Initiation of Stress Corrosion Cracking in Unidirectional Glass/Polymer Composite Materials

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Abstract

The purpose of this research is to determine the resistance to the stress corrosion cracking (SCC) of three unidirectional (pultruded) E-glass/polymer composites based on modified polyester, epoxy and vinyl ester resins. The composites have been subjected to a nitric acid solution of pH 1.2 in a newly designed four-point bend fixture. The stress corrosion process was initiated on the as supplied surfaces of the composites. The process has been monitored using acoustic emission and the stress corrosion surface damage in the specimens has been investigated using scanning electron microscopy techniques. Experimental results indicate that the stress corrosion cracks originate predominantly from exposed glass fibers on the surfaces of the composites. The process can be successfully monitored using acoustic emission. Three stages of SCC, crack initiation, sub-critical crack extension and stable crack propagation, can be distinguished by carefully examining the acoustic emission (number of events) versus time curves. For the first and second stages of SCC, the acoustic emission outputs are linear functions of time. The slopes of the acoustic emission versus time curves for the first and second stages have been used to determine quantitatively both the resistance of the composites to crack initiation and sub-critical crack extension, respectively. It has been shown in this research that the resistance to the initiation of SCC in nitric acid of the E-glass/vinyl ester composite is approximately ten times higher than for the E-glass/epoxy composite. Furthermore, the E-glass/epoxy system exhibits approximately five times higher resistance to the initiation of SCC than the E-glass/modified polyester system. The sub-critical crack extension process is also significantly more rapid in the E-glass/modified polyester than in the E-glass/epoxy composite.

1. Introduction

Composite suspension insulators are commonly used in overhead transmission lines with line voltages in the range of 69 kV to 735 kV [1-28]. The insulators rely on pultruded glass fiber/polymer matrix rods as the principle load bearing components. There are two metal end-fittings attached to the rod and the surface of the rod is covered with a rubber housing material with multiple weathersheads. One of the major problems related to the application of composite insulators on overhead transmission lines is their mechanical failures in-service by brittle fracture. Brittle fracture of composite insulators results from the stress corrosion cracking (SCC) of the composite rod material [1,2,4-6,
SCC in an E-glass/polymer composite is a consequence of chemical attack on the fibers by an acid (either organic or inorganic) in conjunction with low mechanical tensile stresses applied along the rod axis [29-38]. Recently, it has been shown [24] that the brittle fracture process in composite insulators can be caused by the formation of nitric acid solutions in-service due to the presence of moisture and corona discharges. If the acid penetrates the end-fitting and reaches the surface of the composite rod, the brittle fracture process can be initiated leading to the insulator failure in service. In Figure 1, an insulator which failed in service by brittle fracture is shown. The most typical feature of the brittle fracture failures is the presence of large planar fracture surfaces in the rods which run perpendicular to the glass fibers.

The characteristics of brittle fracture failures of composite insulators have been extensively studied over the years by Kumosa et al. [14,15,19,21,22,24-28]. Numerous testing techniques and numerical models have been designed to explain the brittle fracture process in various designs of composite insulators. Several different stress corrosion methods have been used to duplicate the process under laboratory conditions. Various pultruded E-glass and ECR-glass/polymer composites have been subjected to the combined effect of mechanical, chemical and electrical stresses. In particular, the effect of either organic (oxalic) or inorganic acids (nitric) on the resistance to the stress corrosion process in the glass/polymer composites has been extensively investigated [28,37,38]. However, all the previous testing techniques used in the insulator research did not provide meaningful conclusions regarding the resistance of the composites to the initiation of SCC. Therefore, the ranking of the composites based on E-glass fibers for their resistance to brittle fracture could not be accurately established. Since a vast majority of suspension composite insulators are based on E-glass fiber composites with either polyester, epoxy and vinyl ester resins, the issue of initiation of SCC in these composites when subjected to mechanical tensile loads in the presence of a nitric acid solution (the most probable cause of brittle fracture failures) is extremely important.

The previous tests have shown that stress corrosion process can be initiated in the composites when subjected to nitric acid and mechanical stresses [28,37,38]. Moreover, the process has also been initiated in some of the composites when subjected to the combined effect of mechanical stresses, corona discharges and moisture. Regarding the effect of different glass fibers (ECR vs. E-glass) and polymer resins (modified polyester, polyester, polyester with clay, polyester with calcium carbonate, epoxy, vinyl ester and modified vinyl ester) on the stress corrosion process, the following two major conclusions were drawn [28,37,38]:

1. Neither crack initiation nor propagation could be achieved in the ECR-glass/polymer composites under the influence of a nitric acid solution (pH 1.2) and mechanical stresses.

2. For the E-glass fiber/polymer composites, the type of polymer resin does not significantly affect the stress corrosion process under the stable crack propagation conditions. Stress corrosion cracks in the composites grow almost at the same rate when subjected to mechanical tensile stresses and nitric acid and their crack growth rates can be described using a power law [31,34,35]. Below the stable crack growth
regime, the SCC process is still possible, however, the crack propagation process cannot be described by the power law relation.

Despite the fact that differences have been noticed regarding the initiation of SCC in the E-glass/polymer composites depending on the type of resin the exact relationship between the onset of stress corrosion cracking and the type of resin could not be quantitatively established. Therefore, an attempt was made in this research to evaluate the resistance to SCC in nitric acid, and in particular, the resistance to the initiation of brittle fracture in the three most commonly used pultruded composites in composite suspension insulators. These composites are based on E-glass fibers with either modified polyester, epoxy or vinyl ester resins. The resistance to SCC in nitric acid of the composites was investigated by exposing the as supplied surfaces of the composites to the acid under four point bend testing conditions.

