

# Influence of pre-exposition and pre-loading on the environmental stress cracking of a PBT/PBA copoly(ester ester)

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**ABSTRACT:** Previous research showed Environmental Stress Cracking (ESC), i.e. mutual intensification of the destructive effect of loading and environment, of a chemical nature of poly(butylene terephthalate)/poly(butylene adipate) (PBT/PBA) copoly(ester ester) in water and phosphoric acid solution at 353 K. The ESC was studied by means of constant-load time-to-failure (TTF) experiments performed on sharply notched tensile specimens. In most practical situations the application of stress and initial contact with a potential ESC fluid do not coincide. It is known that in the case of physical ESC the order of loading as well as immersion and the time in between can influence the severity of attack. To investigate if this is also the case with chemical ESC of PBT/PBA in water and phosphoric acid solution, the interaction between environment and deformation is tested by means of exposition or loading before the actual ESC testing (TTF tests in environment). The tests are performed at 2.5 MPa, within the stress range where chemical ESC occurs. Previous research [1] without pre-exposition and pre-loading showed a heavy reduction in the TTF, indicating an acceleration of the ESC, due to the presence of acid. Also a lifetime inversion region is found (longer TTF for higher load) indicating competition between crack growth and blunting mechanisms. These results, in combination with the results of the pre-exposition and pre-loading experiments described in this paper, lead to the hypothesis that early mechanical loading causes crack tip blunting and local strain hardening due to orientation, resulting in a TTF increase. Accordingly, early chemical exposition, especially exposition to acid solution, reduces the favourable effect of blunting and orientation resulting in a decrease of TTF.

## INTRODUCTION

Environmental Stress Cracking (ESC) in polymer materials can lead to the sudden and unpredicted failure of constructions. It is unpredicted since it is neither the loading nor the environmental factors alone that damage the material, but rather the combination that is fatal. The effects of ESC range from the cosmetic to the catastrophic and life-threatening as well as frequently being costly [1]. Having a knowledge of ESC mechanisms is essential to prevent this.

Previous research proved chemical ESC of a PBT/PBA copoly(ester ester) in water and in phosphoric acid solution, by showing that there is a mutual intensification of the destructive effect of loading and the environment [2] that can not be explained by a pure physical influence of the environment. Chemical aspects were found to be dominant over (other) physical aspects. Also the influence of the load on the time to failure (TTF) and the failure mechanism was investigated.

The research presented in this paper is focused on further investigation of the failure mechanisms by measuring the influence of pre-exposition and pre-loading.

## MATERIAL, SPECIMENS AND HYDROLYSIS

### *Material*

Copoly(ester ester)s belong to the family of thermoplastic elastomers (TPEs) and consist in general of thermo-reversible hard and elastic soft domains [3]. The copoly(ester ester) used here consists of 60% poly(butylene terephthalate), 35% poly(butylene adipate) and 5% 4,4'-methylenebis(phenyl isocyanate), and shows domain sizes of about 20 nm [4]. The material possesses a rubber plateau between the glass transition temperature of the mixed amorphous PBA/PBT phase (the PBT phase is semi-crystalline) at about 243 K and the melting point of the PBT at about 493 K. The amorphous PBA/PBT soft domains are expected to be vulnerable to water attack [5]. The PBT/PBA copoly(ester ester) is used here to study the existence of ESC related to chemical rather than physical factors. In view of completeness it should be mentioned that no additives were used in the copoly(ester ester) described here.

### *Specimens*

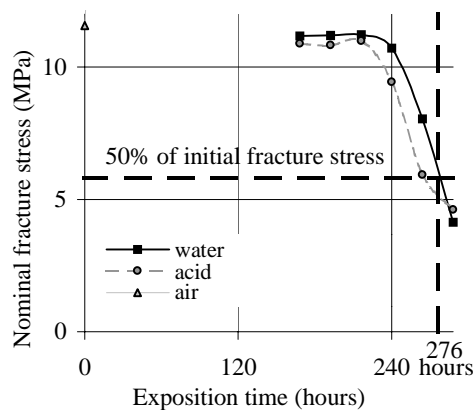
The PBT/PBA copoly(ester ester) was injection moulded into dogbone tensile specimens. The cross section in the tapered area of the specimen is 4 mm by 10 mm. The gauge length is 50 mm.

