

**Characterisation of Environment Stress Cracking  
Susceptibility of Weld-line Defects by the Chemical Probe  
Technique**

**Project DME 3.2:**

**Environment Stress Cracking  
of Polymeric Materials.**

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### **ABSTRACT**

An investigation has been undertaken to assess the effectiveness of the chemical probe technique in identifying the susceptibility of complex polymeric mouldings to environment stress cracking (ESC). PMMA samples were produced with weld-line defects using a double-gated mould. The variation in relative ESC susceptibility of the weld-line with distance from the gates was readily identified by the chemical probe technique. In addition, quenched and air-cooled samples were easily distinguished. It is envisaged that the chemical probe technique could be used to detect poorly processed samples with respect to ESC susceptibility.

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Approved on behalf of Managing Director, NPL by Dr C Lea,  
Head of the Materials Centre

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## **1 Introduction**

In previous work [1] the chemical probe technique was shown to be effective in determining near-surface residual tensile stresses in simple injection moulded components. The technique is based on establishing reference environment stress cracking (ESC) data for the relationship between stress and time to crazing and/or cracking for specific polymer-environment combinations with the polymers in the annealed state. When a plastic with unknown residual stress is exposed for a specific period to an environment, the existence or otherwise of crazing and/or cracking will indicate that the surface, or near surface, stress is above or below the reference value. This exercise is then repeated for environments of varying aggressivity in a progressive manner to estimate the magnitude of the residual tensile stress. The range of environments is selected according to the accuracy of measurement required.

A potential limitation of the method as described is the implicit constraint to materials which are microstructurally homogeneous. Hence, there is potential uncertainty in its applicability to welded material and also to complex mouldings, with more than one gate, for which weld/knit lines will arise. Evaluation of residual stress may not then be feasible. Nevertheless, the chemical probe method can still be used to identify regions of potential susceptibility to ESC, whether due to residual stress, microstructural sensitivity or a combination of both. The value of the technique then will be in distinguishing poor quality processing, similar to the method used for ABS [2]. This report explores the effectiveness of the chemical probe method, using PMMA samples produced using a double-gated mould. A comparison is made between the results obtained from the chemical probe technique and those obtained from slow strain rate testing. The influence of microstructure and residual stress on the chemical probe technique is assessed and a procedure for more general application of the technique is indicated.

## **2 Experimental**

### **2.1 Materials**

Injection moulded plates of PMMA (Plexiglass 7N) containing weld-line defects were produced using a double-gated mould (Figure 1) mounted on a Mannesmann-Demag

Kunststofftechnik NC111 150 tonne injection moulding machine. The processing parameters are summarised in Appendix 1. The double-gated mould consists of a flat rectangular plate 150 mm square with two gates on one side through which the molten polymer enters. The weld-line forms down the centre of the mould half-way between the two gates, as can be seen in Figure 1. Due to difficulties in controlling the moulding process, all the specimens were produced using the same moulding parameters. However, in order that “poor” and “good” quality mouldings could be examined one set of samples was immediately quenched in liquid nitrogen whilst a second set was air-cooled before being stored in liquid nitrogen.

## 2.2 Slow strain rate tests

Slow strain rate tests were conducted using a tensile test machine at a constant displacement rate of  $4.5 \times 10^{-4} \text{ mms}^{-1}$ . Details of the procedure have been described elsewhere [3]. Standard tensile test specimens [4] (Figure 2) were removed from both the air-cooled and quenched plate samples at four different positions (labelled 1 to 4 in Figure 1) along the weld-line. Position 1 was located closest to the gates where the residual stresses and microstructural influences of the weld-line are expected to be most significant. Near to the gates the two melt fronts tend to meet “head-on” whereas they are able to mix more gradually further away from the gates. Short-shots produced while moulding the plates indicate that the two melt fronts meet before Position 1 in the weld-line. Position 4 is located at the opposite end of the weld-line where the influence of the weld is expected to be least significant. “Weld-free” specimens were also prepared from sections of the plate remote from the weld-line.

The machined edges of all the specimens were ground with 1200 grit-paper, cleaned with distilled water and tissue dried. Preparation of the specimens was achieved within 2 hours after which the specimens were replaced in the liquid nitrogen prior to testing. To avoid relaxation of residual stress prior to testing, the time following removal of the specimens from the liquid nitrogen was minimised.

For comparative purposes, some weld-free specimens were annealed in an air-oven at  $110^\circ\text{C}$  for 8 hours to remove the residual stresses. As these specimens were taken from a region of the plate remote from the weld-line the specimens may also be

assumed to be microstructurally homogeneous. These specimens are referred to as “annealed weld-free” specimens.