2. Experimental Procedure

2.1 Fixture design

The stress corrosion experiments on the unidirectional E-glass/polymer composites were performed using a newly designed four point bend fixture. A schematic of the fixture is shown in Figure 2. The load was applied to the specimen by placing weights on the top plate using the pin to ensure they are completely centered. Both the spacing between the load pins and the diameter of the load pins were determined using ASTM specification D790-86 standard [39]. Bearings were inserted in the ends of the load pins so they would roll on the surface of the specimen and not slide. Guide pins and linear bearings were used to ensure that that specimen was loaded in a vertical manner. Sufficient clearance between the guide pins and the specimen allow acoustic emission transducers to be mounted on each end of the specimen. Displacement of the center of the specimen was measured using a linear variable displacement transducer (LVDT) attached to the specimen as shown in Figure 2. A tank made out of poly methyl methacralate is attached around the center of the specimen to hold nitric acid.

In the fixture, composite specimens can be tested for their resistance to SCC and the process can be monitored using both acoustic emission and a LVDT transducer. The experimental set-up is acoustically quiet therefore acoustic emission from the stress corrosion process can be monitored independent of any other sources of acoustic emission that might interfere with the experiment. The fixture allows the testing of various composite materials under a wide range of loading conditions in different corrosive environments.

2.2 Specimen geometry optimization and finite element analysis

Composite specimens for the stress corrosion experiments were machined from the pultruded unidirectional composite plates supplied by Glasforms, Inc. The plates were 304 mm long, 50.8 mm wide with a thickness of 6.35 mm. The direction of the fibers
was along the long axis of the plates. The final dimensions of the stress corrosion specimens were selected based on the following criteria:

1. The specimens should respond linearly to the applied load without significant geometric non-linearity effects (linear relationships between loads and displacements as well as stresses and strains).

2. Scaled loads should be used to simulate tensile stresses in the specimen gage section (on one side of the specimen) equivalent to the tensile stresses in composite insulators under in-service loading conditions.

3. The geometry of the specimen should allow monitoring of acoustic emission with the maximum contact area between acoustic emission transducers and the cross section of the specimens.

Initially, a large range of specimen dimensions was considered. The final dimensions (3.2 mm thick, 12.7 wide and 304.8 mm long) were selected based on a parametric study of stresses and displacements in the specimens following the above criteria.

Since the stress corrosion tests had to be performed with the tensile stresses in the composite specimens very similar to the tensile stresses in the insulators, the stress distributions in the specimens were numerically analyzed to ensure the linear behavior of the specimens for the load range considered. A finite element model of the specimen with the supporting pins was constructed using ANSYS 5.4 (see Figure 3a). The finite element computations were non-linear considering the effect of geometric non-linearity on the displacements and stress distributions. In the model the specimen was allowed to slide along the supporting pins by using contact elements and the pins were allowed to rotate with their middle points fixed. A friction coefficient of 0.1 between the pins at the specimen was used to simulate the specimen rolling. The external loads were applied to the inner pins by a set of forces. The following elastic properties were used in the finite element computations:

$$E_{11} = 38.86 \text{ GPa}, \quad E_{22} = 10 \text{ GPa}, \quad G_{12} = 3.8 \text{ GPa} \quad \text{and} \quad v_{12} = 0.29$$

Since the properties of the three composites are very similar only one set of properties (for the E-glass/epoxy composite) was used in the finite element analysis.

The numerical results show that the stresses in the gage section between the inner pins are tensile on the bottom of the specimen and compressive on the top side (see Figure 3b). Moreover, no shear stress occurs in the specimen gage section. The stresses in Figure 3b are presented in the Cartesian coordinates with the x-axis along the long axis of the specimen and the y-axis in the direction perpendicular to the specimen (through the thickness). Since the inner pins are located at a distance 35 mm from the acid tank the local stress concentrations in the specimen near the pins do not affect the uniform stress field in the specimen gage section (within the acid tank). For loads up to 110 N, the displacements and stresses are almost linear functions of load indicating that the effects
of specimen rolling along the pins and geometric non-linearity on the mechanical behavior of the specimen are almost insignificant within this load range. The comparison between the numerical, analytical (using the beam theory) and experimental load/displacement curves is presented and discussed in the section below.

2.3 Experimental verification

To verify the numerical and analytical predictions of the load/displacement and corresponding stress/strain curves, mechanical four point-bend tests were conducted with strain gages mounted to the composite specimen in the center of the gage section along the axis of the fibers. Plots of load versus displacement curves for the analytical, numerical, and experimental results can be seen for a glass/epoxy specimen in Figure 4a. This diagram shows that the numerical and experimental results are in good agreement with the analytical predictions. Moreover, the experimental and numerical load-displacement curves are almost linear for the load range in which the acid tests will be performed. In addition, the stress verses load curves from the numerical and experimental approaches are shown in Figure 4b. This also shows that the system is almost linear up to 110 N with a slight disagreement between the finite element model and experiment. Since the elastic properties of the three composites are almost the same the same mechanical behavior can be expected in the cases of the E-glass/modified polyester and E-glass/vinyl ester specimens.

