

FATIGUE CRACK GROWTH IN EPOXY POLYMER NANOCOMPOSITES

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Abstract

The present paper has described detailed analyses of experimental data for the cyclic-fatigue behaviour of epoxy nanocomposite polymers. It has been shown that the data may be interpreted using the Hartman-Schijve relationship to yield a unique, ‘master’, linear relationship for each epoxy nanocomposite polymer. By fitting the experimental data to the Hartman-Schijve relationship, two key materials parameters may be deduced: (a) the term A , which may be thought of as the fatigue equivalent to the quasi-static value of the fracture energy, G_c , and (b) the fatigue threshold value, $\Delta\sqrt{G_{thr}}$, below which no significant fatigue crack growth (FCG) occurs. It has then been established that the values of these parameters, together with the slope, n , and intercept, D , of the Hartman-Schijve master relationship, may be used (a) to compute the experimental results measured for the fatigue behaviour of the epoxy nanocomposite polymers, (b) to understand the observed fracture and fatigue behaviour of these materials with respect to the structure of the epoxy nanocomposite polymers and (c) to deduce the ‘upper-bound’, i.e. ‘worst-case’, FCG rate curve which may be used by industry as a material development, material selection, design and service-life prediction tool when these epoxy nanocomposite polymers are used in engineering applications such as structural adhesives and/or as matrices in fibre-reinforced composites.

Keywords: adhesives, fatigue crack growth, fracture, polymer nanocomposites

1. Introduction

Epoxy polymers are widely used for the matrices of fibre-reinforced composite materials and as structural adhesives. When cured, epoxy polymers are amorphous and highly-crosslinked (i.e. thermosetting) polymers [1]. This microstructure results in many useful properties for structural engineering applications, such as a high modulus and failure strength, low creep and good performance at elevated temperatures. However, the structure of such epoxy polymers also leads to a highly undesirable property in that they are relatively brittle materials, with a poor resistance to crack initiation and growth. Recently, a new technology has emerged which holds considerable promise for increasing the mechanical performance of such thermosetting polymers, whilst maintaining other important properties such as their elevated temperature resistance. This is via the addition of a nanofiller to the polymer. The nanofillers that have been so employed include silica particles [e.g. 2-5], carbon nanotubes (CNTs) [e.g. 6-8], carbon nanofibres (CNFs) [e.g. 9-11], graphene nanoplatelets (GNPs) [12-16] and other types of platelet structures [17,18]. Depending upon the exact type of nanofiller incorporated, other properties of the epoxy polymer may also be enhanced. For example, the electrical conductivity and barrier properties of the nanocomposite may be significantly improved compared to the neat, i.e. unmodified, epoxy polymer.

However, in the literature there are relatively few papers where the cyclic-fatigue behaviour of such epoxy nanocomposites has been studied. This is a very important aspect of their mechanical properties if these materials are to be used in engineering applications. However, the few studies [6,13,19-23] that may be found have interestingly reported that the cyclic-fatigue behaviour of polymer nanocomposites may indeed be improved compared to that of the neat epoxy polymer. However, no detailed analyses of the experimental data for the cyclic-fatigue behaviour of epoxy nanocomposite polymers have yet been undertaken.

Recently the present authors have developed an approach for analysing the cyclic-fatigue behaviour of polymer-matrix continuous fibre composites [24,25] and structural adhesives [26,27] using a fracture-mechanics approach based upon the Hartman-Schijve equation [28]. The advantages of using this approach are that (a) a unique, ‘master’, linear representation may be obtained which yields the threshold value of the energy release-rate, G , below which no significant fatigue crack growth occurs, (b) having ascertained the values of the constants in the Hartman-Schijve equation the complete curve for the experimentally-measured results may be computed with a relatively high degree of accuracy, and (c) an ‘upper-bound’, i.e. ‘worst-case’, fatigue crack growth (FCG) rate curve may be deduced. This ‘upper-bound’ FCG rate

curve, which encompasses all the experimental results, yields a curve that can be used with confidence by industry for (a) material development, characterisation and comparative studies, and (b) design and lifing studies. Therefore, the aims of the present paper are to analyse cyclic-fatigue data which have been experimentally measured and reported for different types of epoxy nanocomposite polymers employing the Hartman-Schijve methodology.

2. Theoretical

2.1 Introduction

In the present paper we shall use a fracture mechanics approach to study the FCG of nanocomposite materials based upon a thermosetting epoxy polymeric matrix. The basic tenet of fracture mechanics is that the strength of most real solids is governed by the presence of flaws and various theories enable the manner in which they propagate to be analysed mathematically. Two main, inter-relatable, conditions have been proposed. Firstly, the energy criterion arising from Griffith [29], the ‘founder of fracture mechanics’, in 1920 which assumes that fracture occurs when sufficient energy is released (from the stress field) by growth of the crack to supply the requirements of the new fracture surfaces. The energy released comes from stored or potential energy of the loading system and can, in principle, be calculated for any type of test specimen or component. This approach, which assumes that a naturally-sharp crack or flaw is present in the material, therefore provides a measure of the energy required to extend a crack over unit area. For monotonic loading, this is termed the fracture energy, or the critical energy-release rate, and is denoted as G_c . Secondly, Irwin [30], the ‘father of fracture mechanics’, reported in 1957 that the stress field around a sharp crack in a linear-elastic material could be uniquely defined by a parameter termed the stress-intensity factor, K , and he stated that fracture occurred when the value of K exceeds some critical value, K_c . These two fracture parameters are inter-related via the modulus, E , of the material and, for plane-strain:

$$K_c^2 = G_c E / (1 - \nu^2) \quad (1)$$

where ν is Poisson’s ratio.

