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Environmental stress corrosion behavior of polyamides and their composites with short glass fiber and glass swirl mat

A comparison

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ABSTRACT

Environmental stress corrosion cracking (ESC) behavior of different polyamides (PA) without and with short and glass fiber mat reinforcements was studied in air,water and diluted sulfuric acid and compared. Whereas the neat polymers and their short glass fiber reinforced versions failed by crack growth, the breakdown of the glass mat reinforced polyamide block copolymer (NBC) depended on the corrosion loading history, i.e. on the immersing time.The ESC response of the systems studied was analysed and summarized schematically indicating the effects of matrix structure, type and amount of the reinforcement and environment. Characteristic failure events were also revealed and included in related models.Guide-lines for further material improvements were deduced.

INTRODUCTION

Structural parts of polyamides (PA) and their composites, produced by injection molding techniques, are often exposed to the combined influence of an applied stress and a given environment.This process, referred as static fatigue in air and environmental or stress corrosion cracking (further ESC) in various environments, may result in a considerable reduction of the part lifetime depending on the susceptibility of the matrix and reinforcement in the specific medium.Informations about the possible effects of aggressive environments on glass fiber reinforced plastics can be taken from reviews [1-2].The ESC measurements are generally carried out according to the the principles of the fracture mechanics in the subcritical range [1-4].Although results on the ESC performance of rubber toughened PA-6.6 and its short glass fiber (GF) reinforced grades, both in alkaline and acidic mediums, have been reported [4] a comparison among dfferent PA matrices is still missing.In addition, the effect of a continuous GF strand (swirl) mat incorporated into the PA is unknown at present.The purpose of this paper is to contribute to this topic.

EXPERIMENTAL

Materials

Three different PAs were studied:commercially available PA-6 (Danamid-E,Magyar Viscosa,H), rubber toughened PA-6 (RTPA-6; Durethan BC 402, Bayer,D) and a polyamide block copolymer (NBC) containing 20 wt.% polyether segment produced via reaction injection molding (RIM) using Nyrim^{R} 2000 components of DSM (Maastricht,NL).As composites 20 and 30 wt.% short GF filled grades of the above PA-6; 15 and 35 wt.% short GF (SGF) containing high-impact PA-6 (HIPA-6; Durethan BKV 115 and 135,Bayer,D) and NBC-based composites with 20,40 and 50 wt.% GF swirl mat were used.Further details about the materials applied can be taken from references [5], [6] and [7], respectively.

Tests

For the ESC investigations compact tension (CT) specimens were cut from the injection molded plaques and notched parallel (L) to the mold filling direction (MFD) as it can be seen in Figure 1.

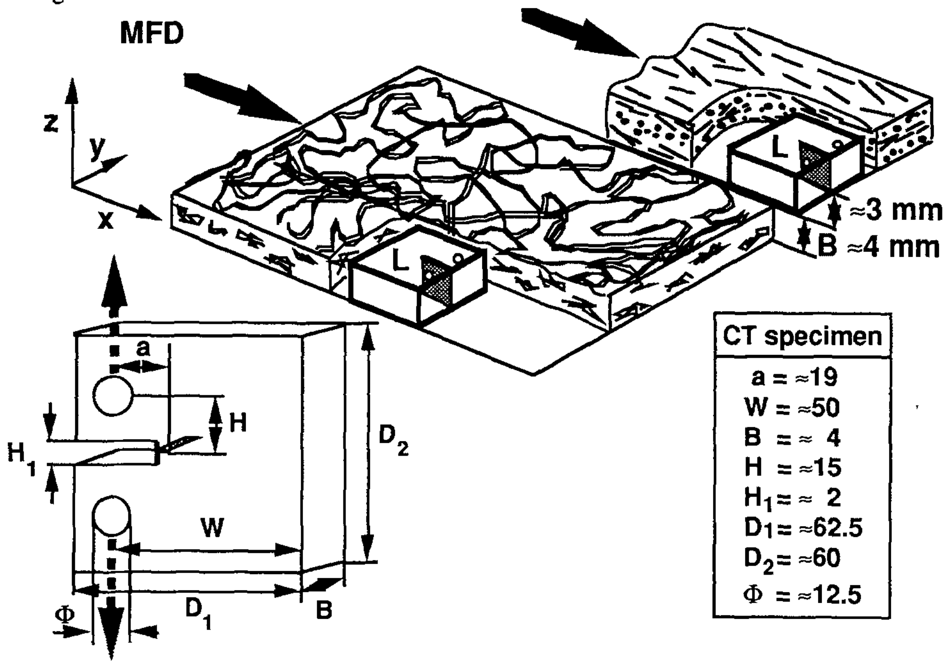

Figure 1.
Machining,notching and dimension of the CT specimens used
(Note:the fiber layering in the SGF-composites due to injection molding could be approximated by a 3-ply laminate structure in accordance with literature descriptions [8])

