DISCONTINUOUS CRACK GROWTH DURING ENVIRONMENTAL STRESS CRACKING OF A PBT/PBA CO-POLY(ESTER ESTER)

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Abstract

Environmental Stress Cracking (ESC) is the cause of approximately 15% of all failures of plastic components. Previous research showed ESC of a chemical nature of a poly(butylene terephthalate)/poly(butylene adipate) (PBT/PBA) copoly(ester ester) in water and phosphoric acid solution at 80°C. Investigation of the fracture surfaces, using a Scanning Electron Microscope, SEM, revealed bands indicating successive crack front positions and thus discontinuous crack growth. Video recordings of crack growth in other specimens confirmed this.

The fracture mechanism is further investigated by interrupting an ESC test before fracture. The crack process is examined using an Environmental SEM with a built-in tensile machine. No indication of crazing is found. Since the band spacing is of the order of the plastic zone dimension, a plausible explanation is that the influence of the medium is stronger within the yielded zone leading to a quick fracture of (a substantial part of) this zone.

1. 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. Wright [1] points out that the effects of ESC range from the cosmetic to the catastrophic and life threatening as well as frequently being costly. Having a knowledge of ESC mechanisms is essential to prevent this.

Previous research by Kuipers et al. [2] 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 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. Examination of fracture surfaces using a Scanning Electron Microscope, SEM, revealed failure due to hydrolysis at 0.6 MPa, while ductile failure was found at 5 MPa and higher loads. Brittle failure is observed in-
between, from 0.6 MPa to 4 MPa. SEM photos of brittle fracture surfaces showed bands indicating successive crack front positions and thus discontinuous crack growth. This could be due to craze formation, however no crazes are found in PBT/PBA during static and fatigue tests by Marissen et al. [3].

The research presented in this paper answers two remaining questions: is discontinuous crack growth present and, if the answer is yes, which mechanism causes this discontinuous crack growth.

2. Material
Copoly(ester ester)s belong to the family of thermoplastic elastomers (TPEs) and generally consist of thermo-reversible hard and elastic soft domains like described by Adams, Hoeschele and Witsiepe [4]. The copoly(ester ester) used here consists of 60% poly(butylene terephthalate), 35% poly(butylene adipate) and 5% 4,4’-methylenebis(phenyl isocyanate), and according to van Berkel et al. [5] shows domain sizes of about 20 nm. The material possesses a rubber plateau between the glass transition temperature of the mixed amorphous PBT/PBA phase (the PBT phase is semi-crystalline) at about –30°C and the melting point of the PBT at about 220°C. The amorphous PBT/PBA soft domains are expected to be vulnerable to water attack similar to the copolymers described by March [6]. 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.

3. Experimental
For all test methods the specimens are placed in a glass container containing demineralised water or phosphoric acid solution (pH=1.6). All tests are performed at 80°C. An elevated temperature is used to accelerate the tests and also to reflect the service conditions that PBT/PBA copoly(ester ester)s normally experience.

3.1 ESC tests on DENT specimens
These tests are part of the previous tests, mentioned in the introduction, which proved ESC. Essential information is summarized in this paper for convenience of the reader. Previous publications are available for further reference [2, 8].

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 notchin procedure was conducted according to the notch method used with polyethylene specimens, ASTM F1473 [9]. The notches (2.5 mm) reduce the cross-section of the specimen by 50% (from 40 mm² to 20 mm²).

Time-to-failure, TTF, tests on notched specimens are used to characterise environmental stress cracking as a function of the load and environment. Hough and Wright [7] demonstrated that TTF tests discriminate, to a high resolution, the ESC resistance of polymer/fluid combinations. The TTF is the total period of time needed for a crack to initiate
and grow until final fracture occurs. The applied nominal stress, \textit{i.e.} the load divided by the unnotched cross-section of 40 mm\textsuperscript{2}, is within the range of 0.60 to 7 MPa.

