Environmental Stress Cracking of Polymers Monitored by Fatigue Crack Growth Experiments

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Summary: This article describes fatigue crack growth experiments to investigate the degradation of the durability of polymers due to fluid environments. The degrading effect of media causing stress cracking can be observed on the fracture surfaces of tested samples by scanning electron microscopy. Strategies to improve environmental stress cracking like changes in molecular weight, orientation, toughening with rubber particles of different sizes are discussed. Fatigue crack growth experiments can be employed as a very fast and effective screening method.

Keywords: fatigue crack growth; mechanical properties

Introduction

Fatigue crack propagation (FCP) experiments can be employed as a fast and effective screening method for determining long-term mechanical properties of polymers. Advantages of this method, like the need for a very small quantity of test material (<10 g), the broad range of fatigue crack propagation rates (from 10^{-2} mm/cycle to 10^{-7} mm/cycle) measured within one specimen and a well defined stress state at the crack tip favor the use of FCP experiments instead of traditional S-N curves [1]. These experiments can also be conducted in the presence of a specific environment and are

© 2004 International Union of Pure and Applied Chemistry DOI: 10.1002/masy.200451004

able to provide valuable information about environmental effects on crack propagation.

If the FCP experiment is carried out in the presence of a critical fluid environment, a more or less progressive degradation of mechanical properties (embrittlement), depending on the polymer, can be observed. This degradation is caused by enhanced disentanglement and chain scission of the molecules affected by a solving liquid. The process is called environmental stress cracking (ESC). ESC is defined as the simultaneous action of stress and contact with specific fluids. Approximately 15 % of all failures of polymer components are due to ESC. Since prediction in many cases is exceedingly difficult, assessment through suitable laboratory tests becomes important [2]. Standard tests for environmental stress cracking of polymers are the *Ball or Impression Method* (ISO 4600), the *Bent Strip Method* (ISO 4599) and the *Constant Tensile Stress Method* (ISO 6252).

In these standards either a constant static load or a constant deformation is applied. In the case of the bent strip method and the impression method the residual strength is quantified through a succeeding impact or tensile test. This, however, does not imply that the stress state at the crack tip in the moment of failure is well defined. Moreover, the common standardized test methods do not consider a well defined stress state within the test specimen. This could be achieved by applying the principles of linear elastic fracture mechanics to ESC test procedures in combination with a compact tension (CT) specimen. In contrast to tensile or impact tests, the stress state at the crack tip of a CT-specimen is well defined. A specific fluid is able to penetrate to the front of the crack tip. Under cyclic loading, the propagation of a fatigue crack through the bulk material of a CT-specimen is affected by the presence of the fluid. From the dynamics of crack propagation, information about the interaction between the crack tip, designated as a microscopically small probe, the fluid environment and the ESC sensitivity of a specific polymer, polymer blend or polymer composite, can be achieved.

Fatigue crack growth

All fatigue failures in polymers or polymer composites involve one phase in which a defect zone such as a craze or microcrack initiates, followed by a propagation phase to final fracture. Based on the assumption that the fatigue lifetime is determined by the propagation phase, a preexisting flaw is assumed. The stress state at the tip of the crack is defined by the stress intensity factor range ΔK. For the case of fatigue, Paris [3] showed that a linear relationship predicted by a simple power law for a double logarithmic scale exists between the FCP rate da/dN and the applied ΔK (Figure 1).

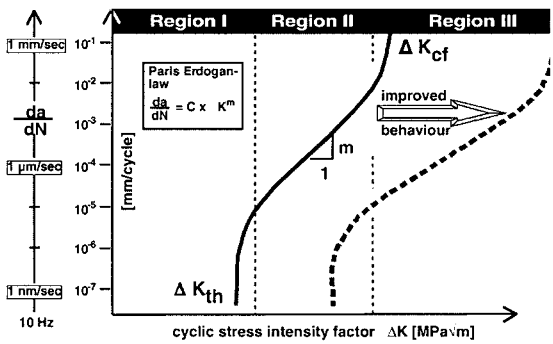

Figure 1. Scheme of fatigue crack propagation diagram.

The linear dependence is frequently observed only over an intermediate range of growth rates. When investigating a wide range of da/dN, deviations from this linear behavior may be observed, as illustrated schematically in Figure 1. That is, FCP-rates decrease rapidly to vanishingly small values as ΔK approaches the threshold value ΔK_{th}. This ΔK level defines a design criterion that is analogous to the fatigue limit determined from traditional S-N curves [4,5]. FCP rates increase markedly as ΔK approaches ΔK_c, at which unstable fracture occurs within one loading cycle. From the standpoint of evaluating a materials fatigue resistance, any decrease in FCP rates at a given value of ΔK or, alternately, any increase in ΔK to drive a crack at a given speed is, of course, beneficial.