To assess the influence of residual stress on ESC susceptibility, as opposed to microstructure, specimens were removed from the weld-line at Position 1 and annealed at 95°C for 100 hours. Annealing at this temperature is high enough to remove the residual stresses from the specimens without significantly altering the microstructure. The annealing conditions chosen were determined by measuring the shrinkage in specimens that had been annealed over a range of different conditions. Observation of shrinkage in a sample is a good indication that the microstructure of the polymer has been altered. The annealing temperature selected was therefore the highest temperature that could be achieved without causing significant shrinkage. These specimens therefore have their original microstructure but minimal residual stresses and are known as “annealed weld-line” specimens.

Grips with a rippled surface were used to prevent slippage of the specimen and were examined visually before and after the test to ensure the ends of the specimen were in their original position. Care was taken to align the specimens in the grips. The load was measured using a calibrated load-cell and the displacement of the crosshead measured using a calibrated displacement transducer with an accuracy greater than 0.4%. The strain in the gauge length of the specimen,  $\varepsilon$ , was calculated from the crosshead displacement measurement using the following relationship [3].

$$\varepsilon = \delta_{\text{total}} / (l_1 + 2 A_1 \Sigma \Delta l_2 / A_2)$$

where,  $\delta_{\text{total}}$  is the measured crosshead displacement,  $l_1$  and  $A_1$  are respectively the length and the cross-sectional area of the narrow parallel-sided section of the specimen and  $l_2$  and  $A_2$  are the length and cross-sectional area of one of the tapered ends.

Slow strain rate tests were conducted for the air-cooled and quenched specimens in air and in ethanol. In addition, testing of the annealed PMMA specimens was undertaken in each of the chemicals chosen for the chemical probe technique, these

being selected using the NPL ESC database [5]. In order of increasing aggressivity the chemicals were: ethyl hexanol, ethanol, propanol and acetic acid. Analytical reagent grade chemicals were used in each case.

In an environment inducing ESC, the stress-strain curve deviates from that obtained in air as a consequence of the enhanced extension due to crazing [3]. The stress at which deviation first occurs, the departure stress, reflects the onset of crazing and can be used as an index to rank the aggressiveness of different environments. The departure stress was defined as the stress at which the gradient of the stress-strain curve in the environment was reduced to 75% of that measured in air. The results from these tests and more extensive tests on other materials [3,5] indicate that the variability in departure stress in the slow strain rate tests is  $\pm 0.5$ MPa.

### **2.3 Chemical probe technique**

The plate samples to be tested by the chemical probe technique were removed from the liquid nitrogen and allowed to attain room temperature (a period of about 30 minutes). A test cell consisting of a cylindrical ring 25mm in diameter was attached with sealant to the region of the weld-line under investigation. The sealant was not aggressive to the test material and was allowed to cure for 2 hours before conducting the test. The chemical to be used in the test was then poured into the test cell. After 10 minutes, the surface of the specimen was visually inspected for the presence of crazes. If crazing was observed the test was repeated using less aggressive chemical environments. If no crazing was detected the test was repeated using more aggressive environments until crazing was observed.

## **3 Results and Discussion**

### **3.1 Slow strain rate tests**

The ESC susceptibility of the weld-lines was assessed by conducting slow strain rate tests of the PMMA in ethanol. Figures 3 and 4 show the effect of the weld-line and weld-line location on the slow strain rate behaviour in the air-cooled and quenched specimens, respectively. Slow strain rate curves for the air-cooled specimen at position 1 and the quenched specimens at positions 1, 2 & 3 were not obtained as the specimens fractured in the ethanol before any measurements could be made. The stress applied to

these specimens would be that used for taking up the initial slack in the machine, typically between 1 and 2MPa.

Values of the departure stress for the different specimens in Figures 3 and 4 are summarised in Tables 1 and 2 respectively. Repeat tests indicate that these departure stresses are accurate to  $\pm 0.5$ MPa. The results for the weld-free specimens highlight the marked decrease in departure stress along the weld-line with proximity to the gates, as expected. In addition, the departure stresses in the quenched specimens are smaller than those in the air-cooled specimens, reflecting the increased residual stress introduced by quenching. Furthermore, a close inspection of the fractured specimens revealed that the annealed specimens contain many more small crazes than the un-annealed specimens, whereas the weld-line specimens contained just one craze along the weld-line. These results clearly demonstrate the high ESC susceptibility of the weld-line and the marked variation that occurs in these plates with distance from the gates.