The stress corrosion experiments have to be performed as a function of time. Therefore there is a possibility that displacements, stresses and strains could be time dependent with significant creep, especially for long tests. To examine the potential creep effects two tests under the same constant load of 83.97 N were performed to determine the effect of material non-linearity (creep) on the displacement measurements in the case of the E-glass/epoxy composite. One test was performed under dry conditions whereas in the other test, the acid tank was filled with water. The displacement-time curves from the dry and wet experiments are shown in Figures 5a and 5b, respectively. Third order polynomials were fitted to the experimental data. The composite specimens exhibit a steady state displacement of about 0.35 mm. There is an approximate difference of 0.025 mm between the steady state part of the curves for the wet and dry specimens. This result indicates that the composite does not absorb enough moisture in 110 hours to significantly change the material properties. This is not surprising since the maximum moisture content for this composite tested at room temperature in distilled water has been found to be approximately 0.6% [25]. For the E-glass/modified polyester and E-glass/vinyl ester the maximum moisture contents have been reported to be 1.2% and 0.25%, respectively. Therefore, it could be expected that the creep effects in the wet tests might be slightly more significant in the case of the E-glass/modified polyester composite and less significant for the E-glass/vinyl ester relative to the E-glass/epoxy system.

3. Stress Corrosion Test Results and Discussion

Three E-glass/polymer systems, namely E-glass/epoxy, E-glass/modified polyester, and E-glass/vinyl ester were tested for their resistance to the SCC in nitric acid.
3.1. Stress corrosion tests procedure

Three specimens of each composite machined with the dimensions specified in section 2.2 were tested. Since three sides of the specimen were machined to obtain the required geometry, these three sides inside the acid tank were coated with a petroleum jelly to ensure the acid only attacked the as-manufactured surface. Then, the acid tank was mounted to each specimen using silicon rubber as a sealant and subsequently filled with a nitric acid solution. The acid used had a pH of 1.20 (6.3*10\(^{-2}\) moles/liter). In the next stage the LVDT rod was attached to the upper surface of the specimens in the center of the gage section and the tank was sealed from the top. The acoustic emission transducers were then mounted on each end of the specimen using epoxy.

Broad band sensors (20-1500 kHz) where used in the stress corrosion experiments in conjunction with a Digital Wave Corporation system. The signals generated by the stress corrosion process (predominantly fiber fractures) propagating through the sample to the sensors were recorded. The trigger bandpass was set between 50 and 500 kHz. The recorded signals were filtered between 20-4000 kHz. Total gain was 55 dB for the recorded signal. The gain on the trigger was set to 67 dB with a 0.1 V threshold level corresponding to a 25 mV threshold at 55 dB or 44 \(\mu\)V at the sensor. The signals were measured at 5 MHz per point for 2048 points 256 points recorded before the trigger. Maximum recorded voltage level was \(\pm 1.0\) V.

Each specimen was loaded in the fixture with a constant load of 83.97 N generating an axial stress along the fibers of 134 MPa (see Figure 4b) which corresponded to 26.7 kN applied to a composite insulator in-service with a rod diameter of 16 mm. Each test lasted for 72 hours at room temperature and ambient humidity. After testing, each specimen was removed from the fixture, cleaned using an alcohol and prepared for SEM analysis.

3.2 Stress corrosion experiments under constant loads

The acoustic emission signals versus time from all nine stress corrosion experiments are shown in Figure 6. Three significantly different trends in the AE versus time curves are apparent. The curves for the E-glass/modified polyester composite specimens are steeper than the curves for the E-glass/epoxy composite, all of which are steeper than the E-glass/vinyl ester curves. In spite of sample dependent variation apparent in the data for a given composite, the overall shape of the curves is essentially the same. In Figure 7 the average acoustic emission number of events vs. time for each composite are presented. In addition, the number of acoustic emission events for each test are listed after 24, 48 and 72 hours in Table 1. It can be seen from the data presented in Figures 6,7 and Table 1 that the rates of acoustic emission (slopes of the curves) were always the highest for the E-glass/modified polyester and the lowest for the E-glass/vinyl ester composite. The AE rates for the E-glass/epoxy composite fell somewhere between those of the E-glass/modified polyester and those of E-glass/vinyl ester composite samples.

Since the displacement curves for each composite were very similar, one set of examples of the displacement versus time curve for each composite is shown in Figure 8. Again, a
trend can be seen. After 72 hours, E-glass/modified polyester has the highest displacement, E-glass/vinyl ester has the lowest displacement and that of E-glass/epoxy falls somewhere in between. Examining Figures 7 and 8, a relationship can be seen between the acoustic emission event vs. time curves generated by a composite specimen and the corresponding displacement vs. time curves. This relationship can be further illustrated by plotting AE events versus displacement. Figure 9a presents the AE events versus displacement curve for E-glass/vinyl ester. Although much scatter is seen here due to insufficient data points, a trendline shows a mostly linear curve. Figure 9b presents the AE events versus displacement curve for the E-glass/epoxy composite. Here, the linear fit is much better, displaying the linear relationship between acoustic emission events and displacement. The initial portion of the curve is not linear up to a displacement of 0.35 mm which could be caused by creep or measurement error. Figure 9c displays the AE events versus displacement curve for E-glass/modified polyester. Again, a linear fit shows a relationship between acoustic emission events and displacement, except the initial region. However, in this curve displacement starts increasing faster than acoustic emission events after approximately 65 hours. Similar non-linear behavior of the acoustic emission versus displacement curve was also observed in the case of one of the E-glass/epoxy specimen (test 1). In both cases large stress corrosion cracks were detected propagating across the specimen.

