Stress Cracking from Medical Fluids

Materials Testing. Environmental stress cracking is one of the most frequent causes of failure of plastic parts under load. Plastics commonly used in medical technology were tested using various methods as to their resistance to stress cracking in contact with medical fluids.

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As part of a project sponsored by the German Federal Ministry of Economics and Technology (BMWi), experimental studies into the stress cracking resistance of polymers in contact with medical fluids were performed at the Institute of Medical and Polymer Engineering (MedTech) at the Technische Universität München, Munich (chair: Prof. Dr. Dr. E. Wintermantel). Furthermore, Das Kunststoff-Zentrum (SKZ) in Würzburg, Germany, cooperation partner of the research project, analyzed the suitability of the phased-array ultrasonic technology for non-destructive detection of stress cracking in plastics.

Environmental stress cracking is one of the most frequent causes of failure of plastic parts under load. Roughly 25 % of all documented part failures are attributable to this aging phenomenon [1]. It is not unusual for it to occur suddenly and unexpectedly, and it can have serious consequences. In order to minimize the hazard potential of stress cracking, it is extremely important to have detailed information about the field of application of the polymer materials and about the environmental influences occurring in practice. Existing resistance tables for plastic/media combinations, however, are frequently incomplete and the necessary test procedures are time-consuming and costly. It is also often not possible to exactly determine and evaluate the individual constituents and mixtures of liquids using the table. A further problem is that many resistance tests are performed over an extremely limited period of time – not seldom with exposure times of less than five days [2]. The long-term effect is thereby more or less ignored. Particularly in the field of medical technology, however, it is crucial for the development process to be able to assess the characteristics and behavior of a material during use in order to minimize the risk for the patient.

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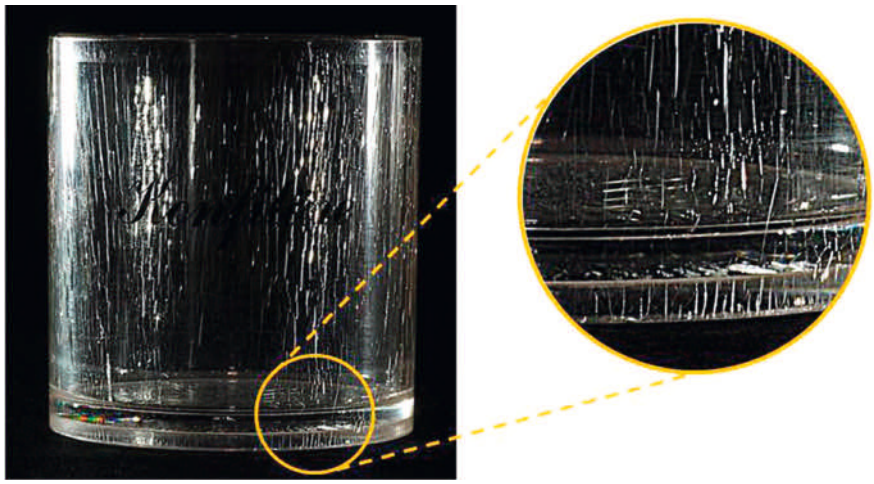

Fig. 1. Stress cracks in a transparent cup. Stress cracks can occur in plastic parts subjected to an internal and/or external mechanical load with simultaneous exposure to a surrounding medium (e.g. tensides). This frequently leads to spontaneous part failure (figs. 1 to 6: TU Munich)

Cracking as an Aging Phenomenon

The cracking of polymer parts due to aging is classified into two categories: Environmental stress cracking (ESC) and stress corrosion cracking (SCC). If a medium acts physically on the polymer at the same time as a mechanical load, the secondary valency forces are affected, a phenomenon that can lead to the occurrence of stress cracking **(Fig. 1)** [3–4]. In this case we speak of environmental stress cracking. If cracking is caused by the medium due to chemical ageing, i.e. due to the impact on the primary valency bonds, then we speak of stress corrosion cracking.