**Table 1 Departure stress of air-cooled specimens**

<b>Position of specimen along weld-line</b>	<b>Departure stress in ethanol (MPa)</b>
Weld-line position 1	<2
Weld-line position 2	4
Weld-line position 3	12
Weld-line position 4	15
Weld-free specimen	17.5
Annealed weld-free specimen	19

**Table 2 Departure stress of quenched specimens**

<b>Position of specimen along weld-line</b>	<b>Departure stress in ethanol (MPa)</b>
Weld-line position 1	<2
Weld-line position 2	<2
Weld-line position 3	<2
Weld-line position 4	11
Weld-free specimen	15
Annealed weld-free specimen	19

To assess the influence on the departure stress of the weld-line microstructure, two tests were conducted on specimens containing weld-line defects (Position 1) which had been

annealed at 95°C. This temperature is high enough to relieve the residual stresses in the specimen without causing significant re-orientation of the polymer chains. The slow strain rate behaviour of these annealed specimens is shown in Figure 5. The departure stress in these annealed weld-line specimens is similar to that of an annealed weld-free specimen. This would indicate that the microstructure of the weld-lines in this particular mould has little effect on the ESC susceptibility of the specimens. Moreover, it should be noted that fracture occurs at extremely low stresses <2MPa in weld-line specimens that have not been annealed. This clearly demonstrates that in these specimens it is the residual stresses associated with the weld-line and not the microstructure that is responsible for the ESC susceptibility.

The slow strain rate results for *annealed* PMMA, without weld-line defects, in a range of environments are shown in Figure 6 and Table 3. The data show a reasonable range of departure stress values, sufficient for application of the chemical probe method.

**Table 3** Departure stresses of annealed weld-free specimens in the different environments used in the chemical probe technique.

Chemical Environment	Departure stress (MPa)
Ethyl hexanol	23
Ethanol	19
Propanol	15
Acetic Acid	12

### 3.2 Chemical Probe

The results obtained from the chemical probe technique at different positions along the weld-lines are shown in Tables 4 and 5. Specimens in which crazing was observed after 10 minutes are indicated as a “fail” and those in which no crazing was observed with a “pass”. The restriction to 10 minutes is a little arbitrary but was chosen to address the requirement for a rapid test. Less aggressive chemicals are required to cause crazing next to the mould gates (Position 1) as expected. Moreover, it can be seen that stronger ESC agents are required to initiate crazing in the air-cooled specimens than in the quenched specimens. This is due to the large residual stresses that form during the quenching process and is consistent also with the lower departure

stresses that are observed in the quenched specimens during slow strain rate testing (Figures 3 and 4).

**Table 4 Results from the chemical probe technique applied to the quenched PMMA weld-line specimens.**

<b>Weld-line</b>	<b>Chemical Probe Chemicals</b>			
<b>Position</b>	<b>Ethyl hexanol</b>	<b>Ethanol</b>	<b>Propanol</b>	<b>Acetic Acid</b>
1	Pass	Fail	-	-
2	Pass	Fail	-	-
3	-	Pass	Fail	-
4	-	-	Pass	Fail

**Table 5 Results from the chemical probe technique applied to the air-cooled PMMA weld-line specimens.**

<b>Weld-line</b>	<b>Chemical Probe Chemicals</b>			
<b>Position</b>	<b>Ethyl hexanol</b>	<b>Ethanol</b>	<b>Propanol</b>	<b>Acetic Acid</b>
1	-	Pass	Fail	-
2	-	Pass	Fail	-
3	-	-	Pass	Fail
4	-	-	-	Pass

A further observation made during the chemical probe tests was that the crazes formed either along or parallel to the weld-line indicating that the dominant residual stresses are perpendicular to the weld-line.

If the air-cooled and quenched samples are considered *notionally* to represent a well-processed material and a poorly processed batch respectively, the desire is to have a chemical which passes the good material but fails the deficient product. In that context, ethanol would be deduced to be the appropriate exposure chemical for PMMA since failure occurred only for the quenched material.

There is some inconsistency of the chemical probe results of the air-cooled samples in ethanol with respect to the slow strain rate testing. In the latter, a specimen at Position 1 failed at low stress levels under small static loads. It would suggest that the pass accorded by the chemical probe at that position was marginal. However, it should be noted that the machined sides of the slow strain rate specimens are exposed

to the chemical and if the material is more sensitive internally, this may explain the low departure stress.

Finally, to enable the chemical probe technique to be used with products produced from other materials it is necessary to identify the relevant test environment. These must initiate crazing in poorly-produced mouldings but not in well-produced mouldings. To aid in the selection process a short test procedure has been produced (Appendix 2).