Subsequently, the acoustic emission vs. time curves for each composite specimen were carefully examined. It was found that the curves for the E-glass/modified polyester and E-glass/epoxy specimens could be separated into three distinctly different sections. The first section (stage 1) was shown to be linear with a much smaller slope than the rest of the curve. The second section (stage 2) was also linear, but with a larger slope. The third section for both composites, the AE vs. time curves were either linear or non-linear with a lot of variability in the slopes observed.

For the E-glass/vinyl ester composite only one linear section (stage 1) was identified for each sample tested. In Figures 10, 11 and 12 the acoustic emission vs. time curves for stage 1 for the E-glass/vinyl ester, E-glass/epoxy and E-glass/modified polyester specimens are presented, respectively. It can be seen in these figures that the AE vs. time curves for stage 1 are very linear (disregarding the initial regions caused by creep and/or measurement errors), especially for the E-glass/epoxy and E-glass/modified polyester specimens. For the E-glass/vinyl ester specimens the fits were not as linear (see Figure 10) due to an insufficient number of data points and the fact that creep and displacement measurement errors could play a large role in this region. The stage 1 slopes for all nine tests are presented in Figure 13. The data presented in Figures 10-13 clearly demonstrate that the slopes of the AE vs. time curves in stage 1 are very consistent for each composite tested. It can also be observed that the average slope for the E-glass/modified polyester is 10.37 which is approximately 5 times larger than the average slope for the E-glass/epoxy composites (2.18). The average slope for the E-glass/vinyl ester specimens is 0.24 which is approximately 10 times lower than for the E-glass/epoxy and 50 times lower than for the E-glass/modified polyester.
The AE vs. time curves for stage 2 are presented in Figures 14 and 15 for the E-glass/epoxy and E-glass/modified polyester specimens. The linear trends of these six curves are even better than for stage one for these two composites. The slopes of the six curves are illustrated in Figure 16. Comparing with stage 1 the scatter in the slopes for stage 2 is larger. Similar to the slopes in stage 1, the average slope for the E-glass/modified polyester (41.68) is significantly larger than the average slope for the E-glass/epoxy specimens (8.61).

The rates of increase in the number of acoustic emission events vs. time for stage 3 could not be accurately compared for the E-glass/epoxy and E-glass/modified polyester specimens since the curves in some cases were linear and in some cases non-linear. As an example, the curves for stage 3 for the three E-glass/modified polyester specimens are shown in Figure 17. It can be seen that the curve for Test 1 is clearly exponential, whereas the other two curves for Test 2 and Test 3 are linear.

3.3 Load effect on the initiation of the stress corrosion cracking

In this part of the study an attempt was made to determine the critical loads in the four point bend test on the initiation of stress corrosion cracking in the E-glass/modified polyester composite. This composite system was selected because it is the most susceptible to the stress corrosion cracking as has been shown in the previous section. A series of 72-hour stress corrosion experiments were performed with the applied load changing from 0 N to 80N with 13.3 N load increments. For high loads the stress corrosion process could be monitored using acoustic emission with the acoustic emission system set-up according to the configuration described in section 3.1. However, at lower loads the system did not record any acoustic emission signals caused by the process. This might indicate that there was no initiation and propagation of stress corrosion cracks below a certain threshold load. There is also another possibility. The gain and trigger level of the acoustic emission system were selected for monitoring acoustic emission from fracturing fibers under high applied loads. Unfortunately, the AE system had a limited dynamic range, which means that only a small range of AE signal energies can be accurately detected. Since the energy released from the fractured fibers depends very strongly on the applied load, the energy of the signals coming from broken fibers at low loads has to be significantly lower compared to the energy released at high loads [37,38]. Therefore, by setting up the system for high loads (i.e., higher energy signals) the system was not sensitive to the lower energy signals generated during low load test. In order to resolve which of the two possibilities (no stress corrosion or no AE signals but stress corrosion), SEM analysis of the gage section of the test samples was performed as described in the following section.

3.4 SEM analysis of surface damage

After the stress corrosion experiments the gage sections of the specimens were examined using scanning electron microscopy techniques. The following two issues were addressed:
The overall surface conditions for each composite were examined.

Second, the morphology of stress corrosion damage was evaluated on the surface of each specimen.

The three composite materials had various amounts of exposed fibers on the specimen surface. The E-glass/modified polyester appeared to have more exposed fibers than both the E-glass/epoxy and E-glass/vinyl ester composites. The epoxy and vinyl ester based composites had approximately the same amount of fibers exposed. A quantitative study of the total surface area of the exposed fibers for each composite was not performed therefore the above two statements are only qualitative based on very general observations.

Each composite surface contained a significant number of misaligned fibers (see Figure 18). The misalignment of the surface fibers varied from one specimen to another. In addition, the specimens showed signs of mechanical damage consisting of a few surface holes and scratches. The amount of mechanical surface damage also varied from specimen to specimen. It is likely that all of these surface imperfections (fiber misalignment and surface defects) are artifacts of the pultrusion process. It can be expected that they might contribute to the stress corrosion process.

