

The Effect of Degradation in Aqueous Media on Viscosity Average Molecular Weight of Single Polymer Polyester Composites

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In present study the authors determine the impact of active environment on destruction processes developing in single polymer polyester composites. The processes impact on the structure and selected (e.g. viscosity) mechanical features of these composites were examined. The work included the following stages: manufacturing of ordered and disordered linear fiber single polyester composites, preparation of samples in accordance with applicable testing standards, performing composites' degradation tests in different media (distilled water and sea water at 30°C,). Literature review has shown that this kind of material has not been examined in reference to active media impact on degradation processes. This work is part of the research on discussed composites' properties and recycling.

Keywords: single polymer polyester composites, degradation.

In corrosion resistance tests we often use the concepts of material resistance and durability. These properties are interrelated; resistance being a primary property, and durability is a secondary property. Resistance of a material is the resistance a material shows against destructive action of a chemical, physical, physico-chemical or biological agent. This characteristic is undefined and cannot be expressed as a specified unit of measure. Durability, a secondary property, is expressed unequivocally by a unit of time. This characteristic is regarded as the time of safe use, and its value is determined by statistical methods. We can therefore conclude that, unlike resistance, durability is a property that can be measured unequivocally and precisely.

These days, due to product safety during use, manufacturers of polymer-based products estimate their durability. The focus is on the impact of the environment, where the effect of combined external factors may change the appearance (e.g. discoloring, dulling or cracking) and/or loss of the desired, e.g. mechanical properties, usually as a result of the degradation of the material resulting from the changes in its chemical structure (including oxidation, reduced molecular weight due to cracking of macromolecule chains or increased chain sizes by crosslinking or branching) [1].

There are three basic destruction processes affecting polymer chains, leading to reduced molecular weight of polymers [2-6]. These are depolymerisation, destruction and degradation processes. The depolymerization reaction is the opposite of polymerization and consists in thermal disintegration of polymer into monomer(s). The process of destruction is the disintegration of polymer chains, where low molecular compounds other than monomer are precipitated.

Polymer destruction can be caused by physical agents (heat, light and high-energy radiation) or chemical (oxygen, acids and alkalis). Degradation of polymers, in turn, is a process by which macromolecules decompose into smaller fragments [2-6]. These can be particles with less molecular weight or products of partial decomposition with reformulated chemical composition, created as a result of

splitting off or conversion of certain substituents. Depolymerization reaction is a particular case of polymer decomposition leading to the formation of monomer. Depolymerization as a deliberate and controlled process can have practical relevance, facilitating processing or recovery operations, aimed at obtaining mers from polymers, e.g. methyl methacrylate from methyl polymethacrylate. However, uncontrolled degradation of polymers is a harmful process, limiting their practical application [2-6].

Degradation is the process of structural change, that may be the result of physical or chemical transformations in polymer materials under the long term operation of external factors, such as: heat, oxygen, ozone, light and high-energy radiation, UV rays, chemicals, including water and steam and mechanical stress, particularly cyclically changing dynamic stresses (leading to material fatigue), generating deterioration of original functional properties [4-10].

Most of these effects are synergistic and result in interactions between individual stimuli. Such course of degradation occurs in most applications of hardenable plastics and their composites, e.g. heat accelerates fatigue degradation, internal stresses intensify thermal degradation, while aggressive environment leads to accelerated thermal degradation or composite fatigue. In practice, systems of degradation-inducing factors are much more complicated [4-14].

