Fatigue Behavior of Vinyl Ester Polymer and Effects of Carbon Nanofiber Reinforcement

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ABSTRACT

Fatigue and cyclic deformation behaviors of vinyl ester and its nanocomposite with 0.5 wt% functionalized carbon nanofiber were obtained by performing tension-tension cyclic tests at different constant stress amplitude levels. Strains were predominantly elastic for both materials, even at high strain amplitudes. There was a small decrease in the cyclic modulus of elasticity of both materials with increasing fatigue cycles, possibly due to the breaking of some polymer chains during the cycling process. Considerable scatter was observed in the fatigue data because of the materials brittleness, necessitating the use of a large number of tests and statistical analysis.

Comparisons between vinyl ester and nanocomposite for different probabilities of survival based on log-normal distribution of life showed that the nanocomposite had shorter life than vinyl-ester at higher stress amplitudes, while it had higher life than vinyl ester at lower stress amplitudes. Fracture surfaces observed by SEM consisted of a crack initiation region followed by a smooth region leading to steps or river-like pattern. The fatigue fracture surfaces also contained a series of concentric crack growth bands surrounding the surface source. Cracks initiated subsurface in the nanocomposite specimens and small patches of nanofibers and nanofiber pullouts were observed in the crack initiation area.

1. INTRODUCTION

Polymers and their nanocomposites are increasingly used with the potential for application in high performance structures and vehicles. Such structures must typically operate under fluctuating loading conditions. It is, therefore, essential to understand the fatigue and failure mechanisms of these materials by conducting fatigue tests, to enable designing against fatigue failures. Fatigue tests are important to mechanical characterization of the material, since the maximum cyclic load that a material can sustain is a fraction of its tensile strength.

Among the parameters that influence the fatigue performance of composites are fiber type, matrix type, environmental conditions (temperature and moisture absorption), and loading conditions (stress ratio, cycling frequency, etc). There are some difficulties which have to be overcome when fatigue life prediction of composite materials is pursued; including the fact that the governing damage mechanism is not the same for all stress level states and failure can vary with cyclic stress level and even with number of cycles to failure. The frequency can have a major impact on the fatigue life because of the sensitivity of matrix to the loading rate and because of the internal heat generation and temperature rise [1].

Compared to non-reinforced polymers most fiber-reinforced polymers are stiffer and less susceptible to fatigue failure and have lower hysteretic heating effects [2]. Fatigue properties of short fiber reinforced polymers depend on fiber volume fraction, fiber orientation, matrix properties, fiber-matrix interfacial strength, and fiber aspect ratio (l_f/d_f). Short fiber reinforced polymers are notch sensitive and are much likely to fail by the propagation of a single macroscopic crack. The failure mechanism is a combination of interfacial debonding and matrix cracking. Although there are many studies on fatigue behavior of thermoplastic polymers and continuous as well as short fiber composites, these studies are rare for fatigue of nanocomposites.

This paper discusses the fatigue behavior of vinyl ester polymer and its nanocomposite with 0.5 wt% functionalized carbon nanofiber under tension-tension cyclic loads. These materials have high scatter in their fatigue lives due to the surface condition, machining defects, porosity, residual stresses, material brittleness, and sensitivity to moisture and temperature, and in the case of nanocomposite the variation in fiber dispersion in the matrix. Hence statistical analysis of the stress-life data was required. Microfractograph images of the fatigue fracture surfaces are also illustrated and analyzed.

The work reported in this paper was a part of an overall project with the goal of determining the mechanical behavior of the vinyl ester polymer and its carbon nanofiber reinforced composite. Extensive experimental work other than fatigue tests consisted of tensile, flexure, and creep tests, while analytical efforts included modeling deformation, creep, and stress-strain behavior of these materials. Experimental data considering strain rate and temperature effects as well as stress-strain and creep models are reported elsewhere [3-6].

