings in the polyethylene terephthalate foil, it can be stated that absorption of water did not happen to such an extent to cause stresses on the border between the crystalline and the amorphous phase of the structure that would lead to the formation of cracks.[16].

Nothing pointed out that hydrophilisation process i.e. softening of polyethylene terephthalate had happened.

Conclusions

Based on the analysis of the obtained results of the investigation of the polyethylene terephthalate foil, it can be concluded that the described treatment of change in temperature and humidity:

- causes drop of tensile strength (longitudinal and perpendicular) and tearing force (in both directions) for about 10%; this decrease of the mentioned mechanical characteristics was caused by hydrolysis and interfacial decohesion processes
- does not cause important change of tensile elongation (in both directions);
- does not initiate change of color, thickness, flexibility at low temperature and integral light transparency;
- does not lead to absorption of water to the extent which would cause formation of microcracks and cracking of material.

Literature

- [1] ASHBY,F.M.: *Materials selection in mechanical design*, Butterworth-Heinemann, Oxford, 1999.
- [2] SORENSON,W.R., CAMPBELL,T.W.: *Preparative methods of Polymer Chemistry*, Interscience Publishers, John Wiley and Sons, New York, 1986

- [3] CHEN, Y., LIN, Z., YANG, S.: *Plasticization and crystallization of poly(ethylene terephthalate) induced by water*, Journal of thermal analysis and calorimetry, 1998. Vol.52, No.2, pp.565-568.
- [4] SCHNABEL, W.: *Polymer Degradation, Principles and Practical Application*, Academic Verlag, Berlin, 1981.
- [5] RADULOVIĆ, J.: *Investigation of the influence of natural weathering factors on the properties of polyamide thermoplastic materials*, Scientific Technical Review, 2005, Vol.LV, No.3-4, pp.21-28.
- [6] DAVIS, A., SIMS, D.: *Weathering of Polymers*, Applied science publishers, London and New York, 1983.
- [7] SUMMER, W.J., RABINOVITSCH, B.E.: *Weatherability of Vinyl and Other Plastics in Weathering of Plastics*, Editor WYPICH G., ChemTec Publishing, Norwich, 1999.
- [8] FAGERBURG, R.D., DONELSON, E.M.: *Effects of Water Spray and Irradiance Level on Changes in Copolyester Sheeting with Xenon Arc Exposure in Weathering of Plastics*, Editor WYPICH G., ChemTec Publishing, Norwich, 1999.
- [9] ZHAO, J., WANG, J., LI, C., FAN, Q.: *Macromolecules*, 2002, 35 (8), 3097-3103.
- [10] BARTOLOMEO, P.: *Deriving a prediction of the life cycle of geosynthetic polymers*, Bulletin des laboratoires des Ponts et Chaussées-243-Mars-Avril-47-69, 2003.
- [11] CAMINO, G., POLISCHUK, A.Y., LUDA, M.P., REVELINO, M., BLANCON, R., MARTINEZ VEGA, J.J.: *Water ageing of SMC composite materials: a tool for material characterisation*, *Polymer Degradation and Stability*, 1998, 61, pp.53-64.
- [12] RADULOVIĆ, J., KARKALIĆ, R.: *Uticaj temperature i vlažnosti na promenu svojstava polietilentereftalatne folije*, Zbornik radova 5. Kongresa inženjera plastičara i gumara KIPG-2008, Društvo inženjera plastičara i gumara, Zrenjanin, 2008.
- [13] SRPS G. S2. 733 Plastične mase. *ODREĐIVANJE DEBLJINE FOLJIA*, Savezni zavod za standardizaciju, Beograd, 1972.
- [14] SRPS G. S2. 734 Plastične mase. *ISPITIVANJE FOLJIA ZATEZANJEM*, Savezni zavod za standardizaciju, Beograd, 1971.
- [15] SRPS G. S2. 735 Fizikalna ispitivanja gume i plastičnih masa *ISPITIVANJE OTPORA PREMA CEPANJU GUME, FOLJIA IZ PLASTIČNIH MASA I ELASTIČNIH PENASTIH PROIZVODA*, Savezni zavod za standardizaciju, Beograd, 1970.
- [16] BASTIOLI, C., GUANELLA, I., ROMANO, G.: *Effects of water sorption on the physical properties of PET, PBT and their long fibres composites*, *Polymer Composites*, 1990, 11 (1), pp.1-12.

Received: 11.11.2008.

Otpornost polietilentereftalatne folije prema uticaju temperature i vlažnosti

Ispitivana je otpornost polietilentereftalatne folije prema dejstvu promene temperature i vlažnosti. Prikazane su vrednosti fizičkih, mehaničkih i optičkih karakteristika folije polietilentereftalata pre i posle dejstva uticaja navedenih parametara. Opisani su faktori koji utiču na promenu osobina ovog materijala. Zaključeno je da je došlo da pada prekidne čvrstoće i sile cepanja, ali da materijal nije degradirao u tolikoj meri da bi se javile prskotine odnosno pucanje polietilentereftalatne folije.

Кljučне речи: polimeri, termoplastični polimeri, polietilentereftalat, folija, uticaj temperature, uticaj vlage, osobine materijala.

Сопротивление полиэтиленотерефталатной фольги к влиянию температуры и влажности

В настоящей работе исследовано сопротивление полиэтиленотерефталатной фольги к влиянию перемен температуры и влажности. Также показаны величины физических, механических и оптических характеристик фольги полиэтиленотерефталата до и после влияния упомянутых параметров. В том числе и описаны и факторы влияющие на изменение характеристик этого материала.

В работе сделан вывод, что произошло резкое понижение предела прочности на разрыв и силы задырания, но что материал не ухудшался в той степени, чтобы появились трещины, т.е. щёлканье полиэтиленотерефталатной фольги.

Ключевые слова: полимеры, термопластические полимеры, фольга, полиэтиленотерефталат, влияние температуры, влияния влаги, характеристики материалов.

La résistance de la feuille en polyéthylène téréphtalate

La résistance d'une feuille en polyéthylène téréphtalate sur l'influence de la température et l'humidité a été étudiée. On a présenté les propriétés des caractéristiques physiques, mécaniques et optiques de la feuille en polyéthylène téréphtalate avant et après l'action de l'influence des paramètres cités. Les facteurs qui font l'influence au changement des propriétés de ce matériau ont été décrits. La conclusion est qu'il eu a lieu une baisse de la résistance à la rupture et à la force de déchirure, mais le matériau même n'était pas dégradé à ce point d'avoir les ruptures visibles c'est-à-dire la rupture de la feuille étudiée ne s'est pas produite.

Mots clés: polymères, polymères thermoplastiques, polyéthylène téréphtalate, feuille, influence de la température, influence de l'humidité, caractéristiques des matériaux.