## **4 Conclusions**

The chemical probe technique has potential as a method for rapidly distinguishing good and poorly produced weld-lines in complex polymeric mouldings with respect to ESC susceptibility. However, the short time of exposure means that only near-surface susceptibility can be determined.

In addition, by annealing the specimens to relieve the residual stresses it was shown that the dominant influence on the ESC susceptibility of the weld-line specimens of PMMA was the residual stress rather than the microstructure.

## **References**

1. Turnbull A., Maxwell A.S., Pillai S., J. Mat. Sci. 451-459, 34, (1999).
2. ASTM D 1939-84: Determining residual stress in extruded or molded acrylonitrile-butadiene-styrene (ABS) parts by immersion in glacial acetic acid.
3. Turnbull A., Maxwell A.S. and Pillai S., Polymer Testing, 19, 117-129, (2000).
4. ISO 527-2: 1966, Plastics - Determination of tensile properties.
5. NPL Environment Stress Cracking database, National Physical Laboratory (1998).

## Appendix 1 - Moulding Conditions

### SUMMARY OF PROCESSING PARAMETERS FOR PMMA WELDLINES

<u>Material Code:</u>	EPW
<u>Machine Parameters</u>	
Max Machine clamp force:	160 tonne
Max Machine Injection volume:	110 cm <sup>3</sup>
Max machine Injection pressure:	244 MPa
Max Machine Injection rate:	157 cm <sup>3</sup> /s
<u>Process Parameters</u>	
Material Drying Time:	4 hours
Set barrel temperature:	200 °C
Set mold temperature:	
(coolant temp)	41 °C
Coolant flow rate:	11 L/min
Measured melt temperature:	225-240 °C
(air shot)	
Fill time:	3.96 sec
Time for hold pressure:	20.0 sec

## **Appendix 2 - Test Procedure**

### **1 Introduction**

The chemical probe technique can be used in principle to distinguish between well-processed and poorly-processed weld-lines in polymeric mouldings and can be considered for use as a quality control test for assessing the ESC susceptibility of injection moulded components. The technique is not recommended as a substitute for other tests but does yield valuable information as to the ESC susceptibility of complex moulded components.

### **2 Normative Reference**

- 2.1. The following standard provides useful background for conducting this test procedure. At the time of publication, the edition indicated was valid. All standards are subject to revision and the most recent edition of the standard should be consulted.

ASTM D 1939-84: Determining residual stress in extruded or molded acrylonitrile-butadiene-styrene (ABS) parts by immersion in glacial acetic acid.

### **3 Test Specimens**

- 3.1. Prepare two sets of mouldings one set under conditions known to produce “well-processed” mouldings and the other under conditions known to produce a “poorly-processed” product.

Note: The size and shape of the mouldings should be the same as those for which the test is to be used.

### **4 Environments**

- 4.1. Select a range of chemicals and grade them according to aggressivity; for example, using the NPL database.

Note: Care should be taken to ensure that the chemicals do not *chemically* attack the polymer.

4.2. Analytical reagent grade chemicals should be used in all the tests.

4.3. The temperature of the testing shall normally be  $23 \pm 2$  °C.

## **5 Selection of test environment**

5.1. Initially select a chemical of moderate ESC aggressivity.

5.2. Attach a test cell to the surface of one of the mouldings and add the test environment to the cell.

5.3. Visually inspect the surface of the material for crazing and note its condition after 10 minutes.

5.4. If crazing is observed the procedure should be repeated on identical mouldings with less aggressive chemicals until crazing is not observed.

5.5. If no crazing is observed the procedure should be repeated on identical mouldings with more aggressive chemicals until crazing is observed.

5.6. Repeat this procedure for both sets of mouldings to produce a table similar to those shown in Tables 4 and 5.

5.7. Using these results, identify a chemical environment that will cause crazing in a poorly-processed moulding but not in well-processed mouldings.