### 3.2 ESC tests on SENT specimens

These tests and results are published, Kuipers \textit{et al.} [10], in a different context. Details concerning discontinuous crack growth are repeated in this paper. The dimensions of the SENT specimens are 130 x 50 x 6.1 mm. One side is notched in the same way as the DENT specimens. Various notch depths (3.07-9.02 mm) are used. The specimens are side grooved (depth 0.8 mm, root tip radius = 0.4 mm) with a milling machine to enhance the straightness of the crack front. The effective thickness of the specimen is calculated with:

\[
b_{\text{eff}} = \sqrt{b_{\text{bruto}} \cdot b_{\text{netto}}} \tag{1}
\]

With: \( b_{\text{eff}} = \) effective thickness, \( b_{\text{bruto}} = \) original thickness and \( b_{\text{netto}} = \) original thickness minus the depth of the side grooves.

The far ends of the specimen are clamped between steel plates. The clamps are loaded through rotation points, designed according to ASTM E399-97 [11]. A nominal stress, calculated with the effective thickness of equation 1, of 0.79-1.95 is used.

Images are made with a digital camera. From these images the crack length is measured as a function of time. The systematic error in the crack length measurement, related to the pixel size, is 0.06 mm.

### 3.3 Interrupted ESC test on DENT specimens

The fracture mechanism is further investigated by interrupting an ESC test before fracture. An ESC test on a DENT specimen is preformed as described in paragraph 3.1 only the glass container is mounted on a tensile test machine (Instron 5500R) with a climate chamber. Video images are made as described in the previous paragraph.

A preliminary recorded ESC test showed signs of failure after 5 hours and 10 minutes, while the final fracture took place after 7 hours and 45 minutes. A second test is stopped after 7 hours and three minutes based on this information and based on observation of the crack progress. The specimen is taken out of the climate chamber.

Half of the specimen thickness is removed with a milling machine in order to be able to view the middle of the crack (see Fig. 1). Before the milling the specimen is clamped and frozen in liquid nitrogen to prevent damage of the material during the milling.

The specimen is clamped in the tensile testing machine of the Environmental SEM, ESEM. The specimen and tensile machine are place into the ESEM, Philips XL30, and the fracture surface is monitored during the opening of the crack. One advantage of the ESEM over the SEM is the reduced build-up of static electricity. Therefore there was no need to apply a gold coating, which would tear during the opening of the crack.
4. Results and discussion
Fig. 2a and Fig. 2b are SEM photos of brittle fracture surfaces respectively at 2.2 MPa in phosphoric acid solution and at 3.5 MPa in water. The photos display only half of the fracture surface of the DENT specimens. Bands are visible on both fracture surfaces.

Figure 2: Fracture surfaces of a DENT specimens:
 a) tested in phosphoric acid solution at 2.2 MPa and b) tested in water at 3.5 MPa.
 Crack growth from the right to the left on the photo (indicated with arrow in Fig. 2b).
 The arrows in Fig. 2a indicate the end of the first five bands.

Bands are also found on the fracture surface of SENT specimens. During these experiments the crack is monitored using a video camera. The crack length is measured on the video recordings. Fig. 3 shows the crack length as a function of the time. Part of this curve is enlarged and next to it the SEM image of the corresponding crack area is shown. The notch depth of this SENT specimen is 4.55 mm and the specimen is tested at a nominal stress of 1.82 MPa in a phosphoric acid solution (pH = 1.6) at 80°C ± 0.2°C.

The measurement of the crack length as a function of the time proves discontinuous crack growth. Fig. 3 shows, with a good correlation between the steps in the crack growth and the fracture band pattern, that the bands are a result of discontinuous crack growth.
FIGURE 3. The measured crack growth curve of a SENT specimen and part of this curve with the SEM image of the corresponding crack area reveal discontinuous crack growth and a fracture band pattern with approximately the same spacing.

Possible explanations for discontinuous crack growth are the forming of crazes created and broken one after another and/or the stronger influence of the medium within the yielded zone leading to fracture of (part of) this zone.