The stress corrosion surface damage in the E-glass/vinyl ester specimens consisted of several stress corrosion cracks on the surfaces of exposed fibers. An example of these cracks can be seen in Figure 19. These cracks were located in individual fibers without any crack extension into the neighboring fibers. Comparing with the other two composites the E-glass/vinyl ester specimens had the least amount of stress corrosion damage on their surfaces. On the other hand, the amount of stress corrosion damage was the highest in the E-glass/modified polyester. This damage consisted of numerous cracks in exposed individual fibers (see Figure 20a), cracks extending into neighboring fibers (see Figure 20b), a few straight long cracks extending through several fibers (see Figure 20c) and a couple of long irregular cracks (see Figure 20d). The morphology of the stress corrosion damage on the surfaces of the E-glass/epoxy specimens was similar to the E-glass/modified polyester samples. However, the amount of damage in the E-glass/epoxy composite was noticeably smaller than for the E-glass/modified polyester material.

All of the surface cracking initiated on the surfaces of exposed fibers. In a few cases it was noticed that the cracks initiated from surface imperfections such as surface holes. In E-glass/epoxy Test 1, one of these cracks lead to the failure of the specimen (see Figure 21). In one case of a single fiber failure a shear damage band consisting of several tensile cracks in the layer of epoxy between the fibers was detected (see Figure 22). After the fiber failure, the stress corrosion process was reinitiated away from the initial crack. This might explain why in some cases the stress corrosion cracks are not straight and change their propagation plane.

The surface damage in the E-glass/modified polyester specimens tested at various loads was also examined in order to determine the critical loading conditions for the initiation
of stress corrosion cracks. It was found that cracks formed on the surfaces of the specimens for all loads. Most importantly, single fiber cracks were observed even in the specimen tested without any mechanical load. An example of these cracks can be seen in Figure 23a. In this case, the specimen was tested outside the fixture with the acid tank attached. This very strongly indicates that there is no critical applied load for the initiation of stress corrosion cracks for this particular composite. The first indication of crack extension traversing more than two fibers was observed in the tests performed under 13.3 N and 26.6 N (see Figure 23 b).

3.5 Discussion

It has been shown in this research that the acoustic emission results are significantly different for each composite tested in nitric acid. The highest rates of acoustic emission signals were observed for the E-glass/modified polyester composite, with the lowest for the E-glass/vinyl ester composite material. There is a strong relation between the amount of stress corrosion surface damage observed on the surfaces of the specimens and the acoustic emission data. The largest amount of surface damage (cracks in individual fibers, cracks across several fibers and large macro-cracks) was observed in the E-glass/modified polyester specimens, with the smallest number of stress corrosion cracks in the E-glass/vinyl ester composites. Both the acoustic emission rates and the amount of surface damage caused by stress corrosion for the E-glass/epoxy specimens fell somewhere between the data for the composites based on modified polyester and vinyl ester resins.

It has been indicated in section 3.2 that the acoustic emission vs. time curves can be separated into three different stages. In stages 1 and 2 the number of acoustic emission events seem to be linear functions of time with the slopes significantly different for each composite in each stage. In stage 3, the event vs. time curves are either linear or non-linear. If large cracks are observed on the composite surfaces (see Figure 21) the AE curves are always highly non-linear. It is stipulated that in stage 1 predominantly single fiber cracks are formed on the composite surface (stage 1, Figure 24a) and the process is random. This generates linear acoustic emission events with time. This stage was obvious in the cases of the E-glass/vinyl ester composite specimens which did not develop the second stage of cracking. Only single fiber cracks were observed for this composite. In the second stage, (stage 2, Figure 24b) more single fiber cracks randomly develop. At the same time, the previously formed single fiber cracks begin to grow slowly into the neighboring fibers. Since the acoustic emission vs. time curves are still linear in stage 2 the combined single crack and crack extension process must also be random. At some point, one of the larger cracks reaches a critical size and propagates in a stable fashion across the specimen (stage 3, Figure 24c). The SEM analysis of the tested specimens strongly supports the proposed 3-stage model of the stress corrosion process.

Some of the possible factors which contribute to the initiation of individual fiber cracks on the surfaces of the three tested composite are:
1. The total surface area of the exposed fibers on the composite surfaces,
2. Applied and residual stresses,
3. Deterioration of the polymer due to acid attack,
4. Diffusion of acid through the polymer matrix and glass/matrix interfaces,
5. Fiber sizing.

It has been shown by Qiu and Kumosa [33] that E-glass fibers (the same fibers as the fibers in the composites investigated in this study) will not develop any noticeable surface damage when exposed to nitric acid, pH1, for two weeks without any tensile stresses. In sulfuric and oxalic acids, the glass fibers developed either longitudinal or spiral cracks depending on the acid type and concentration. The stress corrosion process of glass fibers is caused by leaching of aluminum and calcium out of the glass (ion exchange mechanism) [33] with the hydrogen ions replacing the metal ions in the glass. Since after 3 days of testing single fiber cracks were observed on the surfaces, their initiation process must be mostly controlled by the leaching process and the mechanical tensile stresses. However, these cracks were also observed in the specimen tested without load in the acid environment. This might indicate that the initiation of stress corrosion cracks is also possible without externally applied mechanical loads if significant residual stresses are present in a unidirectional E-glass/polymer composite.