2. EXPERIMENTAL DETAILS

Thermoset vinyl ester resin with high strength and stiffness was chosen as the matrix material in this study. The polymer material used in this research was HETRON 942/35 (65 wt% Vinyl ester - 35 wt% Styrene). The additives manufactured by Ashland Chemical Company and added based on the total weight of the vinyl ester - styrene material included 0.02 wt% N-dimethylaniline (DMA) and 0.2 wt% cobalt napthoate (CoNap) as promoters, and 1.25 wt% Luperox® DDM-9 methyl ethyl ketone peroxide (MEKP) as initiator.

Styrene was added to vinyl ester to provide viscosity required for addition and uniform dispersion of carbon nanofibers. Vinyl ester resin with a composition of 55 wt% Vinyl ester - 45 wt% Styrene (by dilution of HETRON 942/35 with styrene) was used in this work to make plaques of test materials to be cut into test specimens. This composition was chosen due to its common industrial application as well as suitable viscosity required for addition of carbon nanofibers. The nanofibers used in this study were provided by Applied Sciences Inc. (ASI) and had an aspect ratio (l_f / d_f) of about 200. To make nanocomposite material, the functionalized carbon nanofibers were added into vinyl ester resin and dispersed inside the resin by sonication.

A closed-loop servo-hydraulic axial load frame in conjunction with a digital servo-controller was used to conduct fatigue tests. The gripping system used was the wedge action type suitable for flat specimens. The smooth gripping faces used for the experiments were modified by inserting an emery paper between the jaw faces and the test specimen with the rough paper surface facing the test specimen. Repeatability of the grips ensured the alignment of the test specimen in the direction of strain without any bending. Any twisting of the specimens was avoided by using an anti-rotation device mounted on the lower grip's arm.

Significant effort was put forth to align the load train (load cell, grips, specimen, and actuator). According to ASTM Standard E 606-92 [7], the maximum bending strains should not exceed 5% of the minimum axial strain range imposed during

fatigue test program. ASTM Standard E 1012-93 [8] was followed to verify specimen alignment. For this verification, a 12.7 mm (0.5 in) × 5.1 mm (0.2 in) rectangular cross section bar with eight strain gages was used.

Uniaxial tension-tension fatigue tests to avoid buckling under compression were performed according to ASTM Standard D 3479-76 [9]. The dogbone-shaped flat specimen with rectangular cross section shown in (Fig. 1) was used. The stress concentration factor was calculated to be about 1.06 at the radius, which was reasonable. All fatigue tests were in load-control and conducted using a triangular waveform and with a minimum load of 90 N. The test frequency was chosen in a way to keep the strain rate nearly constant for all fatigue tests. However, the frequency was increased at lowest stress level and longer lives in order to reduce test duration. At least 8 repeat tests were carried out at two stress levels of 24.3 MPa and 20.6 MPa and one test at 17.4 MPa stress level. These tests were selected to produce failures over the range of 100 to 10^6 cycles. From stress amplitude versus number of cycles to failure curves, fatigue properties were generated. These tests were conducted at room temperature and humidity.

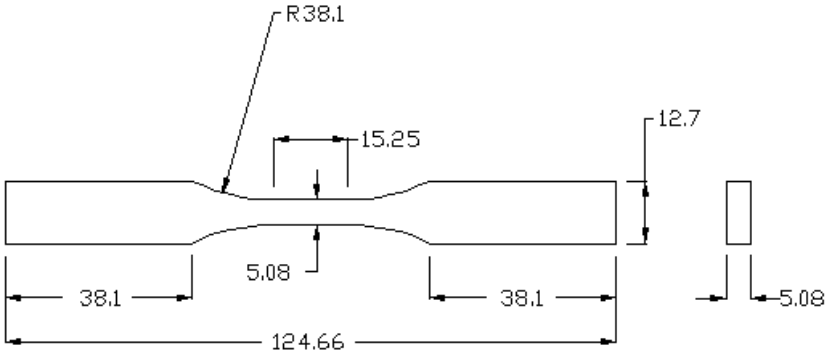


Fig. 1. Specimen configuration for fatigue tests (dimensions are in mm)

3. CYCLIC DEFORMATION BEHAVIOR

Cyclic elastic modulus measured from stress-strain loops showed higher value at loading than that at unloading. The cyclic modulus as the average of loading and unloading moduli at 0.5% strain was found from hysteresis loops at different cycles. The strain of 0.5% is where the stress-strain curve starts to become nonlinear. Modulus of elasticity of vinyl ester decreases by increasing fatigue cycles. These small changes in the modulus of elasticity are perhaps because of the breaking of some polymer chains during the cycling process.