Tests were performed in air, water and diluted sulfuric acid solution (5%), respectively, by loading the CT specimens with different dead weights (F).The initial stress intensity factor (K_o) set by this way was in the range of (0.25-0.9)K_c, where K_c denotes the critical stress intensity factor or fracture toughness derived from measurements at monotonic increased load.Aim of the tests was to establish either the threshold value ($K_{I,ESC}$) below which "infinite" life is expected or to determine the ESC growth characteristics (crack growth plotted against the actual stress intensity factor; da/dt vs. K_I), or both.K_o and K_I were calculated by the Equation given in Figure 2, which illustrates for the ESC test,too.
Failure mode of the materials was studied by light and scanning electron microscopy (SEM).Any other details related with the testing were published previously [2-4].

RESULTS AND DISCUSSION

Matrices

In order to cover a relative broad subcritical range, it is necessary to carry out measurements either on the same specimen at stepwise increased load or on several specimens, each of them loaded by different K_o.The static fatigue response may differ upon the testing conditions (single or multiple specimen technique) as it is demonstrated in Figure 3a.Very often, however, the results can be described by an envelope curve, illustrated schematically in Figure 3b.

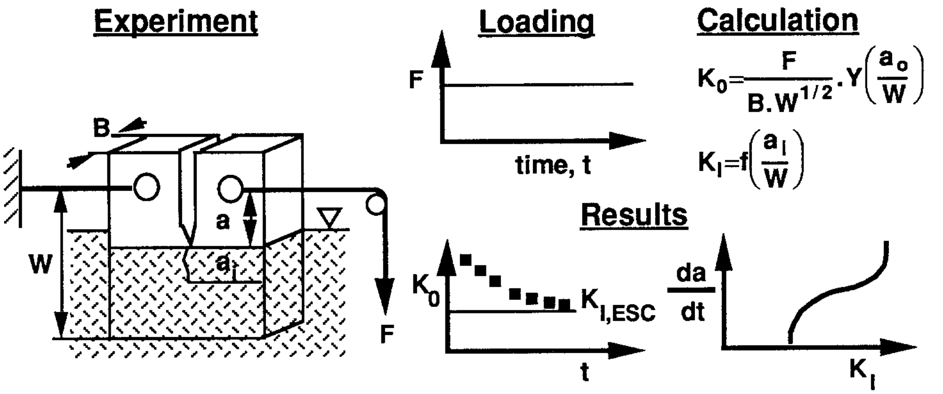

Figure 2.
Loading mode of the CT specimens and results got from ESC testing
(Note:the Y term in the Equation is the finite width correction factor according to the ASTM E 399 standard; all other parameters were defined before)

Range I in Figure 3b composed from microscale acceleration and deceleration processs can be evidenced mostly by single specimen technique.Appearance of range I strongly depends on the stress-strain behavior as well as on its alteration (strain hardening,recrystallization etc.) during the test.It can be stated that these acceleration-deceleration stages are related with a change in the sharpness of the crack tip in the damage or processing zone.Below a material- and testing-dependant threshold K_I value crack tip blunting and sharpening takes place subsequently upon stepwise increased loading, which manifests in a stick-slip type crack growth.The onset of range I therefore should depend on the ductility and deformation mode and ability of the matrix on microscopic level (crazing, voiding, shear deformation, recrystallization, strain- or solvent-induced recrystallization,texture rearrangement etc.).