In Stage 1, nitric acid attacks the glass fibers on their exposed surfaces starting the leaching process (Figure 25). The acid can also penetrate from the composite surface into the fibers located underneath the surface through a layer of polymer. In addition, for partially exposed fibers the acid can also penetrate the composite along the fiber/matrix interfaces (point A in Figure 25). Therefore, the single fiber crack initiation process is controlled by the surface conditions of the exposed fibers (both mechanical and chemical), the interfacial chemical properties of the glass fiber/polymer interfaces and the physical properties of the resin (diffusion and the resistance of a polymer to degradation due to acid attack). The mechanical tensile stresses are also important in stage 1. Since cracks were observed in this research in the unloaded E-glass/modified polyester specimen after 3 days of exposure to nitric acid but not in fiber bundle tests after 2 weeks of exposure to the same acid in the research performed by Qiu and Kumosa [33] (with the same acid concentration), this might indicate that the initiation process is influenced by the presence of residual stresses generated during the pultrusion process.

It has been recently suggested [40] that the three polymer matrices tested in this project can have significantly different properties as far their deterioration under nitric acid attack. The most vulnerable sites for chemical attack are the ester linkages [40]. A typical Bis A epoxy vinyl ester (vinyl ester used in the E-glass fiber composite) has an ester content of 5-10%, while an isophthalic polyester has a 20-30% ester content. The absence of an ester linkage in the epoxy backbone of vinyl esters makes them less susceptible than polyester resins to attack by strong acid. These statements might further explain the observed difference in the initiation of stress corrosion cracking of the composites based on these resins. Since the deterioration rates of polyester should be higher than of epoxy with no deterioration of a vinyl ester resin, the deterioration process of the resins on the composite surfaces might also contribute to the initiation of stress...
corrosion cracks by exposing more fiber area on the composite surface. An additional factor which could contribute to the deterioration rates of the modified polyester, epoxy and vinyl ester resins when exposed to nitric acid is the rate of moisture diffusion in these resins. It has been shown [25] that moisture diffusion in modified polyester is higher than in epoxy and that the diffusion of water in epoxy is higher than in vinyl ester.

Based on the SEM and acoustic emission data presented in this work, the three most commonly used E-glass/polymer pultruded composites in high voltage composite insulators can be ranked for their resistance to the stress corrosion cracking and thus the resistance to brittle fracture. In particular, the resistance to the initiation of stress corrosion cracks of the composites when subjected to the combined effect of mechanical tensile stresses and a nitric acid solution can be accurately established. It is obvious that the E-glass/modified polyester composite has the lowest resistance to the initiation of stress corrosion cracking in nitric acid. This statement can be made based on the highest rates of acoustic emission and the largest amount of surface damage observed for this material. The E-glass/epoxy composite exhibited higher resistance to the stress corrosion cracking in comparison with the E-glass/modified polyester. Out of the three composites, the resistance to the initiation of stress corrosion cracking for the E-glass/vinyl ester composite was found to be the highest. Due to the high reproducibly of the acoustic emission data (little scatter in slopes of the acoustic emission vs. time curves in stage 1 except for the vinyl ester composite) for each composite, the quantitative ranking of the composites for their resistance to the initiation of stress corrosion cracking in nitric acid is as follows: the E-glass/vinyl ester composite is approximately 10 times more resistant than the E-glass/epoxy composite system whereas the E-glass/modified polyester is 5 times less resistant than the E-glass/epoxy material (see Figure 13).

Regarding the crack extension stage (stage 2), the E-glass/epoxy composite shows superior properties in comparison with the E-glass/modified polyester (see Figure 16). If the slopes for the second stage of acoustic emission vs. time curves are taken as an indicator of the sub-critical crack growth rates, the resistance to sub-critical crack extension of the E-glass/epoxy composite is approximately 5 times higher than for the E-glass/modified polyester composite. Since stage 2 involves both crack initiation and sub-critical crack extension, the exact comparison of these two composites for their sub-critical crack growth resistance cannot be established very accurately based on the results presented here.

The process of the sub-critical crack growth is not very clear. Based on this research it can be speculated that the process is controlled by the local micro-stresses at the crack front. The crack extension process within the sub-critical regime will accelerate with an increase in the applied load. The process will also accelerate as the cracks elongate. Certainly, the leaching process in glass fibers is also very important at this stage. The leaching process has to weaken the fibers to a greater extent when the stresses at the crack front are low. With further crack extension the stresses at the crack tip are increased and the leaching process does not have to weaken the fibers as much. In terms of SCC formation and propagation, chemical leaching plays a larger role in the failure of fibers in stage 1. On the other hand, due to the presence of stress concentrations, mechanical
stresses become increasingly important in stage 2. There also must be a very strong influence of the matrix material on the fracture process in stage 2 as seen comparing the slopes for the E-glass/modified polyester and E-glass/epoxy in Figure 16. Most likely the fracture toughness properties of a polymer influence the process. To understand the sub-critical crack extension process and the transition from stage 1 to stage 2 further research is required.

The transition from stage 2 to stage 3 and the onset of stable stress corrosion crack growth in the three composites could not be established based on the data obtained from the stress corrosion four point bend tests. In some cases, the acoustic emission vs. time curves exhibited highly non-linear behavior. It is well known that the following power law can accurately describe the stress corrosion crack propagation process when a single stress corrosion crack propagates perpendicular to the fibers and the process is stable which means that the crack propagates sequentially from fiber to fiber [31,34,35]:

\[
\frac{da}{dt} = A K_I^B
\]  

where \( \frac{da}{dt} \) is the crack growth rate and A and B are material constants which depend on acid type and acid concentration and the type of tested composite. \( K_I \) is the mode I stress intensity factor that represents the local stress conditions at the tip of Mode I crack (crack subjected to tension) growing in the direction perpendicular to the fibers.