Similar to vinyl ester polymer, the modulus of elasticity of nanocomposite at 0.5% strain amplitude changes slightly by increasing fatigue cycles. Cyclic elastic modulus for this material is also independent of the strain amplitude. Therefore, addition of functionalized carbon nanofibers to the vinyl ester provides more consistent elastic deformation of the material under cyclic loading conditions.

From plots of steady state hysteresis loops for both materials it was found that even at high strain amplitudes, the strains are predominantly elastic, with very small plastic strain amplitudes. This was evident from the narrow width of the hysteresis loops. Experimental observations indicated different nonlinear deformation behaviors during loading and unloading parts of a cyclic load. The comparison between hysteresis loops for vinyl ester and nanocomposite at strain amplitude of 1.18% showed that both materials have similar stress-strain loops and the plastic strain amplitude was the same for both materials.

4. STRESS-LIFE BEHAVIOR

Constant amplitude load-controlled tension-tension fatigue test data were used to determine the stress-life curves. The fatigue strength coefficient, σ'_f, and the fatigue strength exponent, b, are the intercept and slope of the best line fit to true stress amplitude ($\Delta\sigma/2$) versus reversals to failure ($2N_f$) data in log-log scale:

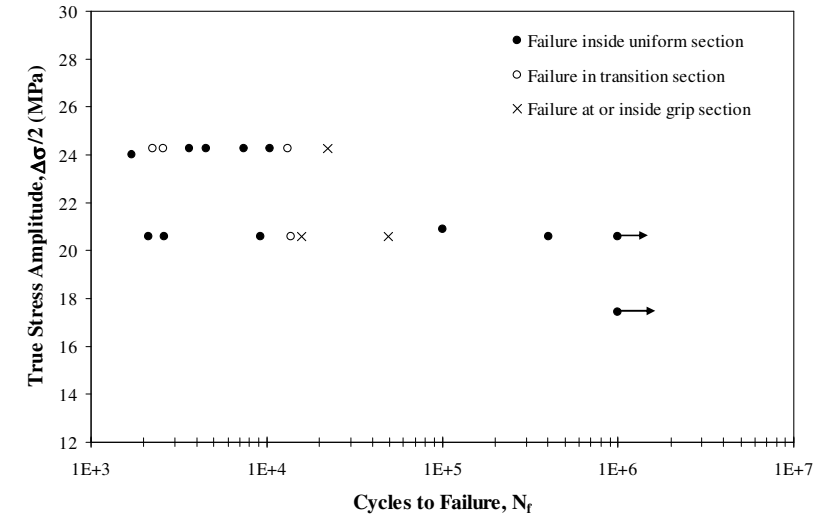
$$\frac{\Delta\sigma}{2} = \sigma'_f (2N_f)^b \qquad (1)$$

The plots of true stress amplitude versus cycles to failure for vinyl ester and its nanocomposite are shown in (Figs. 2(a) and (b)), respectively. As can be seen for both materials, there is considerable scatter in the data necessitating the use of a large number of tests. This scatter in the data could be because of the material's brittleness and high sensitivity to any misalignment of the specimen in the loading machine. Existence of any possible local microscopic defects such as voids on the surface or inside the test specimens, which could not be seen by the naked eyes, might be considered as another source of data scatter. For these scattered data there was no good fit for obtaining the fatigue strength coefficient and exponent. Therefore, a statistical analysis of resulting data was necessary.