Polymer composites used in ships and yacht elements, for example, are exposed to the simultaneous operation of mechanical stresses, radiation (including UV), increased temperature, seawater and micro-organisms [12]. During the degradation in natural climatic conditions it is difficult in most cases to identify which of these factors has a dominant influence, because they act simultaneously, e.g. in industrial districts the air contains aggressive agents, such as sulphur dioxide and trioxide ($-\text{SO}_x$; and SO_2), nitrogen oxides, carbon monoxide, which in combination with moisture form strong inorganic acids [12-13]. The degradation process causes changes in the polymer that are mostly irreversible. This is the result of chemical

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reactions, such as: crosslinking, thermal oxidation, chain cutting, even destruction [4-16]. The degradation of plastics is explained primarily from the viewpoint of changes in the molecular structure of materials, which are largely due to the decrease of molecular weight, reduction of the bond forces of side groups and the reconstruction of morphological structure. Furthermore, the negative effects of material degradation are associated with phase changes, thermal effects and a change of internal stresses. The destruction of polymer composites also results from phenomena occurring at phase boundaries. In that event, the most common effect of degrading factors is the loss of adhesive bond between polymer matrix and reinforcement. However, it should be noted that in some cases in the first degradation phase the degrading factor improves certain material properties, especially mechanical strength. This takes place by additional crosslinking of the material structure, for example, under the influence of heat. Only at a subsequent stage other processes come into play, e.g. excessive crosslinking or reduction of the molecular weight, which deteriorates the tested properties [3-17].

Structural changes in the polymer may be the result of chemical or physical changes during processing, storage and operation [14]. They cause loss of original properties, with the first visible sign being discoloring, e.g. turning yellow, or loss of gloss - dulling, occurring on polymer surface. In order to increase the resistance of polymer to the above mentioned factors, various chemical and physical methods of polymer modification are used [3-16].

Polymers differ in their susceptibility to degradation. The process of degradation may be caused by various physical, chemical and biological factors. Each type of polymer degradation is characterized by specific molecular mechanism; however, the degradation of one polymer may involve different mechanisms simultaneously. The rate of depolymerization depends primarily on their physical and chemical properties. Amorphous polymers are more susceptible to degradation than crystalline ones. Besides, polymers with linear structure undergo faster degradation than branched polymers. The higher molecular weight of the polymer, the slower depolymerization is. Degradability is dependent on the presence of certain chemical groups in the molecule. Easily hydrolyzing urea, ester or amide groups accelerate polymer degradation [13-15].

There are strong relations between individual types of degradation. Usually, we deal with several types of degradation at the same time. A typical example of such a situation can be simultaneous light, oxygen and other weather factors, or parallel influence of heat, mechanical forces and oxygen [14-16].

Physical and chemical properties of macromolecular compounds deteriorate during the degradation process. Both in the case of synthetic polymers and biopolymers the term degradation means deterioration of functional properties of the polymeric material. Due to the manner of initiation, degradation processes are divided into: mechanical, thermal fatigue, photo-chemical, atmospheric, induced by high-energy radiation, biological and chemical [7-17].

Molecular degradation is a leading cause of plastic component failure, with a study indicating that 17% [18] of plastic failures are associated with a degradation mechanism. In the generic terms, the molecular degradation of a plastic is the deleterious alteration of the molecular structure within the polymer as the result of chemical reaction. Importantly, degradation mechanism

principally involves a permanent reduction in the molecular weight as a result of the chemical reaction. There are numerous molecular degradation mechanisms, but the most common are thermal oxidation, ultraviolet radiation, chain scission, and hydrolysis.

Hydrolysis usually means the cleavage of chemical bonds by the addition of water, specifically the hydrogen cations (H^+) or hydroxyl anions (OH^-). Hydrolysis can be the reverse of a condensation reaction in which two molecules join together into a larger one and eject a water molecule. Thus hydrolysis adds water to break down, whereas condensation builds up by removing water and any other solvents. Hydrolytic degradation can occur within plastic materials as result of submersion in water, progression through condensation cycles, or by exposure to steam. It can also result from contact with acids (high H^+ concentration) or bases (high OH^- concentration), which can dramatically accelerate the process [10-18].

Condensation polymers are inherently susceptible to hydrolysis, given their molecular structure. Specifically, such as polyesters, polycarbonate, nylons, polyurethane [2-15].

Molecular degradation represents a chemical reaction the results in a permanent change within the molecular structure of the polymer. The hydrolysis mechanism proceeds through the reaction of the polymer with water, resulting in the cleavage of the susceptible functional group, commonly into chemical species that resemble the initial reactants used in the original polymerization process. With some polymers, water is produced as a byproduct of the hydrolysis reaction, and in these cases the degradation proceeds relatively rapidly [2-17].