An ESC test on a DENT specimen is interrupted to investigate whether there is a craze present or not. The test is stopped after 7 hours and three minutes, before fracture but after development of a crack. The CMOD at that time was 10.8 mm on the one side and 11.6 mm on the other. This corresponds to a CMOD of about 10 mm at room temperature. Full opening of the crack is assumed when the crosshead, of the small tensile machine in the ESEM, is displaced over 10 mm starting from the position in which there is no tension present in the specimen. Figure 4 shows ESEM images of the opened ESC crack. The displayed surface is at the middle of the crack since half of the specimen thickness is removed. The crack growth direction is from the right to the left. The photos are taken at the
middle of the crack length. The left picture shows the partly opened crack. The right picture shows the same crack at the same place but now the crack is opened further than at the end of the interrupted ESC test.

FIGURE 4. ESEM images of the centre of the crack; in the left picture the crack is partly opened at a displacement of 0.7 mm. while the right picture shows the same crack but now opened more than at the interrupted test, namely at a displacement of 1.4 mm.

No indication of crazes is found in accordance with the findings of Marissen et al. [3]. A plausible explanation for the discontinuous crack growth bands is therefore that the influence of the medium is stronger within the yielded zone leading to fracture of (part of) this zone. If this is the case than the yielded zone dimension is expected to be equal to or bigger than the band spacing.

According to the Dugdale strip yield model, e.g. Janssen et al. [12], the length of the yielded strip \( r_p \) assuming plane stress is given by:

\[
 r_p = \frac{\pi}{8} \left( \frac{K_I}{\sigma_{ys}} \right)^2
\]  

(2)

with:

\( \sigma_{ys} \) = yield strength = 9.8 MPa (at 80°C) for this copoly(ester ester) and \( K_I \) is the stress intensity factor [12] for mode I loading, which for a DENT specimen can be calculated as:

\[
 K_I = C \sigma \sqrt{\pi a}
\]  

(3)

with: \( a \) = crack length, \( \sigma \) = nominal stress and \( C \) = geometry factor, which can be calculated for a DENT specimen according to Tada [13]:

\[
 C_{DENT} = \frac{1.122 - 1.122 \left( \frac{a}{W} \right) - 0.820 \left( \frac{a}{W} \right)^2 + 3.768 \left( \frac{a}{W} \right)^3 - 3.040 \left( \frac{a}{W} \right)^4}{\sqrt{1 - 2a/W}}
\]  

(4)
in which: \( W \) = specimen width. And for a SENT specimen [13]:

\[
C_{\text{SENT}} = \sqrt{\frac{2W}{\pi a}} \tan \frac{\pi a}{2W} \left( \frac{a}{W} \right) + 0.37 \left( 1 - \sin \frac{\pi a}{2W} \right)^3 \cos \frac{\pi a}{2W}
\]  

(5)

The equations 4 and 5 have an accuracy of better than 0.5\% and are valid over the total specimen width.

For example the width of the first band at the fracture surface of the DENT specimen tested at 2.2 MPa in acid solution is approximately 0.14 mm (see Fig. 1). At this point the crack length equals the notch size of 2.5 mm. The corresponding stress intensity factor is 0.23 MPa\(\sqrt{\text{m}}\), calculated with equation 3. This results in a yielded strip size of 0.22 mm according to equation 2. This value is higher than the measured band size of 0.14 mm. This is also the case for the previous discussed SENT specimen; the first band is about 0.13 mm (this band is not visible in Fig. 3), while the calculated yielded strip is 0.28 mm.

One explanation for this discrepancy is that the yielded zone dimension is overestimated using the yield strip model because there is not a plane stress state at the crack tip. Consequently the value for \( r_p \) will become lower. Also formula 2, valid for ideal elastic-plastic materials, will overestimate the length of the yielded strip in case of work-hardening. Another possible reason is that only a part of the yielded zone breaks at once.

5. Conclusions

Discontinuous crack growth during environmental stress cracking of a PBT/PBA co-poly(ester ester) is proven. No indication of crazing is found. A plausible explanation is that the influence of the medium is stronger within the yielded zone leading to a quick fracture of (a substantial part of) this zone, since the band spacing is of the order of the plastic zone dimension for both SENT and DENT specimens.

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References