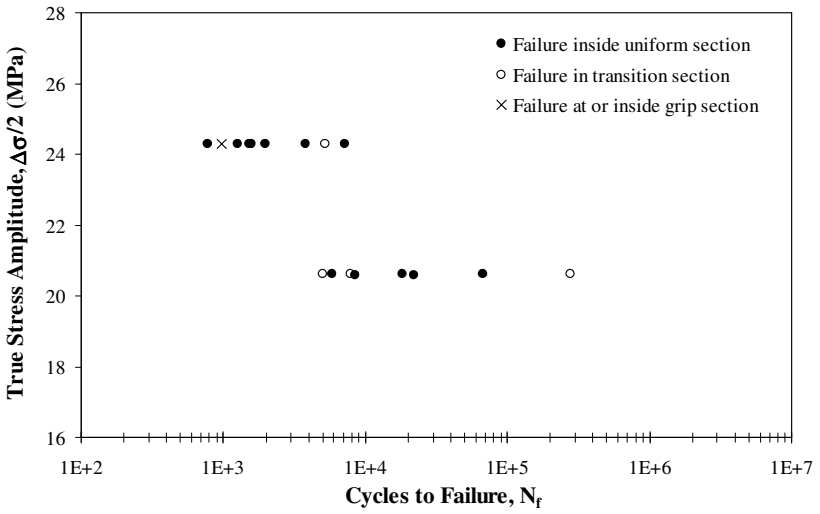
Assuming the normal distribution for the samples, the minimum number of specimens needed to determine 95% confidence interval for a population mean (μ) with standard deviation (σ), is calculated using the following formula [10]:

$$n = \left(\frac{1.96\sigma}{E}\right)^2 \qquad (2)$$

where E is half of the width of interval. Based on Eq. (2), the minimum number of specimens required is 8 for a width of interval of 1.4 σ. Therefore, the minimum number of specimens used at each stress level was 8.



(a)



(b)

Fig. 2. True stress amplitude versus cycles to failure for (a) vinyl ester and (b) functionalized carbon nanofiber reinforced composite at RT

The approach was to find the fatigue life versus probability of failure for both materials at each stress level using different distributions. The results indicated that a Log-normal distribution of life at a constant stress level was a good estimation, even though the number of specimens was calculated based on the

normal distribution assumption. Normal, Weibull, and Gamma distributions were also tried, but none of these distributions fitted as well to the data, compared to the Log-normal distribution in the normal probability plot.

Different probabilities of survival were obtained from fatigue life versus log-normal probability of failure graphs. None of the data points were outliers based on 95% confidence interval. The lower bound was 2.5 percentile, and the upper bound was 97.5 percentile. The data for tests at 20.6 MPa stress level were considered for the vinyl ester specimens up to failure except for those broken inside the grip section. The specimen which did not break up to 10^6 cycles was not considered either. Therefore, for this stress level only 6 specimens were used. With this number of specimens, the width of interval was calculated to be 1.6 σ, which is higher than the case when 8 specimens are used. This number of specimens is acceptable, since the corresponding width of interval in (Eq. 2) is smaller than 1.96 σ.

By connecting the points of equal probability of failure for both materials, curves of constant probability of failure on the S-N plot were obtained, which are shown in (Fig. 3). From this figure at 50% probability of survival, σ'_f and b were obtained for vinyl ester to be 73.3 MPa and -0.121, respectively, and 44.2 MPa and -0.072 for the nanocomposite, respectively.