The work plan includes analyses, use of experimental methods for the determination of degradation mechanisms in single polymer composites. Literature review has shown that this type of materials have not been tested so far for the impact of active media on degradation processes affecting single polymer polyester composites.

Experimental part

Materials and methods

The tested material was a single polymer composite produced by the film stacking method, which consists in placing a reinforcing phase component between two films (matrix) made of the same polymer as the reinforcement, but having lower melt temperature. Then the material is subjected to hot pressing, under conditions allowing plasticizing the films without melting the outer layer of the reinforcement phase. The pressure used must be appropriately high so that the melted matrix polymer completely fills out void spaces between polyester fibers [19, 20]. The material intended for tests will be polyethylene terephthalate (PET), in the form of roving, and the matrix will be made of a 0.5 mm film, made of polyethylene terephthalate glycol modified (PET G).

The use of these components was yield a material with amorphous matrix, reinforced with continuous ordered fibers (fig. 1a) and disordered fibers (fig. 1b).

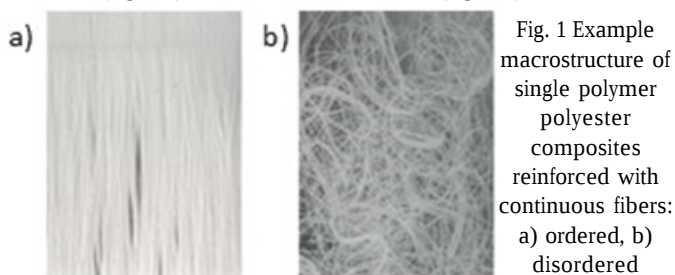


Fig. 1 Example macrostructure of single polymer polyester composites reinforced with continuous fibers: a) ordered, b) disordered

MATERIAL ID	MATRIX	REINFORCEMENT	TYPE OF REINFORCEMENT
A	PETG	-	-
B	PETG	5% PET	<i>Ordered</i>
C	PETG	10% PET	<i>Ordered</i>
D	PETG	15% PET	<i>Ordered</i>
E	PETG	20% PET	<i>Ordered</i>
F	PETG	5% PET	<i>Disordered</i>
G	PETG	10% PET	<i>Disordered</i>
H	PETG	15% PET	<i>Disordered</i>
I	PETG	20% PET	<i>Disordered</i>

Table 1
COMPOSITION OF THE SINGLE
POLYMER POLYESTER
COMPOSITES

Composition of the composites subjected to the studies are shown in the table 1.

The research work include the following test methods:

1) Degradation tests

Exposure is the most time-consuming part in degradation tests. Consequently, exposure is the major factor affecting the duration of tests. A distinction is made between long-lasting corrosion studies, in which exposure occurs in natural, real conditions, and short duration studies, which in turn can be divided into short-term and accelerated tests [21].

In accelerated tests the exposure is reduced by intensifying the destructive action. Methods of accelerating the degradation process include raising the concentrations of aggressive substance, increased temperature or miniaturization of samples. The most reliable and convenient of accelerated methods is the miniaturization of tested items. The estimation of material durability in this method for large-scale elements is done using the relationship, commonly used in civil engineering for calculating the masiveness of elements [21].

The scope of work was include accelerated degradation (miniaturization of tested elements) of single polymer composites, which involves the study of how various media affect the composite:

- type 1 – distilled water at temperature 30°C;
- type 2 - sea water, at temperature 30°C;

The accelerated degradation lasted for a period of three months, in laboratory conditions.

2) The degree of degradation of samples after incubation in water environment was assessed based on:

- Macroscopic surface changes - organoleptic method by naked eye observation and camera capture.
- Loss of weight (in %) - weight method. The weight of clean and dry polymer samples after degradation in both media was compared with respective weight of samples before incubation.