Standardized Test Methods

A number of standardized test methods exist for assessing the resistance to stress cracking of polymer materials which differ according to the type of load, the part or test specimen geometry, the material and the test apparatus involved. The DIN EN ISO 22088 standards series establishes the basic methods for determining the ESC characteristics of standardized test specimens. A few selected results of the series of experimental tests are presented as examples below:

Using various test methods such as the three-point bending method, the polymers commonly used in medical technology, polycarbonate (PC, grade:

Makrolon Rx1805), methyl methacrylate acrylonitrile butadiene styrene (MABS, grade: Terlux 2802 HD), cyclo-olefin copolymer (COC, grade: Topas 6013S-04) and polysulfone (PSU, grade: Udel P-1700) were tested as to their resistance to stress cracking in contact with therapeutic and medicinal fluids (Ringer solution, human blood plasma and various disinfectants).

During these tests, the injection molded plastic test specimens were exposed to different environmental media under static bending loads for several weeks and the cracking resistance or crack propagation were assessed. The determination of the remaining material characteristics allows the residual strength to be assessed in correlation with the degree of damage due to the aging process.

The ESC resistance experiments show that polycarbonate tends to form stress cracks in all the tested test fluids. In contact with the disinfectant ClearSurf (manufacturer: Fresenius Medical Care AG), the test specimens failed already after an exposure time of less than four days **(Fig.2)**. The results show a significant dependence of the crack propagation on the mechanical load. The MABS can be seen to be considerably more resistant to ESC than the tested PC. Noticeable on the other hand is the comparatively low service temperature at which MABS takes on a milky opaqueness in some test fluids (at an elevated test temperature of 55 °C). PSU which belongs to the "high-performance polymers" proved to be resistant to stress cracking in all the tested environmental media. Even significant stretching of the edge fibers (up to 3 %) and elevated test temperature have only a marginal influence on the ageing process due to ESC or the residual strength.

A comparison of the dynamic and static bending load on PC test specimens shows that stress cracks in contact with a crack-initiating medium (here: Incidin Extra N, manufacturer: Ecolab GmbH) are formed significantly faster under a dynamic load than under a purely static load during the three-point bending test **(Fig. 3)**. A reduction in the residual strength of 20 % is to be observed after only six hours' exposure to the test fluid. An early reduction in the part strength due to ESC is therefore to be expected under cyclic load conditions.

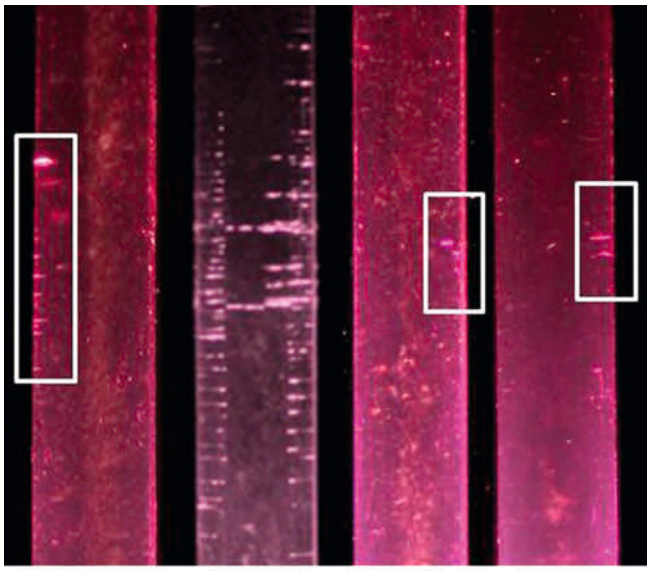

Fig. 2. Stress cracks in polycarbonate test specimens after 62-day media contact. The disinfectant ClearSurf causes severe cracking over the whole test surface after only 19 hours, and leads to failure due to specimen breakage after less than four days