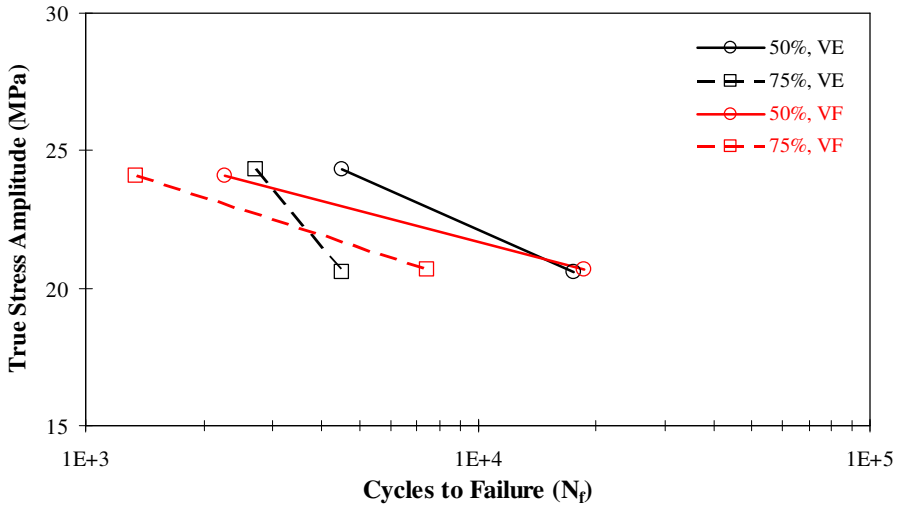


Fig. 3. Stress amplitude versus cycles to failure comparison between vinyl ester (VE) and functionalized carbon nanofiber reinforced composite (VF) at different probabilities of survival at RT

In (Fig. 3) at 50% probability of survival the nanocomposite has shorter life than vinyl ester at stress amplitude higher than about 21 MPa and it has similar life as vinyl ester at stress amplitude of about 21 MPa. The difference is larger for higher probability of survival of 75%. At stress amplitudes lower than about 22 MPa, the life for nanocomposite is higher than vinyl ester. Therefore, at lower stresses nanocomposite has more resistance to cyclic stresses than neat vinyl ester. These brittle materials fail with little or no plastic deformation and have no ability for local yielding, hence abrupt failure occurs.

5. SEM OBSERVATIONS OF THE FRACTURE SURFACES

Fatigue fracture surfaces were examined using Scanning Electron Microscope (SEM) and the images of these fracture surfaces for vinyl ester and nanocomposite at stress level of 24.3 MPa are shown in (Fig. 4). The fracture surfaces under cyclic stresses consist of the crack initiation region followed by a smooth region leading to steps or river-like pattern. The fatigue fracture surfaces also contain a series of concentric crack growth bands surrounding the surface source. These bands are caused by intermittent growth of the crack due to breakdown of a craze. The discontinuous crack growth bands are followed by a region that show radial tear lines, secondary fracture features and increasing surface roughness [11].

Fracture surfaces of the vinyl ester specimens are similar for those broken at higher stress levels and those broken at lower stress levels. The crack was initiated from the corner of these specimens (see Figs. 4(a) and (b)). This is due to higher stresses at the sharp edges of brittle vinyl ester specimens. For the specimens broken outside gage length or at shorter lives, the crack initiation region was larger than for specimens broken inside gage length or at longer lives. The crack growth region with a coarse stacked lamellar structure is the same for all specimens.

Fracture surfaces of the nanocomposite specimens were also similar for those broken at higher stress levels and those broken at lower stress levels. Crack initiated from subsurface on the fracture surface of nanocomposite (see Fig. 4(c)). For this material, the uniform dispersion of nanofibers inside the polymer is important and in some areas agglomeration of nanofibers exists. Even with nanofiber functionalization, it cannot be guaranteed there is no agglomeration of nanofibers in the nanocomposite specimens. At fracture surfaces of the nanocomposites shown in (Fig. 4(d)), disconnection between matrix and nanofibers and pullout of the nanofibers in crack initiation area can be seen. In these areas small patches of nanofibers can also be seen. The crack growth region

with a coarse stacked lamellar structure is the same for all specimens, similar to what is observed in vinyl ester specimens.