In the stress corrosion experiments performed using the four point bend test, the stress corrosion surface damage and the propagation of stress corrosion cracks through the composites could not be accurately monitored for their crack propagation rates, especially in stage 3. Due to the limitation of the test, the exact crack front geometry and crack depths as a function of time could not be established for the cracks growing within the stable crack growth regime (stage 3) in order to determined their crack growth rates. The issue of stable crack propagation under the stress corrosion conditions in the above composite has been recently addressed in a series of papers and reports [28,37,38]. It has been shown that the crack growth rates when a crack propagates steadily perpendicular to the fibers in nitric acid for the three composites investigated in this research does not depend on the type of polymer used. This has been accomplished by performing numerous stress corrosion experiments using the constant \( K_I \) specimen geometry which was specifically designed for the monitoring of stable growth of stress corrosion cracks in unidirectional composites. It has also been detected that the critical stress intensity factors for the onset of stable crack growth under stress corrosion conditions (\( K_{IC,C} \)) in the E-glass/modified polyester composite tested in nitric acid (pH1) was the lowest (\( K_{IC,C} \approx 4.2 \) MPa m\(^{1/2}\)) for the E-glass/modified polyester, the highest for the E-glass/vinyl ester (\( K_{IC,C} \approx 5.3 \) MPa m\(^{1/2}\)) with the critical stress intensity factor for the E-glass/epoxy somewhere between the other two stress intensity factors (\( K_{IC,C} \approx 4.7 \) MPa m\(^{1/2}\)) [28]. Above the critical stress intensities the fracture process followed very closely the relation described by equation 1. Below the critical stress intensities the stress corrosion process was still possible without however obeying the power law (equation 1).
Since the stress corrosion process (for a single crack growing steadily perpendicular to the glass fibers) obeys the power law it is not surprising that the acoustic emission data (number of events) within stage 3 are in some cases nonlinear functions of time. In general, under the constant load conditions the stress intensity factors along the crack front increase as a function of crack geometry, and in particular, as a function of crack depth. Therefore, the process has to accelerate with time if the cracks propagate within the stable crack growth regime for a constant applied load. However, the acoustic emission data can consist of signals generated by several cracks growing according to equation (1). In addition, other sub-critical cracks and single fiber cracks also contribute to the acoustic emission data within stage 3.

The stress corrosion experiments performed in this study were conducted by exposing the surfaces of the composites to nitric acid without any surface modifications. The surfaces were exposed to the acid as supplied. It has been suggested that the initiation of the stress corrosion process is strongly related to the exposed glass fibers on the composite surfaces. The as-supplied composites exhibited significantly different stress corrosion properties with the lowest resistance to the initiation and sub-critical crack extension found for the E-glass/modified polyester. The E-glass/vinyl ester composite seems to have the best resistance to the stress corrosion cracking. However, during the insulator manufacturing process the physical properties of the composites can be significantly altered. In particular, the surfaces of composite rods can be significantly modified. Some insulator manufacturers subject the surfaces to sand blasting, whereas in some cases the rods can be chemically treated in order to increase the chemical bonding between the rods and the rubber housing material. These two procedures have to dramatically change the resistance to stress corrosion cracking and thus brittle fracture of the insulators based on the three composite materials investigated in this project. Both surface treatment procedures will expose more fibers on the composite surfaces. It can be expected that even the best E-glass/vinyl ester composite will lose its superior stress corrosion resistance in comparison with the other composites. By the same token, the E-glass/modified polyester composites (despite its already very low resistance to stress corrosion) might become even more susceptible to the stress corrosion cracking.

Conclusions

1. A series of stress corrosion tests have been performed on three different composite systems based on E-glass-fibers with modified polyester, epoxy and vinyl ester polymer resins in order to evaluate the resistance of the composites to stress corrosion cracking in nitric acid. Particular emphasis has been placed in this research to determine the resistance to the initiation of stress corrosion cracks by subjecting the as supplied surfaces of the composites to nitric acid in the presence of mechanical tensile stresses along the fibers. The test results indicate that the extent of stress corrosion damage on the composite surfaces is strongly dependent on the type of polymer resin used.

2. The stress corrosion process in the unidirectional composites can be separated into three different stages, namely initiation, sub-critical crack growth and stable
propagation. It has been shown that both the initiation stage and the sub-critical crack extension stage are random phenomena and can be distinguished in acoustic emission vs. time curves. The number of acoustic emission signals generated by crack initiation and sub-critical crack growth are linear functions of time and can be used to quantitatively determine the stress corrosion properties of unidirectional glass fiber composites.

3. It appears that the stress corrosion process in unidirectional E-glass fiber/polymer composites subjected to the combined effect of nitric acid and tensile stresses initiates on the surfaces of exposed glass fibers. Depending on the exposed surface area of the fibers on the as supplied surfaces of the composites, different degrees of stress corrosion surface damage are observed.

4. The three most commonly used pultruded composite materials in high voltage composite insulators have been ranked for their resistance to the stress corrosion cracking and thus their resistance to brittle fracture in nitric acid. Regarding the resistance to the initiation of stress corrosion cracking of the composites, the E-glass/vinyl ester composite is approximately 10 times better than the E-glass/epoxy composite whereas the E-glass/modified polyester exhibits approximately 5 times worse resistance to SCC initiation than the E-glass/epoxy system. As far as the sub-critical crack extension process is concerned, the E-glass/epoxy composite exhibits approximately 5 times better resistance than the E-glass/modified polyester system.