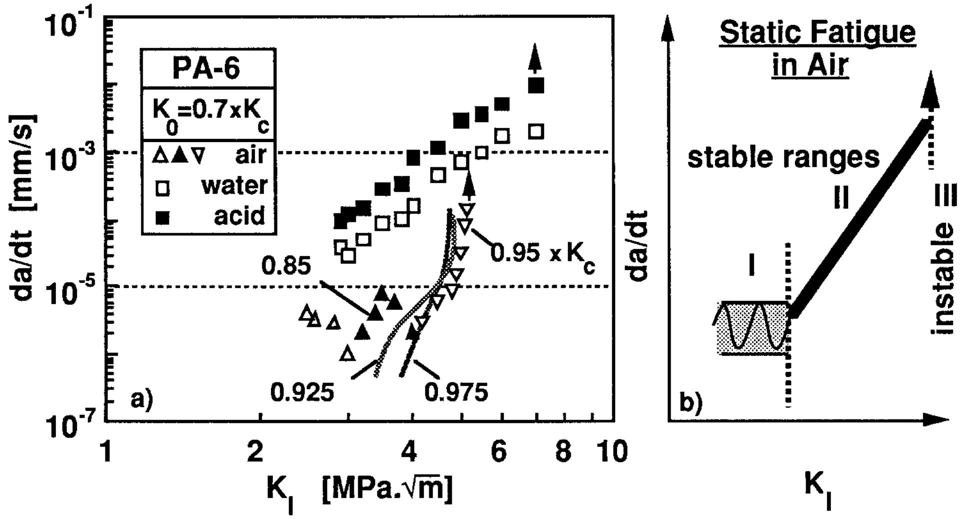

Figure 3.
a) Effect of environments and testing conditions (single or multiple specimen runs in air) on the ESC response of the neat PA-6 with K_c=4.0 MPa.m$^{1/2}$
b) Ranges in the static faigue (air) test results, schematically

Range II,or at least its parts (cf.Figure 3), can be approximated in most cases by the Paris power law:

$$\frac{da}{dt}=A.K_I^m \qquad (1)$$

where A and m are constants, and K_I is the actual crack tip stress intensity factor.

The onset of range III lies generally higher than the corresponding K_c value derived from monotonic increased static fracture tests.It is due to microstructural changes developed in the crack tip and leading to its improved load bearing capacity.External effects influencing the ductility of the specimen and material (e.g. specimen thickness, water uptake) shift range II toward higher K_I values with eventual extension of this range also in lower K_I direction (Figure 4).

The effects of environments studied are shown in Figure 4 which indicates also for changes by water uptake, schematically.Immersion in water and in diluted sulfuric acid results in ESC growth acceleration of about 2 orders of magnitude compared to the corresponding curve in air (cf. Figure 3a).The NBC studied exhibits even faster ESC growth characteristics in comparison to those of PA-6 and RTPA-6.This can be attributed to the enhanced water sorption ability of this block copolymer due to its segmented (polyether and polyamide blocks) build-up.

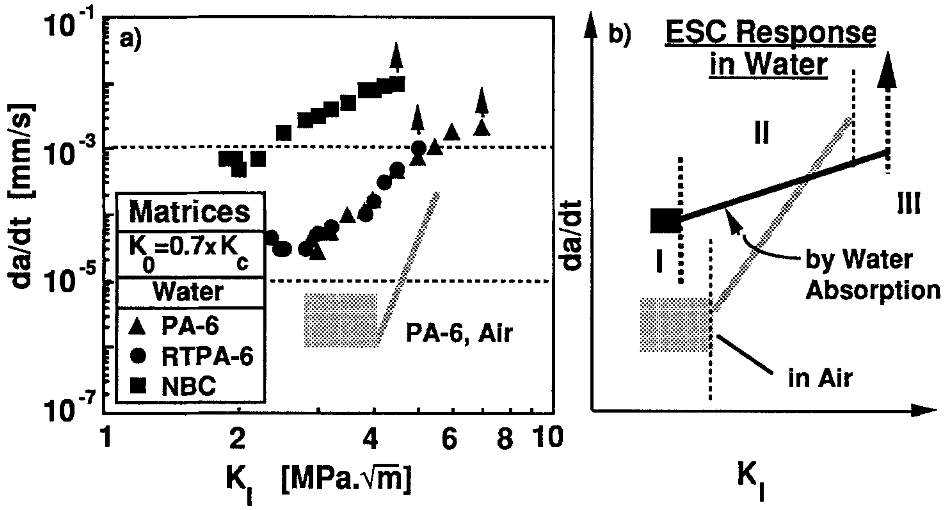

Figure 4.
a) Effect of water uptake on the ESC run of different PAs
b) Effect of water plasticization on the ESC response, schematically.