## **6 Application of the test in service**

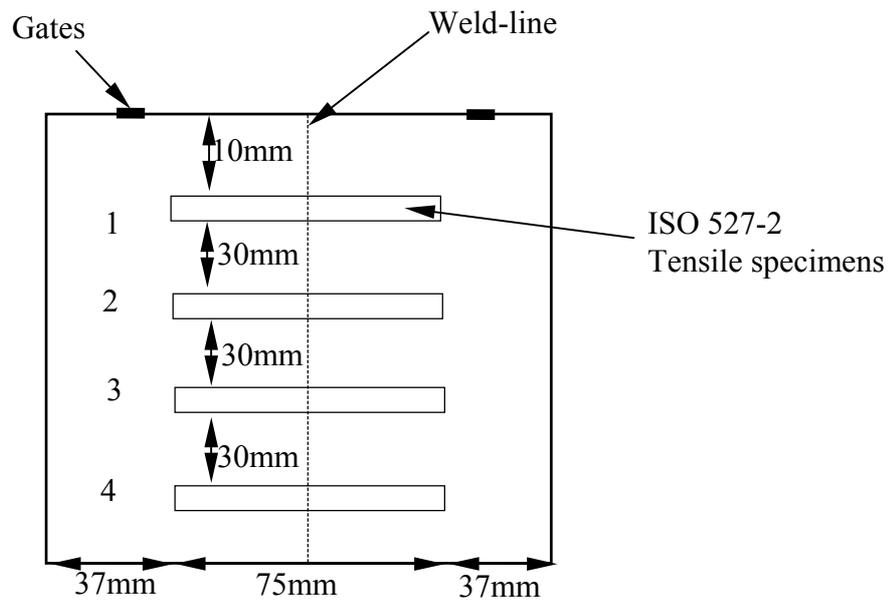
6.1. Attach a test cell to the surface of the moulding under investigation and apply the chemical environment selected in 5.7.

- 6.2. Visually inspect the surface of the material for crazing and note its condition after 10 minutes.
- 6.3. If no crazing is observed the quality of the moulding may be considered as “well-processed” (i.e. there are no significant surface or near surface tensile residual stresses).
- 6.4. If crazing is observed the moulding may be considered as “poorly-processed”.

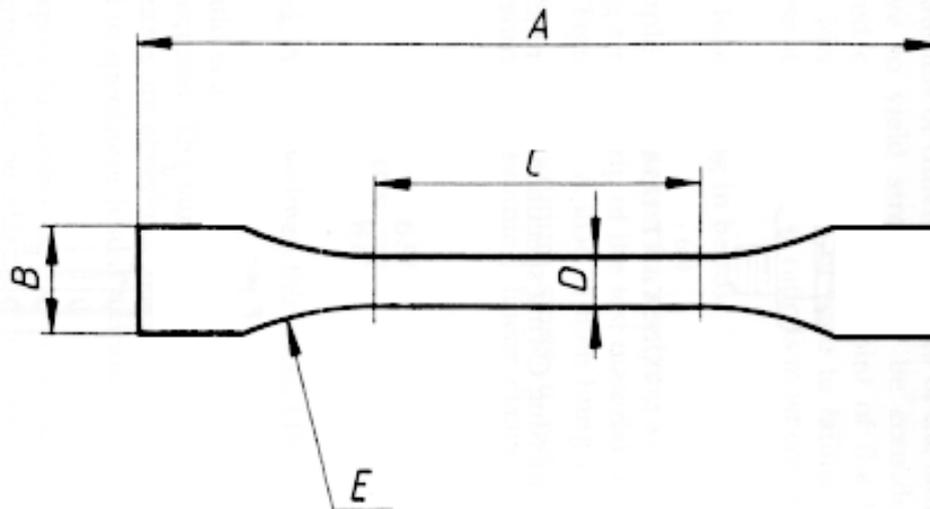
## **7 Report**

- 7.1. Full description of the mouldings and their processing histories;
- 7.2. elapsed time and storage conditions after processing;
- 7.3. location on the moulding where the test cell was attached;
- 7.4. environments tested;
- 7.5. test temperature;
- 7.6. whether crazing was observed in the moulding after 10 minutes exposure.