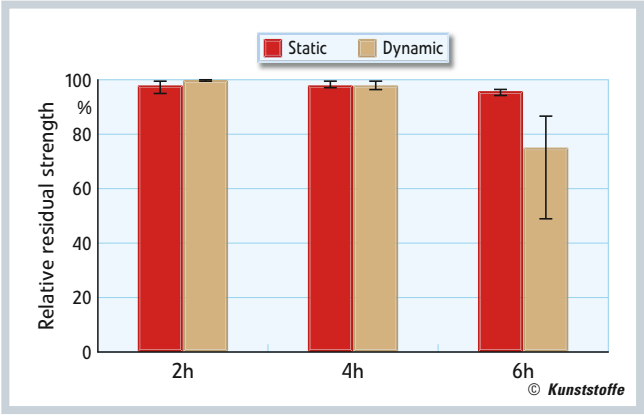

Fig. 3. Relative residual strength of polycarbonate after exposure to static and dynamic load in the disinfectant Incidin Extra N

Influence of Surface Treatment

In addition to the static and dynamic experiments, the influence of common sterilization methods (steam, ethylene oxide and gamma sterilization) and surface activation by Openair plasma on the ESC resistance was also analyzed.

Surface cleaning or activation of the plastic test specimens with atmospheric plasma does not impair the mechanical characteristics in the original condition. Contact with ClearSurf, however, increases the susceptibility to stress cracking of plasma-treated PC and COC specimens significantly due to the increased wettability of the specimen surface. The relative residual strength is thereby reduced by 80 % of the original value →

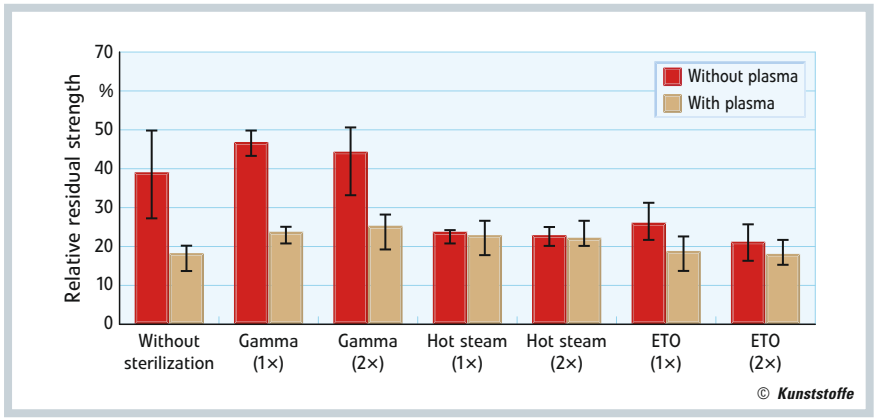

Fig. 4. Relative residual strength of polycarbonate after 48-hours media exposure (ClearSurf) as a function of the sterilization method and the surface pretreatment with Openair plasma. The exposure was performed under mechanical load (three-point bending, bending radius 200 mm)

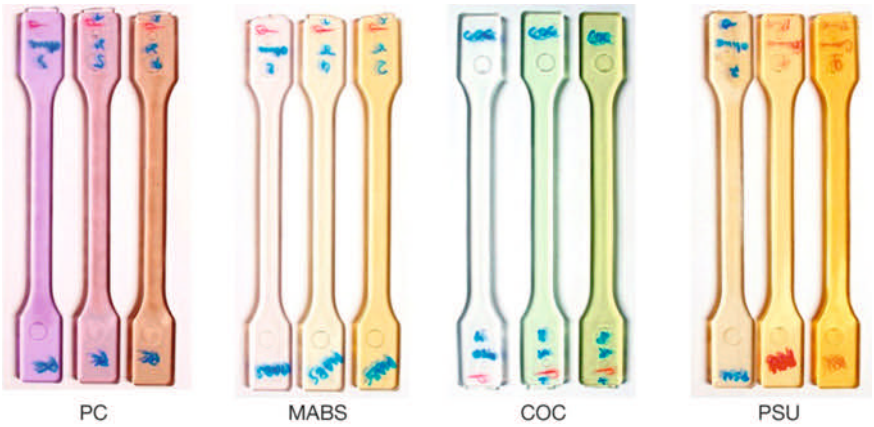

Fig. 5. Color changes due to single and double gamma sterilization (from left to right in each case). The amorphous polymers exhibit a significant change in color (yellowing) after sterilization

(Fig. 4). MABS and PSU, on the other hand, exhibit no changes in their resistance to ESC and in their residual strength after treatment with atmospheric plasma.