Composites
Reinforcement Effects
Short fiber reinforcement

The effect of SGF on the ESC trace is shown in Figure 5.Incorporation of SGF shifts the curves - in the first approximation more or less parallel to each other - toward higher K_I values.Based on the results of fracture toughness this shift is expected, since the K_c of PAs increases due to SGF reinforcements which should be reflected also in resistance against static fatigue or ESC [9].The SGF present affects the ESC response.This can be summarized by using the schemes in Figures 3b and 4b by the following way:

- range I is reduced in both direction and even disappears with further increase in the fiber volume fraction, V_f.On the other hand, plasticizing,toughening effects may contribute to its "recreation"

- range II moves to higher K_I values with increasing V_f and at the same time the slope of the curve in this range becomes steeper
- ductility increase of the matrix due to water uptake and/or toughening reflects in an additional shift of the boarderline between range II and III to the right and generally lowers the slope in range II.Increase in ductility may affect also the onset of range II, which starts then at slightly lower K_I values.

A scheme about these changes will be given later.

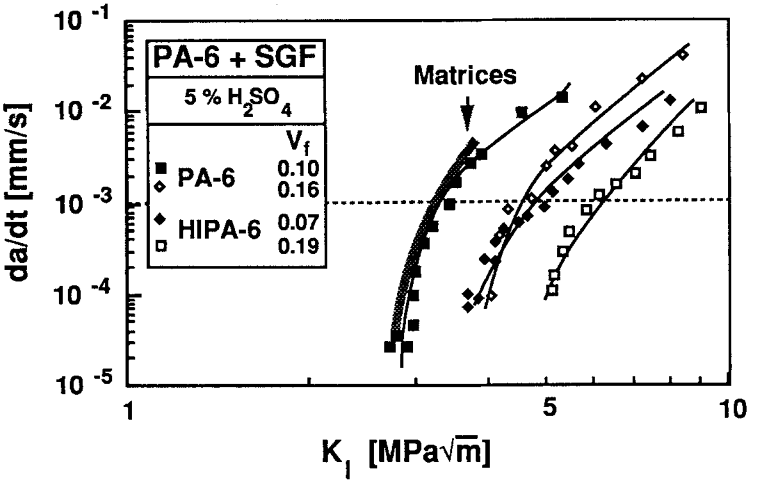

Figure 5.
Effect of V_f on the ESC traces in diluted sulfuric acid on the examples of SGF-reinforced PA-6 and HIPA-6

Mat reinforcement

Figure 6 depicts the characteristic Δa-t curves for NBC-RRIM composites which differ basically from those of the matrix as well as from those of traditional short fiber composites discussed above.

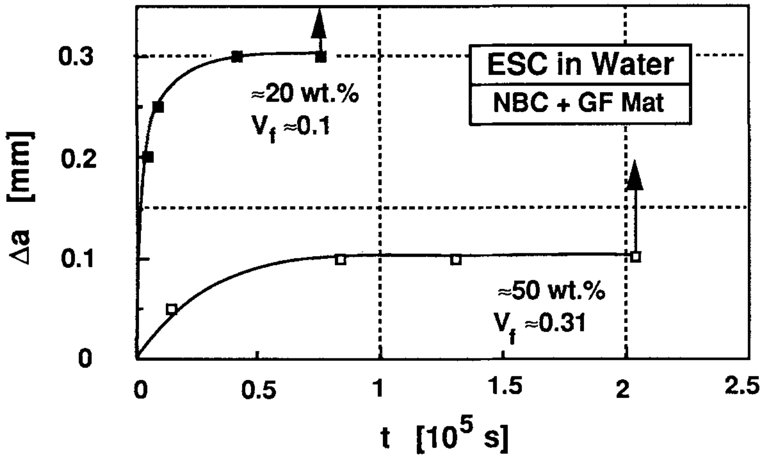

Figure 6.
Crack growth vs. time curves in water for NBC-RRIM of different GF mat loading

It is very striking that the crack extension increases until an upper threshold crack growth is reached.The latter depend on V_f and it has been established that this maximum Δa value agrees reasonably with the mean distance between the GF rovings of the mat.Based on Figure 6 one can conclude that the crack propagates only until attaining the next roving which impedes the crack temporarily.Final breakdown occurs without any further crack growth, which should occur therefore via damage accumulation (see later).Figure 7 compares the crack growth curves of PAs with SGF and GF mat reinforcement at an analogous V_f value.The informations from Figure 7 can be summarized also schematically, provided that the GF mat is regarded as a reinforcement of "infinite" aspect ratio (length to diameter ratio; l/d).Based on Figure 8 which informs about the related effects of discontinuous and "continuous" GF reinforcements, the GF swirl mat reduces the crack growth to a very limited scale (cf. dotted bar, the width of which depends on V_f).This occurs within range I, since final breakdown is preceeded by stable deceleration (cf. Figure 7).
Based on an other representation indicating the stress rupture or time to failure runs (K_0-time; cf.Figure 9) the basic differences between the ESC characteristics of chopped fiber (Figure 9a) and mat reinforced PAs (Figure 9b) are obvious.