### Figures 1-5

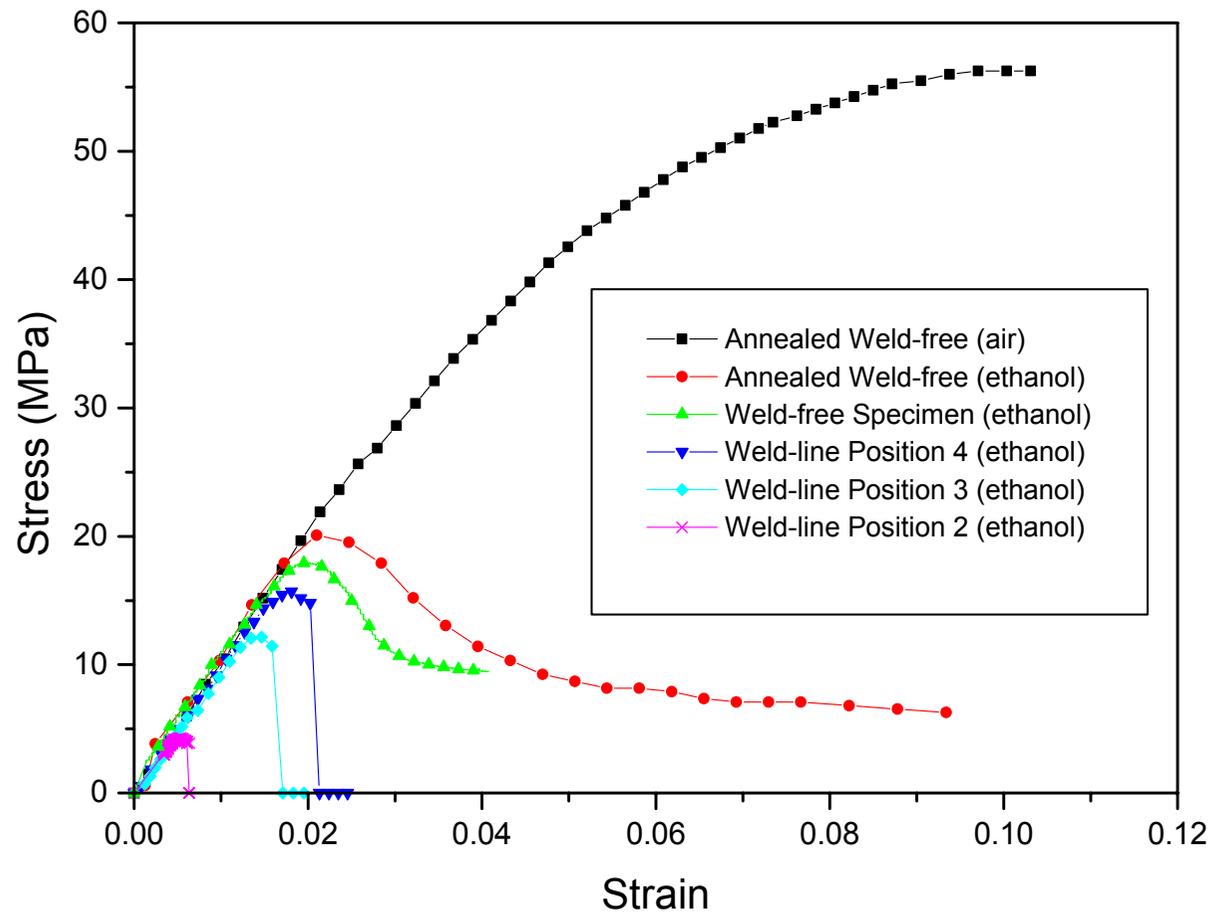


**Figure 1 Position of the specimens machined from the PMMA plates**

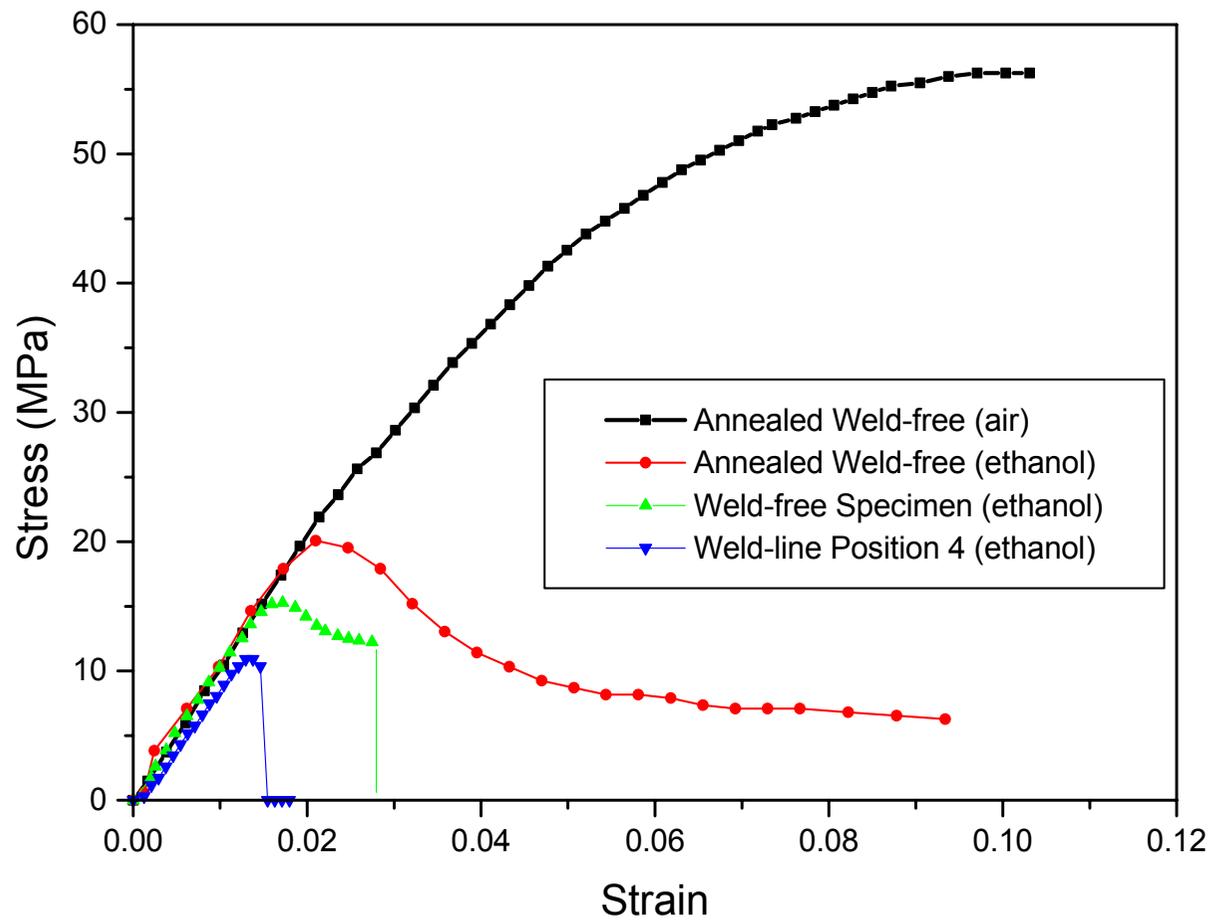
**Key**

- A Overall length, minimum: 75 mm
- B Width at ends: 10 mm  $\pm$  0,5 mm