As shown in Figure 2, the experiments can be conducted also under constant ΔK conditions. In this case, specific influences of a medium could be detected by a change in the crack propagation rate as a function of exposure time. For metallic materials, fatigue crack growth experiments under environmental conditions are described in ASTM E 647, but for polymers, no standard procedure exists until now.

Environmental stress cracking (ESC) of polymers is a phenomenon which has been researched over a period of more than 40 years. The phenomenon involves so many influential variables that the behavior cannot be predicted with sufficient accuracy. The only alternative is testing. It is for this reason that any advances in test methods are important, to make research more efficient and effective.

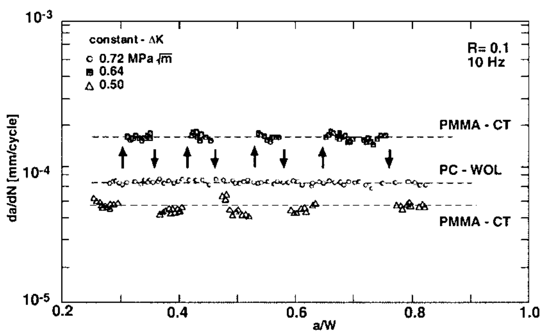

Figure 2. Experiments conducted under constant K [6] conditions.

Experimental

Materials

Amorphous thermoplastics are sensitive to ESC. In particular, polystyrene (PS) is well known to be sensitive to fluid permeation causing crazing [2]. Commercial PS polymers were selected for the investigation of the effect of molecular weight and various types of rubber modification on the ESC behavior under fatigue crack growth conditions. The materials were kindly supplied by BASF AG, Ludwigshafen, Germany and are listed in Table 1.

Two different polycarbonates were used for the investigations regarding lipid resistance. The specimens were kindly supplied by B. Braun Medical AG, Switzerland.

All polymers were processed by injection molding under standard conditions and tested considering the injection molding direction.

Test methods

Compact-type (CT) specimens were cut from rectangular injection moulded plates with 4 mm nominal thickness and precracked by a razor blade. All fatigue crack growth tests were run on a Schenck PSA® servohydraulic test system at a frequency of 10 Hz under sinussoidal loading in tension-tension with a minimum to maximum load ratio (R) of 0.1 at room temperature. The tests were run under ΔK control with a software designed by Fracture Technology Associates, Inc. A ΔK-decreasing portion and a ΔK-increasing portion were measured separately for two different specimens of the same material and combined to one FCP-diagram. The crack length was monitored by a compliance technique, as published by Saxena & Hudak [7].

The tests under environmental conditions were carried out by applying the critical fluid through a soaked sponge, which was fixed on both sides of the specimen as an unlimited source. According to this procedure the crack was always covered with the soaked sponge. For the test with polystyrene (PS) and a commercial sunflower oil (tradename Livio®) were used. The tests with Polycarbonate (PC) were performed with a fat emulsion (Lipofundin® MTC 20 %) for parenteral nutrition.

In this investigation all tests were run within load amplitude limits under ΔK control. The fatigue behavior was expected to deteriorate because, under the softening effect of a liquid medium, the samples would be strained more extensively for each loading cycle.

Table 1. Investigated materials

material	property
PS 148H	polystyrene - M_w 238,000 g/mol
PS 168N	polystyrene - M_w 354,000 g/mol
PS 486M	polystyrene impact modified by small PB particles
PS 2710	polystyrene impact modified by large PB particles

Fractography

Fracture surfaces were studied with a field emission electron microscope LEO 32. The microscope was operated at an accelerating voltage of 0.5-1 kV. Because of the low accelerating voltage no gold coating of the specimen was necessary and the specimens could be investigated directly after fracture of the specimen in the fatigue experiment.

Results and Discussion

Effect of molecular weight

Physical properties of polymers are strongly dependent on the average molecular weight M_W and sequence distribution M_W/M_N, because the presence of molecular entanglements can significantly affect the mechanical behavior. As previously shown by Altstädt [8] for different commercial PS systems prepared by free radical polymerization and by anionic polymerization, the number average M_N of the molecular weight corresponds well to an increase of the fatigue crack growth behavior. Further experiments were conducted in this study to explore the effect of environmental ageing.