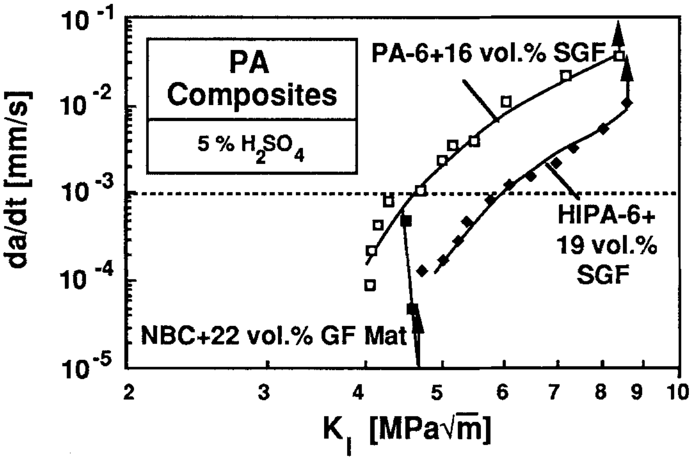

Figure 7.
ESC response of SGF- and GF mat-reinforced PA composites (arrow indicates final failure)

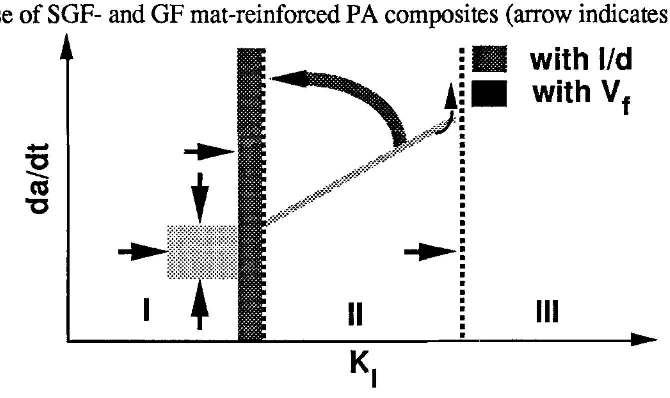

Figure 8.
Effect of the amount and type of GF-reinforcement on the ESC behavior of polyamides, schematically
(Note:the aggressivity of the environment may strongly affect the run of the curve; the position of the bar representing the GF mat reinforcement, depends on K_0, whereas its width is a function of V_f, i.e. of the mean interstrand distance)

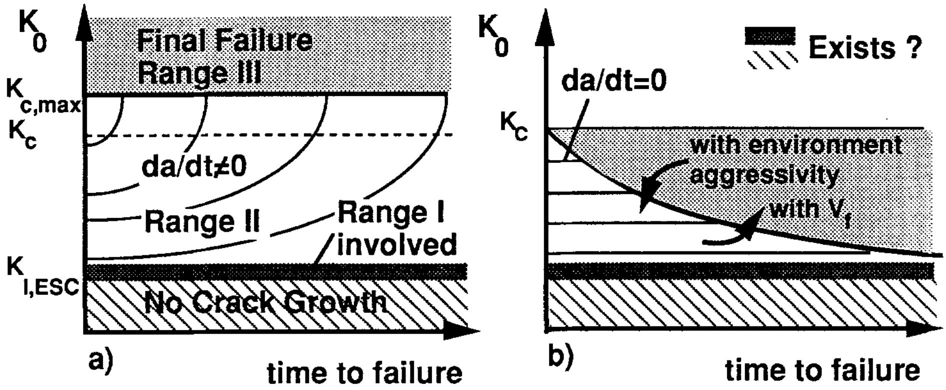

Figure 9.
K_0 vs. time curves highlighting the basic differences in the ESC response between thermoplastics with discontinuous (a) and continuous reinforcement (b)