- C Length of narrow, parallel-sided portion: 30 mm  $\pm$  0,5 mm
- D Width of narrow, parallel-sided portion: 5 mm  $\pm$  0,5 mm
- E Radius, minimum: 30 mm

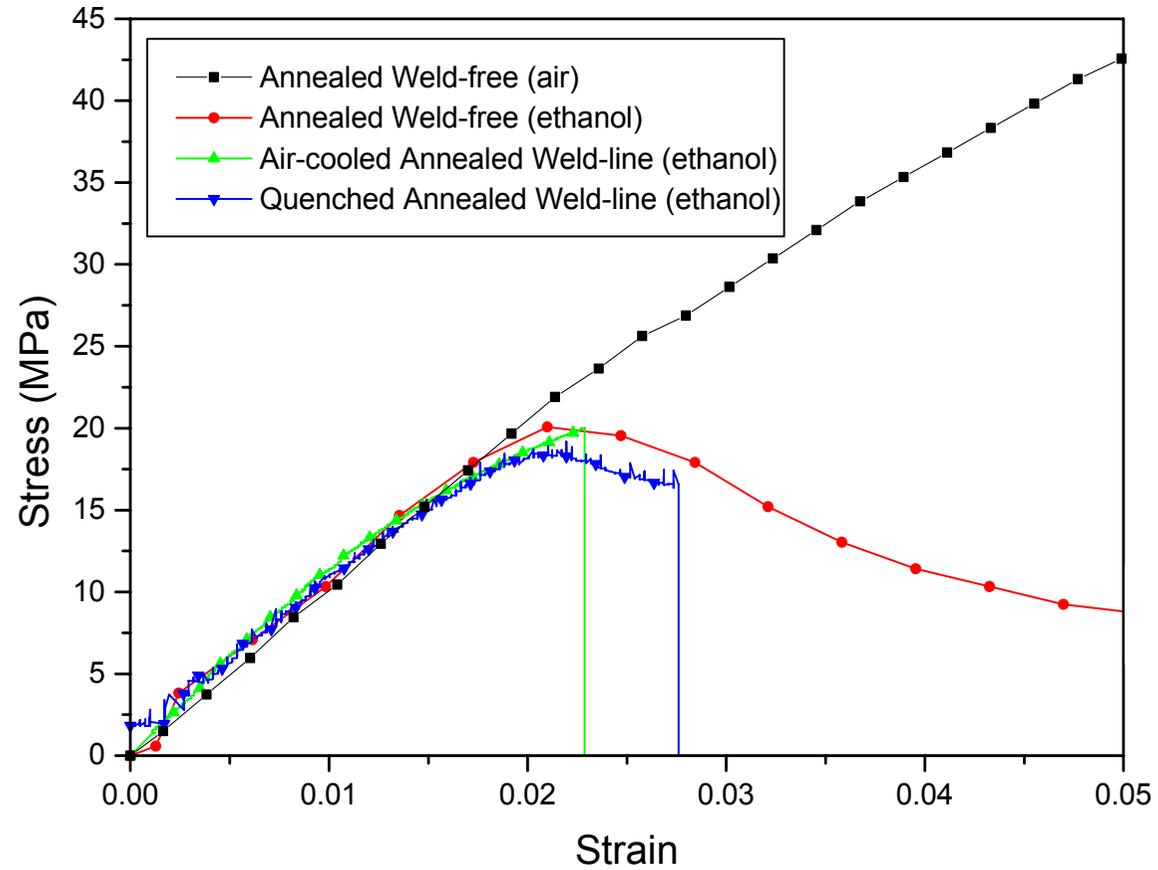
**Figure 2 Standard ISO 527-2 tensile test specimen used in the slow strain rate tests**