The effect of molecular weight on the ESC behavior was investigated for two different PS systems. These were tested with and without an oil environment. As shown in Figures 3 – 4, both PS systems exhibit a severe decrease in fatigue crack growth resistance when tested under oil environment. In both cases, ΔK for a given fatigue crack growth rate is significantly reduced and the slope of the curve is increased. Simultaneously, a decrease in ΔK_{th} is observed. The comparison of both PS systems clearly shows an improved ESC resistance under fatigue loading of the PS with the higher molecular weight. This is reflected in a smaller slope of the linear portion of the FCP-diagram and a higher ΔK_C and ΔK_{th} for PS 168N.

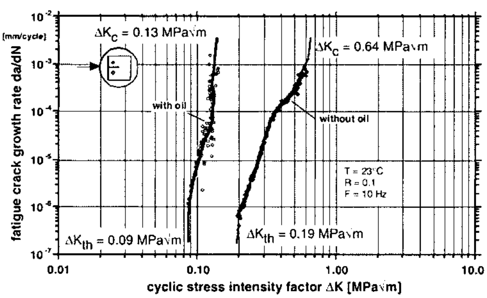

Figure 3. FCP with and without stress cracking media.

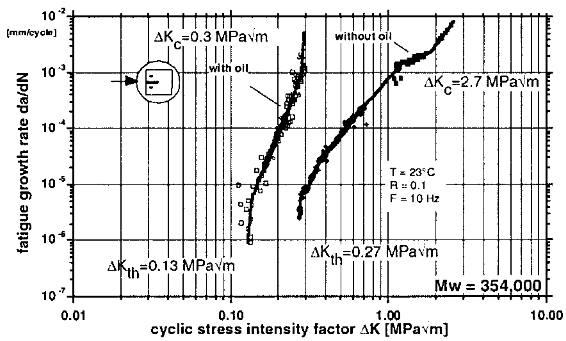

Figure 4. FCP with and without stress cracking media.

Effects of orientation

To investigate possible orientations of the molecules due to the injection moulding process on the ESC resistance under fatigue loading conditions, samples of polystyrene were tested parallel and perpendicular to the injection moulding direction. A specimen prepared from granules by compression molding, which should have a minimum of orientation, was included in the investigation as a reference. To minimize the effect of a plastic deformation possibly induced by precracking with the razor blade, the precrack was extended for a minimum 2 mm by fatigue loading before starting the experiment. In some cases it was difficult to carry out the test, because the crack grew parallel to the injection direction or an additional crack was initiated on the fixing holes of the samples.

As shown in Figure 5 the FCP-diagram of the specimens tested perpendicular to the injection moulding direction is shifted significantly to higher ΔK values compared to the specimens tested parallel. While the reference specimens processed by compression molding behave similar to those with parallel orientation. Obviously it is easier for the fatigue crack to propagate in the direction of the oriented entanglement network. This can be explained by the fact that crack propagation in PS is accompanied by crazing. Molecules which are already stretched in one direction are losing the ability to fibrillate in the other direction. By this, the probability for chain scission is increasing and the breakdown of the material drawn into the process zone occurs at lower ΔK values.

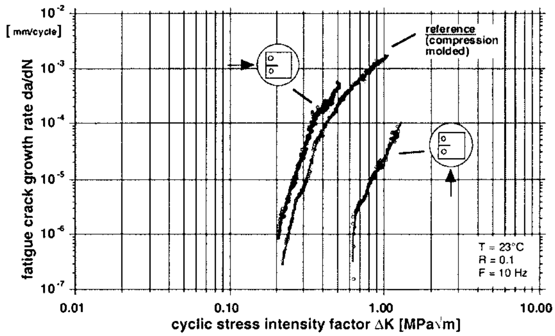

Figure 5. Molecule orientation effects on crack propagation.

If polystyrene is tested perpendicular to the injection molding direction and a stress cracking media is present at the same time, an additional embrittlement can be observed by the steep increase in the FCP-curve, which makes it almost impossible to measure the dynamic of crack propagation in a broad range of crack propagation rates as usual (Figure 6).

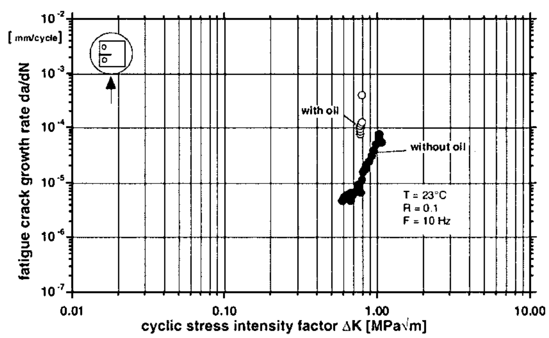

Figure 6. Injection moulded samples tested perpendicular to the injection direction.