Failure Characteristics

It was evidenced by fractography that the size of the damage zone in the crack tip of the matrices was grown at the very beginning of the test.This kind of "crack tip blunting" is responsible for the crack deceleration (range I).Increasing load, eventual in many steps, generates a "stable" damage zone which undergoes stable acceleration in range II.It should be noted here that the shape and size of this damage zone is strongly affected by both microstructural factors (morphology and its alteration during the test) and stress condition circumstances of the matrix (plain strain - plane stress transition due to plasticizing, thickness reduction and the like) which were revealed, indeed.Local rearrangement in the crack tip is demonstrated in Figure 10a taken from a band caused by subsequent de- and reloading.This SEM picture indicates for a fibrillar transition in the previous spherulitic matrix structure induced by the increased molecular mobility of the PA-6 segments due to the depressed T_g (≈ room temperature) by water uptake.

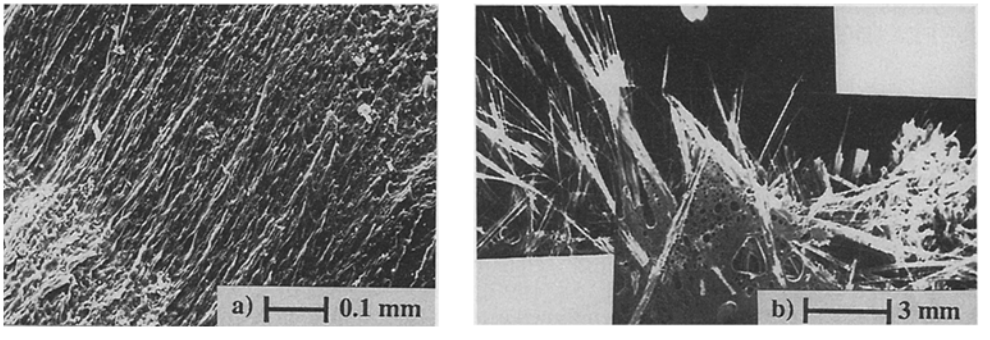

Figure 10.
a) SEM picture from a crack arrest band showing fibrillar structure in the crack tip of PA-6
b) Composed SEM microphotograph from a broken CT specimen of NBC with ≈10 vol.% GF strand mat after testing in water
(Note:crack direction from left to right)

Failure of the composites with short fibers occurs by events grouped into matrix- (crazing,shear yielding,fracture) and fiber-related (debonding, pull-out,fracture) ones [4,8-9]. Improvements in the resistance against ESC growth can be attributed to a fiber avoidance path containing the above mentioned microscopic failure events.Although in the literature there are several indications for the acid-assisted fiber fracture [2,4], fractographic investigations carried out on the broken specimens did not state it in our case.

The peculiar ESC response of the GF mat reinforced NBC can only be explained by a damage accumulation process.Damage accumulation initiates by debonding processes between the matrix and the adherend filaments of the roving.This process is supported by water sorption and diffusion.Penetration of the water is highly promoted by capillary forces acting within the rovings which are not fully impregnated by the matrix.The composite fails when the GF mat looses its reinforcing effect due this fiber/matrix separation process.According to this mechanism the pulled-out roving length should decrease along the free ligament width (W-a; cf. Figures 1 and 2) which was observed, indeed (Figure 10b).

CONCLUSIONS

The response on static fatigue loading in air, in water and in diluted sulfuric acid (environmental stress corrosion ; ESC) of different polyamides (PA) and their composite grades strongly depends on the characetristics both of the matrix and reinforcements.Among the matrix properties, affecting the ESC behavior, the water sorption and toughening mode seems to be of crucial importance.Incorporation of chopped glass fibers improve the resistance of the related matrices against ESC crack growth.Common feature of the neat and chopped fiber reinforced PAs that final failure occurs by crack growth mechanism.In the presence of a swirl glass fiber mat this failure mode alters considerably since it becomes a function of the initial stress intensity factor (K_0) and thus of the immersion time.It means that the fracture mechanics approach can not be used any more.Fracture of the GF mat reinfored polyamide block copolymer (NBC) was initiated by a water-assisted damage accumulation process.Due to this fact, material improvements can be expected from oriented changes in the molecuar build-up (in order to reduce the water sorption capability) and from better interface or -phase coupling between the matrix and the reinforcing GF mat.

ACKNOWLEDGEMENT

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