-Determination of viscosity average molecular weight - Viscometry, i.e. measurement of viscosity, is a convenient method for the determination of viscosity average molecular weight of polymers or the degree of polymerization, mainly due to the simplicity of performance. The relationship describing the molecular weight of a polymer is the Mark-Houwink equation: $[\eta] = KM^\alpha$ where $[\eta]$ means intrinsic viscosity, K and α are parameters dependent on the type of polymer, solvent and temperature. As a result of the measurement we get viscosity average molecular weight [21, 22].

To make the determination of intrinsic viscosity by viscosimetric method, polymers weighing between 0.2475 and 0.2525g were prepared in a 50 mL clean, dry flask. Next, the samples were poured with about 25 mL of

solvent. The next step was to thermostat the samples in the ultrasonic bath until the material was completely dissolved. The temperature of the water bath was kept between 30 and 40°C. Then the solution flasks and the pure solvent were thermostated at 35°C for 24h in the water bath where the measurement was made. After this time the flasks were refilled with 50 mL of solvent [22].

The terms of reference were as follows:

- solvent - a solution of phenol and 1,1,2,2-tetrachloroethane at a concentration of 60/40 wt% (Sigma - Aldrich, Germany);
- concentration of polymer solution: 0.5 g / dL;
- marking temperature: 35°C.

Results and discussions

The pH of sea water was 8.2, and of distilled water was 7.0. The temperature and pH in case of sea water were favorable for the growth of psychrophilic and some psychrotrophic bacteria which should contribute to increased sample degradation [22-25].

Based on samples' surface observation (fig. 2) before and after hydrolytic degradation neither sea water nor distilled water incubated samples showed any significant changes of color or texture. At the edge of the 20% fiber sample (E2) a slight delamination can be observed (fig. 3) caused by water particles that penetrated the material and may cause reversible physical or irreversible chemical changes. At the initial stage, by interrupted exposure to moisture or water, there are usually only physical changes in the form of polymer matrix swelling due to intermolecular space increased by water molecules. In