The centres of the specimens were notched on both sides by inserting a razor blade (American safety single-edge blades, thickness 0.25 mm). The razor blade is inserted with the help of a mechanical testing machine operating at a low speed (0.20 mm/min) in order to minimise the introduction of internal stresses to the specimen. For every notch a new razor blade was used to make sure that every notch had the same sharpness. This notching procedure was conducted according to the notch method used with polyethylene specimens, ASTM F1473 [6]. The notches (2.5 mm) reduce the cross-section of the specimen by 50% (from 40 mm<sup>2</sup> to 20 mm<sup>2</sup>).

### *Hydrolysis*

To distinguish hydrolysis from ESC, the separate influence (i.e. without external stress) of the environment on the mechanical properties is measured during previous research [1]. It is concluded that after 8 hours the specimen is saturated with fluid, both for water and phosphoric acid solution (pH = 1.6) at 353 K. So after 8 hours the specimen becomes vulnerable to hydrolysis over the total cross-section.

Also the influence of hydrolysis on the mechanical properties was determined by measuring the fracture stress as a function of the exposition time. Figure 1 shows the (nominal) fracture stress of the notched specimen as a function of the exposition time in water or phosphoric acid solution, both at 353 K.



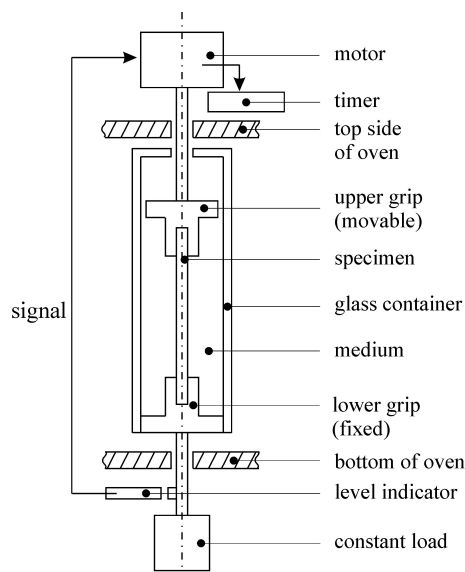
**Figure 1:** Nominal fracture stress of notched specimens as a function of exposition time for water and a phosphoric acid solution (pH 1.6) at 353 K.

The time to hydrolysis, taken as the time corresponding to 50% reduction of the fracture stress, is 276 (+/- 12) hours for both water and the phosphoric acid solution (pH = 1.6). Up to approximately 200 hours no significant influence of hydrolysis on the mechanical properties is measured.

## EXPERIMENTS

Time-to-failure tests on notched specimens are used to characterise environmental stress cracking as a function of the environment and of the pre-exposition time or the pre-loading time. It is demonstrated that time-to-failure experiments discriminate, to a high resolution, the ESC resistance of polymer/fluid combinations [7]. The ESC test consists of a TTF test at 2.5 MPa in water or phosphoric acid solution (pH=1.6) at 353 K.

The experimental set-up is depicted in Figure 2.