After mechanical loading (three-point bending with bending radius 200 mm) and 48-hour exposure to the disinfectant ClearSurf without plasma treatment and sterilization, polycarbonate exhibited isolated cracks on the test surfaces. The plasma pretreatment increased the number of cracks considerably. Furthermore, the sterilization methods employed cause an increase in the stress crack density. The PC specimens show a decrease in the maximum stresses after 48-hour contact with the test fluid – irrespective of the sterilization method and plasma treatment. Only gamma-sterilized specimens (without plasma pretreatment) achieve higher residual strengths (almost 50 %). These decrease further, however, as a result of the plasma treatment (25 % residual strength). The sterilization with hot steam and ethylene oxide causes a similar reduction in the residual strengths in both treated and untreated specimens (25 % of the initial strength).

The common sterilization methods (hot steam, ETO and gamma) also cause in some cases considerable changes in color and/or geometry to the plastic parts **(Fig. 5)**. The pigmented polycarbonate (transparent violet) turns a grayish color, but retains its transparency. MABS, on the other hand, becomes increasingly yellowish in proportion to the number of sterilization cycles. After only one sterilization, the crystal-clear COC takes on a yellowish-green discoloration that becomes more intense after the second sterilization. PSU (transparent amber) becomes more intensely yellow as a result of the sterilization.

Influence of Blood Plasma

In addition, the stress cracking was examined in a case study under realistic conditions using plastic parts of a heart support system and the results were compared with the results generated from the static test specimen experiments.

The polycarbonate part of the heart support system tested for ESC resistance under laboratory conditions (in vitro) in contact with human blood plasma exhibits no signs of aging after a 30-day pulsatile flow of the test fluid. The mechanical load and the internal stresses of the part appear to be too low as to cause stress cracking during the test. As far as the ESC resistance in contact with blood plasma is concerned, the useful life of the heart support system could therefore be prolonged. The comparison with miniature test rods made from the same material show, however, that under elevated mechanical load but otherwise comparable test conditions, cracking already starts after five to ten days **(Fig. 6)**. Specimens subjected to stretching of the edge fibers by 2 % fail after approx. 20 days of contact with human blood plasma.

Non-destructive Test Methods

In order to be able to detect stress cracks in plastics, destructive testing methods generally have to be used, so that the tested parts have to be replaced anyway. Consequently there is a great demand for non-destructive methods which allow estimates to be made as to the residual service life of parts. The phased-array ultrasonic technology (type: OmniScan MX PA ultrasonic tester, manufacturer: Olympus Deutschland GmbH, Hamburg) allows even the smallest cracks to be detected in plastic parts. The run time of the ultrasonic pulse and the amplitude of the fault echo allow conclusions to be drawn as to the location and size of the fault in the part. **Figure 7** shows the ultrasonic images (C scan) of the different levels of damage to the polycarbonate specimens. The amplitude has a color scale and serves as a measure for the size of the crack, where maxima are shown in red. The crack density is indicated by the frequency of the lines.