Toughness modification by rubber particles

A common strategy to improve the mechanical behavior of thermoplastics is to incorporate uniformly distributed rubber particles in the polystyrene matrix. In the case of HIPS (high impact polystyrene) styrene-butadiene block copolymers are used. This strategy is also applied to improve the environmental stress crack resistance of polystyrene.

For this investigation two commercial PS grades with different average diameters of the rubber particles were selected (PS 486M: Ø ≈ 2 μm, PS 2710: Ø ≈ 5 μm).

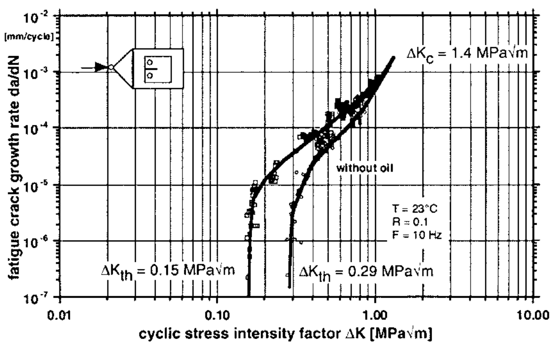

Figure 7. Effect of small styrene-butadiene rubber particles incorporated in PS.

The systems were tested with and without exposure to vegetable oil. The corresponding FCP-diagrams are shown in Figures 7 - 8.

The FCP behavior of the two rubber-modified polystyrenes is comparable in the threshold region and in region III (Figure 1) at high propagation rates. A significant difference is visible in region II of intermediate crack propagation rates 10^{-5} to 10^{-4} mm/cycle. In particular, PS with the larger rubber particles is more effective in decreasing the slope of the crack growth curve.

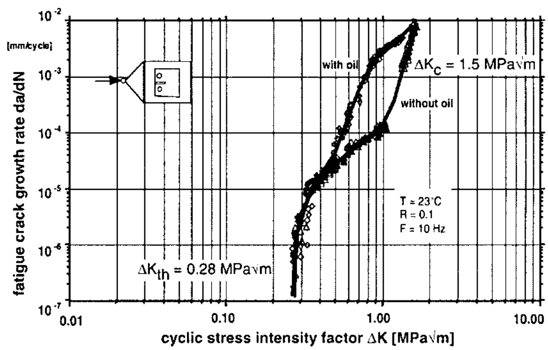

Figure 8. Effect of large styrene-butadiene rubber particles incorporated in PS.

Compared to the unmodified PS 148H and PS 168N (Figures 3 - 4) the observed ranking in terms of FCP behavior is PS 148H < PS 486M = PS 2710 < PS 168N. This ranking is changed completely if the tests are conducted in the presence of vegetable oil: PS 148H << PS 168N < PS 486M < PS 2710. Obviously rubber toughening is more efficient for the improvement of the ESC resistance under fatigue crack growth conditions than the increase in molecular weight corresponding to PS 148H and PS 168N. A remarkable difference between the two rubber modified systems is visible in the threshold region. The ΔK_{th} value of PS 2710 is not affected by the presence of the medium while ΔK_{th} of PS 486M is reduced by a factor of two.

The observation of the fracture surfaces in Figures 9 - 12 reveals the different sizes of the rubber particle of the two PS systems (Figures 9 - 11). Tested in air, in both cases the crack propagates through the rubber particles which is only possible in the case of good interfacial bonding. Tested in vegetable oil, the fracture surface appears to be very smooth. In the case of PS 486M, some marks from the underlying morphology are visible.

It is generally accepted that rubber particles act as stress concentrators, initiate crazes as well as participate in their termination. The contribution of toughness depends on the concentration of the rubber, the particle size and the interfacial bonding. In the case of fatigue crack, growth of small particles is more efficient at low crack propagation rates because the plastic zone size is smaller, while larger particles are more efficient at higher propagation rates and the corresponding larger plastic zone diameter.

Under the influence of a stress cracking medium it seems that in the case of large rubber particles small crazes may easily develop. As a consequence the diffusion rate of oil is reduced, because of the increased fibril density. Small rubber particles show less intensive crazing and the crazes are easier overloaded because of a higher effective opening of the crack tip. In the latter case the oil can penetrate easier through the crazes. This effect is stronger in region I of the FCP curve as compared to region II (Figure 1). At high crack propagation rates, it seems to be possible, that the oil is not able to penetrate fast enough to the crack tip which explains the same ΔK_C values of the two rubber modified systems.

It should be mentioned at this point, that our interest here is rather in the effect of critical fluids on fatigue crack propagation. The total fatigue lifetime of unnotched specimens is determined by a initiation and a propagation phases. The initiation phase could be significantly effected by the presence of rubber particles [9]. The effect of critical fluids on the initiation phase has to be studied separately.