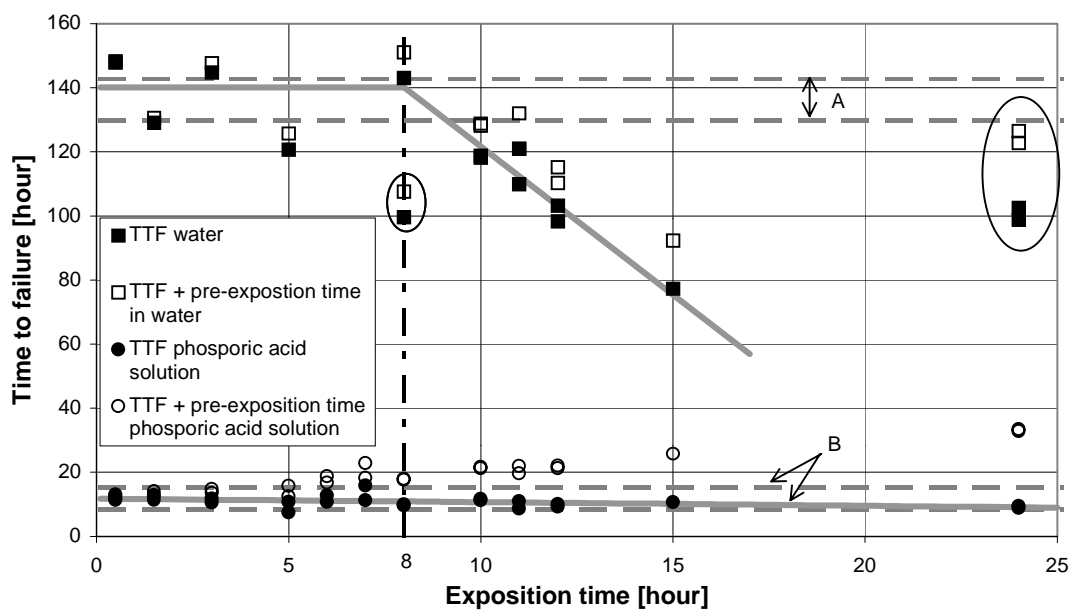
**Figure 2:** A schematic view of the set-up for time-to-failure tests in a medium (water or phosphoric acid solution) in an oven.

The influence of pre-exposition on the ESC behaviour is tested by exposition to the medium before the actual ESC test in the same environment and at the same temperature. The influence of pre-loading is measured by starting a TTF test in air at 353 K and adding the phosphoric acid solution later. At the moment of adding the acid solution, the TTF test becomes an ESC test.

## RESULTS AND DISCUSSION

### *Results of ESC tests with pre-exposition*

The results of the ESC tests obtained with the pre-exposed specimen in demineralised water and phosphoric acid solution are shown in Figure 3. The TTF, the sum of the TTF and the pre-exposition time are plotted against the pre-exposition time. The dotted lines at 8 h denotes the saturation time (both in water and in phosphoric acid). "A" and "B" denote the regions in which the TTF in water and acid solution respectively are found for ESC experiments without pre-exposition. The data trend is indicated by means of a grey line.



**Figure 3:** The TTF and the sum of the TTF and the pre-exposition time versus the pre-exposition time in water or phosphoric acid (pH = -1.6) at 353 K.

The slope of the TTF in water as a function of the exposition time is  $-9 \pm 0.9$  h/h. The encircled points are excluded from this fit because they deviate from the trend shown by the other points. Further research is necessary to determine whether this deviation is structural or whether it is a measurement

error. The slope of the TTF in phosphoric acid solution as a function of the exposition time is about -0.1 h/h.

Pre-exposition to phosphoric acid hardly influences the TTF at 2.5MPa. In water the TTF is also hardly influenced by pre-exposition as long as the pre-exposition time is shorter than the time necessary for saturation of the specimen with the medium. Longer pre-exposition times shorten the TTF significantly. The TTF in water is decreased by approximately 9 times the pre-exposition time after saturation for exposition times of up to 15 hours. So the TTF reduction may be much larger than the pre-exposition time.

Figure 1 shows that the hydrolysis -without loading- will not significantly influence the mechanical properties up to approximately 200 hours. The maximum pre-exposition time used is 24 hours. So it is expected that the mechanical properties will be unaltered by pre-exposition. This explains the fact that pre-exposition does not influence the TTF in phosphoric acid.