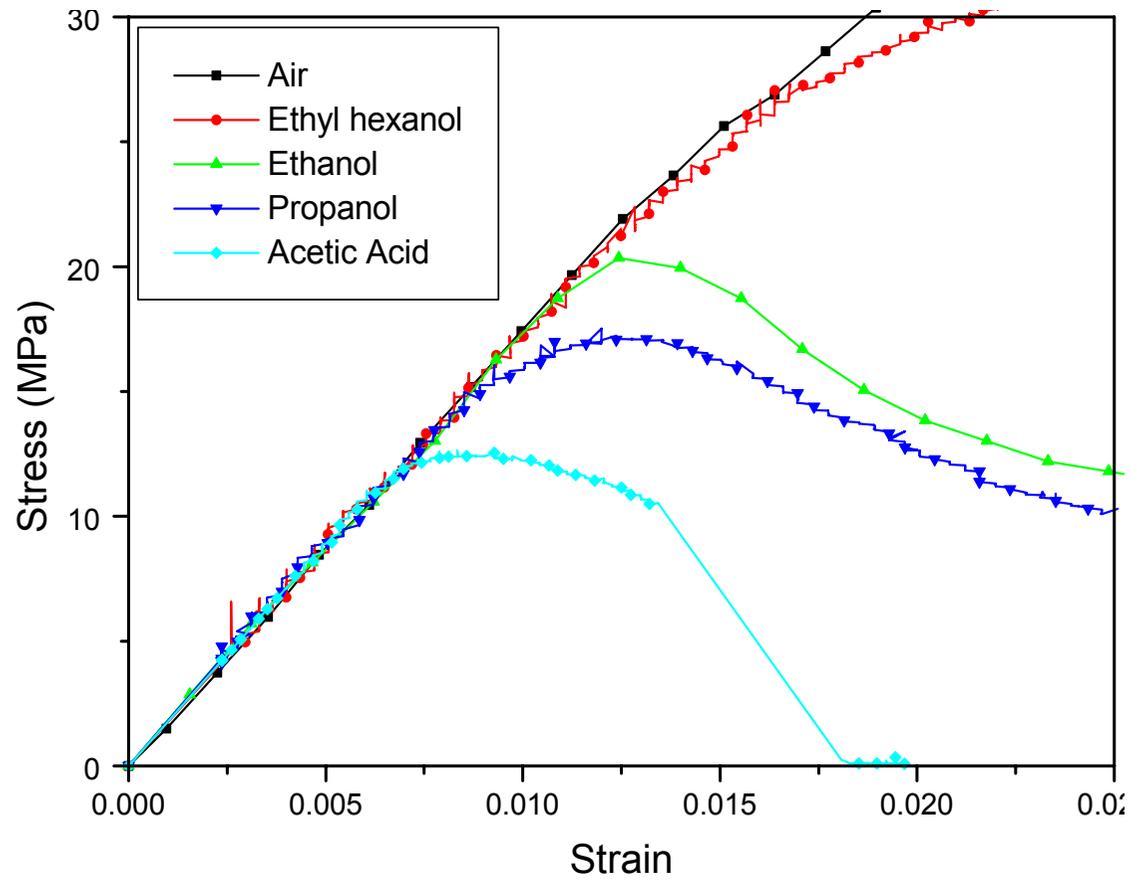
**Figure 3 Effect of the weld-line on the departure stress of air-cooled PMMA specimens**



**Figure 4 Effect of a weld-line on the departure stress of quenched PMMA specimens**



**Figure 5** Slow strain rate behaviour annealed weld-line specimens (Position 1) in ethanol. These specimens were annealed at 95°C for 100 hours to relieve the residual stresses.



**Figure 6** Slow strain rate data obtained from annealed weld-free PMMA specimens