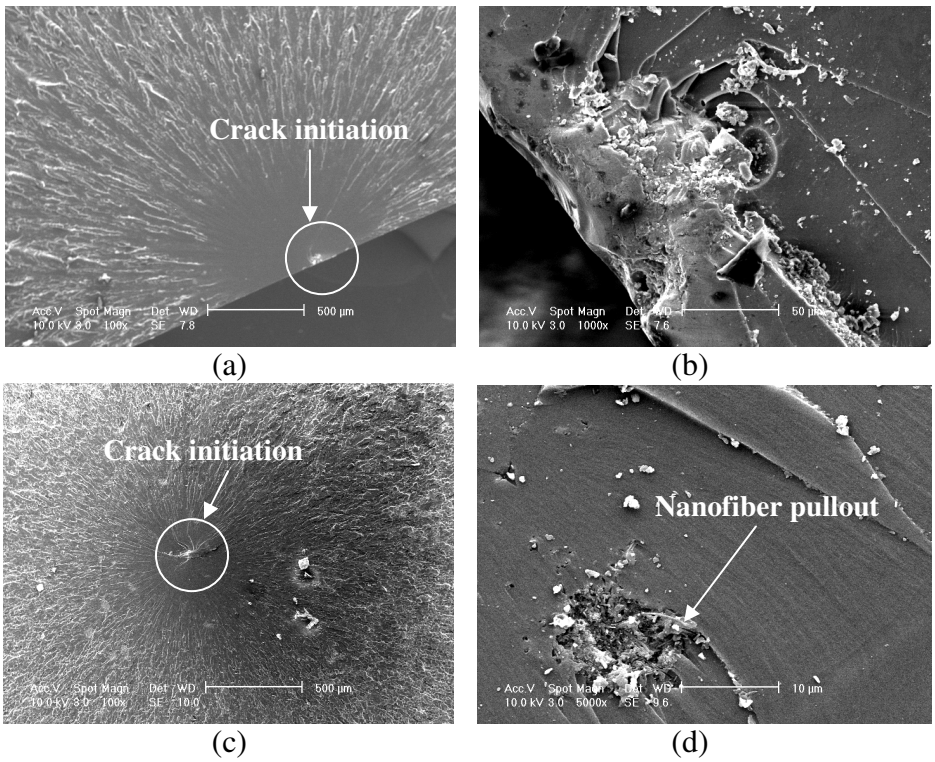


Fig. 4. SEM micrographs of fatigue fracture surface at 24.3 MPa stress amplitude for vinyl ester showing (a) crack initiation and crack growth regions (x100) and (b) large crack initiation region (x1000), and for nanocomposite showing (c) crack initiation and crack growth regions (x100) and (d) crack initiation region with existence of nanofiber agglomeration and some nanofiber pullout (x5000)

6. CONCLUSUIONS

Based on the analysis and discussion of the experimental data presented, the following conclusions can be made:

1. There were very small changes in the cyclic moduli of elasticity of vinyl ester and nanocomposite by increasing fatigue cycles. Cyclic modulus of elasticity for nanocomposite, unlike vinyl ester, was found to be independent of the strain amplitude.
2. For vinyl ester and its nanocomposite, even at high strain amplitudes, the strains were predominantly elastic, with very small plastic strain amplitudes. This was evident from the narrow width of the hysteresis loops.

3. The plot of true stress amplitude versus cycles to failure for vinyl ester and nanocomposite showed that there was considerable scatter in the data because of the materials brittleness necessitating the use of a large number of tests and statistical analysis.
4. From true stress amplitude versus cycles to failure comparisons between vinyl ester and nanocomposite for different probabilities of survival based on Log-normal distribution of life it was found that at lower stresses nanocomposite appears to be more resistant to cyclic stresses than the vinyl ester.
5. Fatigue fracture surfaces of the vinyl ester specimens were similar at lower and higher stress levels. It was shown that for the specimens broken outside gage length or at shorter lives, the crack initiation region was larger than for specimens broken inside gage length or at longer lives. The crack growth region appearance with a coarse stacked lamellar structure was the same for all vinyl ester specimens.
6. Fatigue fracture surfaces of the nanocomposite specimens were also similar at lower and higher stress levels. Crack initiated subsurface and small patches of nanofibers and pullout of the nanofibers in crack initiation area was observed. The crack growth region appearance was the same for all nanocomposite specimens.

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