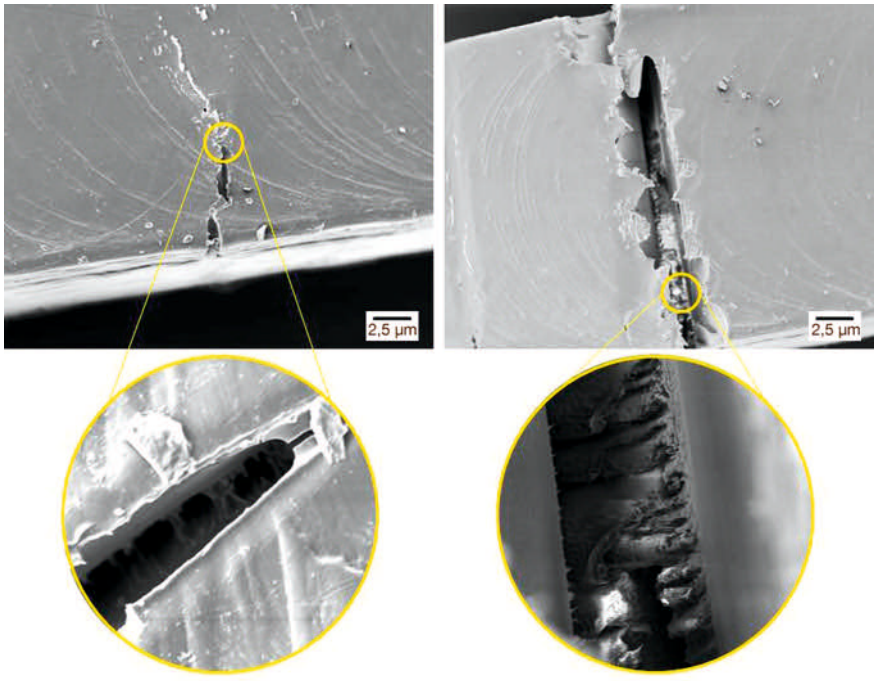

Fig. 6. REM micrographs (top view) of the cracking in miniaturized polycarbonate test specimens after 10-day (left) and 20-day (right) contact with blood plasma

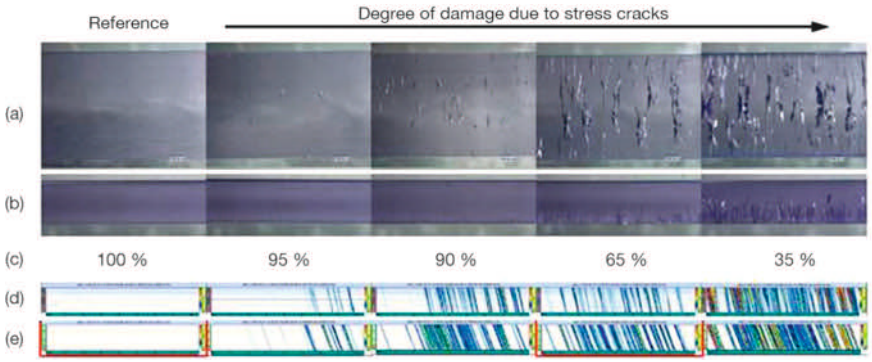

Fig. 7. Non-destructive detection of stress cracking using phased-array ultrasonic technology. The differing degrees of damage to the polycarbonate specimens are shown in the top view (a) and the side view (b) in relation to the relative residual strengths (c). Even individual small cracks can be detected by the contact technology (d) and immersion technology (e) in the sonogram (C scan)
(figure: SKZ)

A comparison of the residual strength shows that stress cracks in PC test specimens can already be detected when a part still has over 95 % residual strength. Even relatively large areas of the part surface can be tested by this means. It is difficult to test parts with an extremely curved, irregular surface using the conventional contact technology as this surface hinders the coupling of the ultrasonic wave into the part. In this case testing using the immersion technology in water offers an alternative.

Conclusion

The findings gained from this study allow conclusions to be drawn as to what extent the selected plastic/fluid combinations are susceptible to environmental stress cracking under given conditions (temperature influence, mechanical load, etc.). These results can, however, only provide a guide for the development of plastic parts in medical technology. Comprehensive, specific experiments which take all the influences and boundary conditions before and during use into consideration have to be performed in order to assess the resistance of medical parts under real application conditions. It was also possible to show that the phased-array ultrasonic technology represents a suitable non-destructive testing method for early detection of stress cracking in plastic parts. ■

This article is dedicated to Prof. Dr.-Ing. Dr.-Ing. E. h. Walter Michaeli on the occasion of his 65th birthday and his retirement.

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