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Figure 1. Brittle fracture failure of a 500 kV composite suspension insulator.
Figure 2. Schematic of the four point-bend fixture.
Figure 3a. Finite element model of a composite specimen subjected to four point bending in the fixture.
Figure 3b. Stresses across a specimen under four point bending.
Figure 4a. Experimental, numerical and analytical load-displacement diagrams.
Axial Stress Vs. Load

Figure 4b. Numerical and experimental stress-strain diagrams.
Figure 5a. Displacement vs. time diagrams; dry conditions.
Figure 5b. Displacement vs. time diagrams; wet conditions.
Figure 6. Acoustic emission (number of events) vs. time for the E-glass/modified polyester, E-glass/epoxy and E-glass/vinyl ester composites from nine stress corrosion tests.
Figure 7. Average acoustic emission outputs vs. time for the E-glass/modified polyester, E-glass/epoxy and E-glass/vinyl ester composites.
Figure 8. Displacement vs. time curves for the E-glass/modified polyester, E-glass/epoxy and E-glass/vinyl ester composites.
Figure 9a. Acoustic emission vs. displacement plot with linear fit: E-glass/vinyl ester.
E-glass/Epoxy Test 3: AE Events vs. Displacement

\[ y = 677.17x - 58.795 \]

\[ R^2 = 0.9861 \]

Figure 9b. Acoustic emission vs. displacement curve with linear fit: E-glass/epoxy.
E-glass/Modified Polyester Test 1: AE Events vs. Displacement

Figure 9c. Acoustic emission vs. displacement curve with linear fit: E-glass/modified polyester.

\[ y = 23472x - 3782.4 \]
\[ R^2 = 0.9912 \]
Figure 10. Acoustic emission vs. time diagrams for the E-glass/vinyl ester specimens in stage 1 with linear fits.
E-glass/Epoxy Initiation Stage (1): Events vs. Time Comparison/Three Tests

Figure 11. Acoustic emission vs. time diagrams in stage 1 for the E-glass/epoxy specimens with linear fits.
E-glass/Modified Polyester Initiation Stage (1): Events vs. Time
Comparison/Three Tests

Figure 12. Acoustic emission vs. time diagrams in stage 1 for the E-glass/modified polyester specimens with linear fits.
Figure 13. Crack initiation rates (stage 1) for the E-glass/modified polyester, E-glass/epoxy and E-glass/vinyl ester composites.
Figure 14. Acoustic emission vs. time diagrams in stage 2 for the E-glass/modified polyester specimens with linear fits.
Figure 15. Acoustic emission vs. time diagrams in stage 2 for the E-glass/epoxy specimens with linear fits.
Figure 16. Sub-Critical Crack Extension Rates (stage 2) for the E-glass/modified polyester and E-glass/epoxy composites.
Figure 17. Acoustic emission vs. time curves in stage 3 for the E-glass/modified polyester specimens with linear fits (Tests 2 and 3) and non-linear fit (Test 1).
Figure 18. Surface morphology of an E-glass/epoxy specimen (as supplied).
Figure 19. Single fiber stress corrosion crack in an E-glass/vinyl ester specimen.
Figure 20a. Stages of stress corrosion damage on the surface of an E-glass/modified polyester specimen; single fiber crack.
Figure 20b. Stages of stress corrosion damage on the surface of an E-glass/modified polyester specimen; sub-critical crack across a few fibers.
Figure 20c. Stages of stress corrosion damage on the surface of an E-glass/modified polyester specimen; planar crack across several fibers.
Figure 20d. Stages of stress corrosion damage on the surface of an E-glass/modified polyester specimen; long irregular cracks with multiple steps.
Figure 21. Large stress corrosion crack in an E-glass/epoxy specimen (final failure).
Figure 22. Shear damage zone at the glass fiber/matrix interface between two single fiber cracks.
Figure 23a. A single fiber crack in the E-glass/modified polyester Composite at a 0 N load.
Figure 23b. A crack extending into neighboring fibers in E-glass/modified polyester at a 13.3 N load.
Figure 24a. Schematics of three stages of stress corrosion damage; stage 1 – crack initiation.
Figure 24b. Schematics of three stages of stress corrosion damage; stage 2 – crack initiation and sub-critical extension.
Stage 3: Crack Initiation, Sub-Critical Extension and Stable Propagation

Figure 24c. Schematics of three stages of stress corrosion damage; stage 3 – crack initiation, sub-critical extension and stable propagation.
Figure 25. Acid attack model on glass fiber composites.
Table 1. Number of acoustic emission events at 24, 48 and 72 hour intervals for the E-glass/modified polyester, E-glass/epoxy and E-glass/vinyl ester specimens.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test</th>
<th>24 h</th>
<th>48 h</th>
<th>72 h</th>
</tr>
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<tbody>
<tr>
<td>E-glass/Modified Polyester</td>
<td>1</td>
<td>685</td>
<td>8827</td>
<td>89438</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>296</td>
<td>1558</td>
<td>4812</td>
</tr>
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<td></td>
<td>3</td>
<td>154</td>
<td>1255</td>
<td>4359</td>
</tr>
<tr>
<td>E-glass/Epoxy</td>
<td>1</td>
<td>61</td>
<td>245</td>
<td>1180</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>47</td>
<td>167</td>
<td>612</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>204</td>
<td>504</td>
<td>880</td>
</tr>
<tr>
<td>E-glass/Vinyl Ester</td>
<td>1</td>
<td>6</td>
<td>11</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11</td>
<td>15</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>26</td>
<td>30</td>
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