In water, however, the pre-exposition does decrease the TTF if the pre-exposition time is sufficient to saturate the specimen. As mentioned above the mechanical properties are expected to be unaltered by pre-exposition itself.

There is, however, a significant difference between the start of an ESC test after exposure in water and the start of an ESC test without such pre-exposition; which is that during the pre-exposition hydrolysis results in the formation of acid. Therefore acid is present from the start of the ESC test, while without pre-exposition no acid is present at the start of an ESC test in water. Previous research [1] without pre-exposition and pre-loading showed that ESC is accelerated in acid solution (at 2.5 MPa the TTF in acid solution is 10 times faster when compared to water).

Previous ESC tests without pre-exposition [1] showed a lifetime inversion (longer TTF for higher load) at stresses between about 3 and 4 MPa. This is a strong indication that there might be competition between crack growth and blunting mechanisms. Mechanical loading causes crack tip blunting (which reduces the stress concentration [8]) and local strain hardening that is due to orientation, which results in a TTF increase. Strain-induced crystallisation [9] may even further enhance this strain hardening. Marissen et al. found similar effects without chemical loading [10]. Due to the viscoelastic behaviour of the material orientation will increase as load and time increase. A nominal stress of 2.5 MPa is chosen in the present investigation because it is lower than the stresses at which lifetime inversion is found. However, blunting and strain hardening will still be present.

Without chemical pre-exposure some crack tip strain hardening may occur before the chemical effect is completely felt. With chemical pre-exposure to water, the lead of the initial strain hardening is reduced thus enhancing the damaging ESC process.

Pre-exposition in phosphoric acid, however, hardly influences the TTF. The presence of acid obviously enhances the damage process to such an extent that there is not sufficient time for the viscoelastic material to cause strain hardening. Therefore, the increase in TTF due to blunting and strain hardening is absent in acid.

A check of the hypothesis discussed above is performed: pre-loading without acid will allow time for more blunting and strain hardening. Consequently, a longer TTF should then be expected. To verify this ESC tests are done in acid solution after pre-loading.

#### ***4.2 Results of ESC experiments after pre-loading***

Table 1 gives the results of the ESC tests obtained from the specimens that are loaded before the phosphoric acid solution is added. The TTFs are an average of 3 measurements. The TTF given for the pre-loaded specimen is without the 24 hours pre-loading time in air of 353 K. The influence due to thermal degradation in these 24 hours is found negligible because TTF tests in air at 353 K were stopped after 6620 hours without fracture and because previous experiments in air show a reduction of the nominal fracture stress with less than 10% after 480 hours in air of 353 K.

TABLE 1: TTF in hours with and without 24 hours of pre-loading in air of 353 K for ESC tests at 2.5 MPa in phosphoric acid solution (pH=1.6) at 353 K.

ESC test at 2.5 MPa in acid solution of 353K	TTF (hours)
• without pre-loading	13
• with pre-loading	53

During these pre-loading experiments no acid is added during the first 24 hours, thus giving time for blunting and strain hardening before the ESC starts. According to the hypothesis formulated in the previous paragraph, this should lead to a longer TTF. This is indeed observed; the pre-loading results in a large increase in the TTF, of more than 300%.

## CONCLUSIONS

Pre-exposition to phosphoric acid hardly influences the TTF at 2.5 MPa in a phosphoric acid solution (pH=1.6) 353 K. In water the TTF is also hardly influenced by pre-exposition as long as the pre-exposition time is shorter than 8 hours, which is the time necessary for saturation of the specimen with the medium. Longer pre-exposition times shorten the TTF with a time of up to 9 times the pre-exposition time after saturation for pre-exposition times of up to 15 hours. On the other hand, mechanical pre-loading causes TTF increase. The explanation is that the earlier the chemical attack occurs and the more severe the ESC attack is (due to the presence of acid), the smaller the favourable effect due to blunting and crack tip strain hardening will be.

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