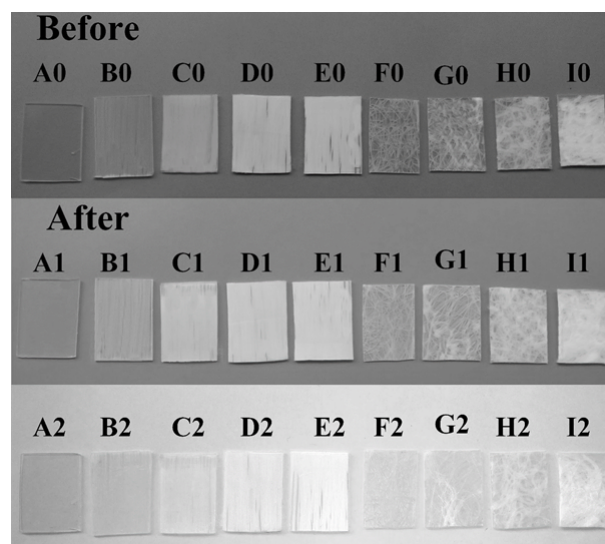


Fig 2.Samples of examined materials

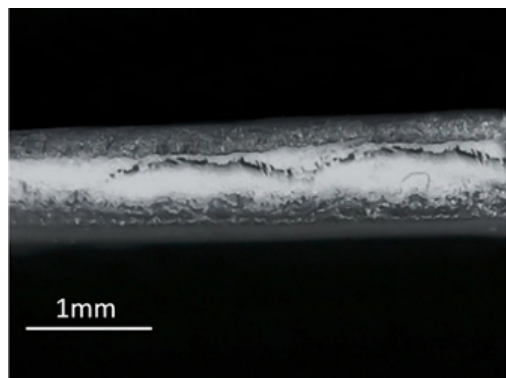


Fig. 3. An example of single polymer composite microstructure delamination

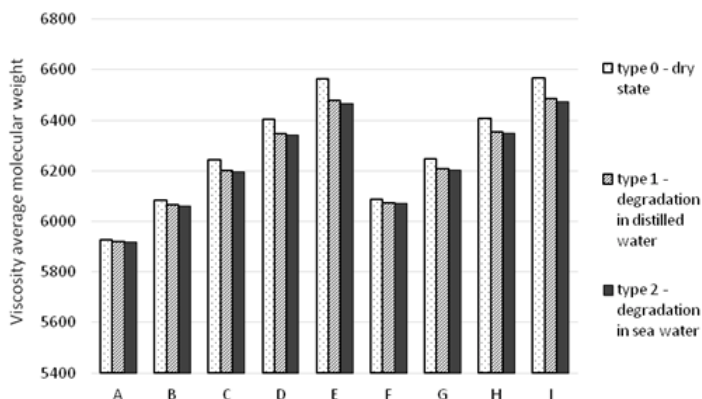


Fig. 4 Summary of viscosity average molecular weight of examined samples

MATERIAL ID	Initial weight [g]	Weight after degradation in distilled water [g]	Weight after degradation in sea water [g]
A	1.2755±0.0001	1.2755±0.0002	1.2756±0.0001
B	1.2463±0.0003	1.2462±0.0004	1.2461±0.0002
C	1.4009±0.0002	1.4008±0.0003	1.4007±0.0005
D	1.4191±0.0004	1.4192±0.0006	1.4193±0.0003
E	1.8593±0.0007	1.8592±0.0004	1.8594±0.0002
F	1.3541±0.0003	1.3542±0.0005	1.3542±0.0003
G	1.4425±0.0003	1.4424±0.0002	1.4423±0.0001
H	1.5202±0.0001	1.5201±0.0002	1.5202±0.0002
I	1.8732±0.0005	1.8735±0.0003	1.8733±0.0004

Table 2
LOSS IN WEIGHT MEASURE RESULTS

the boundary layer breaking of chemical fiber-matrix bonds or entering of water molecules between the adhesively connected fiber and matrix leads to detachment, delamination of fibers from matrix and cracks along the fiber-matrix boundary [23-25].

Loss in weight results (table 2) also confirmed that there are no visible changes of the examined materials. The degree of degradation can be only observed by average molecular weight.

The summary of viscosity average molecular weight of samples examined before incubation after degradation in sea water and degradation in distilled water is presented in figure 4. From the data in the table one can conclude that added fiber promotes degradation of the material. The greater the share of the reinforcement phase the greater the degree of composite degradation. It is caused by the capillary flow to the fiber/matrix boundary layer and leads to the decrease of secondary forces between macromolecules which in consequence increases macromolecules' mobility demonstrated by yielding of the material. At the next phase the water molecules build into the lattice of the matrix material causing the hydrolysis of ester groups.

Based on the picture analysis, the greatest degradation degree by 1.5% occurred to sample E2 - it is the ordered fiber sample of the greatest reinforcement phase share degraded in sea water. The reinforcement phase type has minor influence on composite materials' degradation. Comparing composite E1 and I1 of the same reinforcement phase share one can observe lower degradation of I1 by 0.12% in comparison to composite E1.

Degradation in sea water (E2) is faster by about 0.2% comparing to material (E1) degraded in distilled water. It may be caused by simultaneous impact of chemical

degradation as well as enzyme degradation by psychrophilic and some psychrotrophic bacteria. However no weight loss and no visible surface changes of the examined material do not confirm this conclusion.

Conclusions

It was observed in the course of the research that single polymer polyester composites degrade in natural aqueous environment (sea water and distilled water).

Polymer composites do not dissolve in water but they are able to absorb water in different quantities depending on their composition, enforcement share, matrix chemical structure, matrix and fiber adhesive strength, composite's structural quality. The phenomena related to water absorption can be divided into polymer and fiber surface absorption processes and absorption during which water enters the polymer structure or the fibers' surface layer causing chemical changes including degradation.

The destruction of polymer chains is probably caused by slow chemical degradation. Slightly higher degree of degradation in sea water may be caused, apart from chemical degradation by enzyme degradation. In order to verify this assumption the authors will do further research with longer exposure time.

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