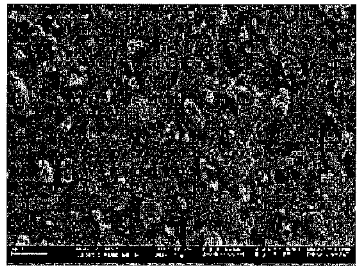

Figure 9. FCP fracture surface of PS 486 486M tested under air environment.

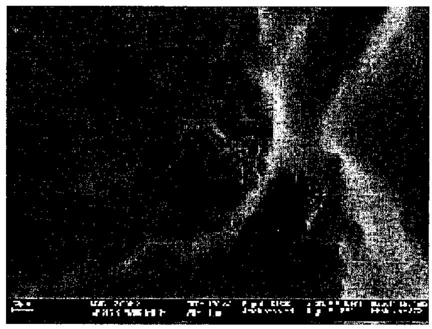

Figure 10. FCP fracture surface of PS 486 486M tested under oil environment.

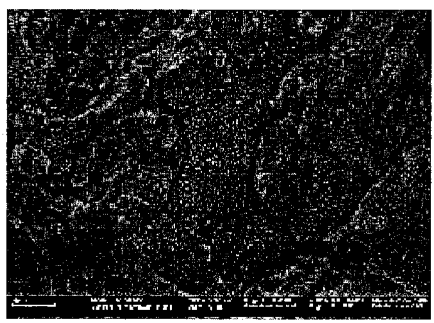

Figure 11. FCP fracture surface of PS 2710 tested under air environment.

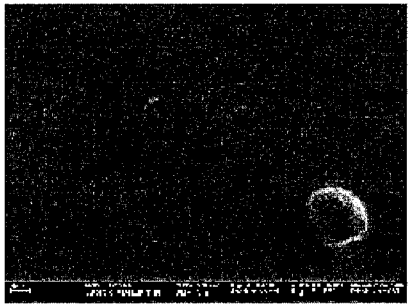

Figure 12. FCP fracture surface of PS 2710 tested under oil environment.

Lipid resistance of medical devices

For medical devices, in particular for components of infusion systems, transparent polymers are indispensable. Because of the multitude of drugs possibly flowing through these systems, the need for disinfection of the devices and the possibility to connect various components by force locking, the ESC resistance plays a decisive roll in the selection of a suitable material. Figure 13 shows a three-way stop cock as a important component of such a system.

In principle, the ESC resistance can be controlled within limitations, which are mostly given by the viscosity for processing, by the molecular weight and molecular weight distribution of the polymer. Because of this, polycarbonate with a molecular weight of above 30,000 g/mol is used for this application.

Specially in the case of parenteral nutrition with lipid-containing emulsions the occurrence of stress cracking by the intravenous infusion in three-way stop cocks made of polycarbonate can not be completely excluded.

Figure 13. Three-way Stop cock as a component for medical infusion systems.

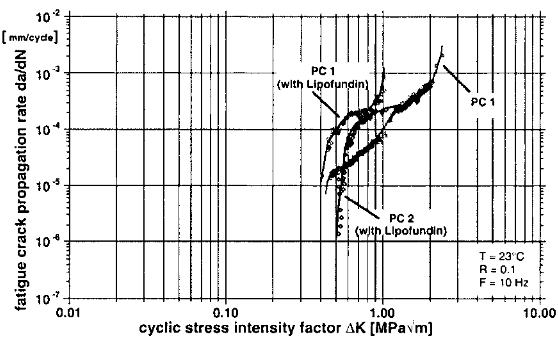

Figure 14. FCP with and without stress cracking media in polycarbonate PC1 (reference) and PC2 (improved).

A significant improvement in the administration of a lipid-containing emulsion was achieved with a special additive to polycarbonate. As shown in Figure 14, the better behavior of the new polycarbonate PC2, proved in practice, could also by verifyed by fracture mechanical fatigue crack growth experiments. In the presence of the fat emulsion the higher lipid resistant PC2 shows a higher fatigue threshold value ΔK_{th}, as well as an improvement by a factor of two for ΔK_c .

Conclusions

Fatigue crack propagation (FCP) experiments can be employed as a fast and effective screening method for the evaluation of environmental effects on crack propagation. As shown for PS, molecular weight, molecular orientation and rubber toughening play an important role in the ESC behavior.

Acknowledgement

We thank Dr. F. Ramsteiner and Dr. W. Loth from BASF AG, Polymer Research Division, Ludwigshafen, Germany for the helpful discussions.

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