2.2 Crack growth under cyclic-fatigue loading

Crack growth in a material is far more likely to occur when it is subject to repeated cyclic loading than under monotonic loading and, therefore, such FCG has been of great interest to materials scientists and engineers for many years. In the late 1950s, when considering FCG in metals, Paris stated [31] that:

“Later in 1957 when I first saw the crack tip stress field equations my reaction was immediate that the fluctuation of the crack tip stress intensity factor, K , causing fluctuations of the crack tip stress field surrounding the plastic zone could correlate growth rates.”

This observation led to the famous Paris Equation [32] which is applicable when linear-elastic fracture-mechanics (LEFM) conditions are satisfied:

$$\frac{da}{dN} = C \Delta K^m \quad (2)$$

where C and m are constants, da/dN is the FCG rate and ΔK is the range of the applied stress-intensity factor such that:

$$\Delta K = K_{max} - K_{min} \quad (3)$$

where K_{max} and the K_{min} are the maximum and minimum values of the applied stress-intensity factor in a fatigue cycle. The Paris Equation is an empirical equation and the constants C and m may also depend upon the test parameters, such as the environment, frequency, stress ratio, etc.

2.3 The G approach and the Hartman-Schijve equation for the FCG

Although for bulk materials the two approaches described above, based either upon G or K , are essentially parallel approaches that may be readily inter-related via Equation (1), the former approach is generally considered to be the more appropriate for relating the fracture and fatigue properties to the microstructure of polymeric materials. Further, due to the inhomogeneity and anisotropy of continuous-fibre composites and the relatively thin layers of structural adhesives, i.e. typically sandwiched between relatively rigid substrates, the energy release-rate, G , approach, rather than the stress-intensity factor, K , approach, is generally considered to be the more valid and useful approach when studying the fracture and fatigue of such materials [33-35].

Considering re-formulating the Paris Equation, see Equations (2) and (3), in terms of G rather than K , then at first sight the most obvious and corresponding parameter against which to plot the measured rate of the FCG, da/dN , is the range of the applied energy release-rate, ΔG .

However, as shown in Equation (1), K is proportional to $\sqrt{G}$. Indeed, recent work, for example by Jones et al. [24,26,27], Rans et al. [36], Pascoe et al. [37], Simon et al. [38] and Yao et al. [25, 39-41] has confirmed that the logical extension of the Paris FCG rate equation in terms of G , rather than K , is in fact to express da/dN as a function of $\Delta\sqrt{G}$, where:

$$\Delta\sqrt{G} = \sqrt{G_{max}} - \sqrt{G_{min}} \quad (4)$$

where G_{max} and G_{min} are the maximum and minimum values of the applied energy release-rate in the fatigue cycle, respectively. The values of G_{max} and G_{min} may, of course, be calculated from the maximum and minimum loads, P_{max} and P_{min} , respectively, in the fatigue cycle and the R -ratio may be defined by $R = P_{min}/P_{max}$. (The value of the R -ratio may also be given in terms of the maximum and minimum displacements, δ_{max} and δ_{min} , respectively, and the R -ratio may now be defined by $R = \delta_{min}/\delta_{max}$.)

The Paris Equation, either in terms of ΔK or $\Delta\sqrt{G}$, gives a linear expression when plotted as logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$. However, whilst the central portions of the FCG relationships that are experimentally measured do invariably follow this linear expression relatively closely, the experimental results for the FCG relationships over the full range of values are usually sigmoidal in shape, for example see Figures 1,4,7 and 9 below. When the FCG rate is relatively high, an acceleration in da/dN is observed as the value of G_{max} approaches that of the fracture energy, G_c , under quasi-static monotonic loading. On the other hand, when the FCG is relatively very low, a deceleration in da/dN is observed as the value of $\Delta\sqrt{G}$ approaches that of a threshold value, $\Delta\sqrt{G_{thr}}$, below which no significant fatigue crack growth occurs. Therefore, as Schwalbe [42] has commented some “*fine tuning of the Paris Equation was needed*”. An expression proposed by Hartman and Schijve [28] in 1970 has proved to be a valid and very useful way to proceed. The form proposed for the Hartman and Schijve equation, which is a variant of the NASGRO equation [43], by Jones et al. [24-27,44] in terms of $\Delta\sqrt{G}$ is:

$$\frac{da}{dN} = D \left[\frac{\Delta\sqrt{G} - \Delta\sqrt{G_{thr}}}{\sqrt{\{1 - \sqrt{G_{max}}/\sqrt{A}\}}} \right]^n \quad (5)$$

where the four terms D , n , A and $\Delta\sqrt{G_{thr}}$ are constants. The parameter A may be thought of as the fatigue equivalent to the quasi-static value of the fracture energy, G_c , and the parameter $\Delta\sqrt{G_{thr}}$ is defined by:

$$\Delta\sqrt{G_{thr}} = \sqrt{G_{thr.max}} - \sqrt{G_{thr.min}} \quad (6)$$

and the subscript ‘*thr*’ in Equations (5) and (6) again refers to the values at threshold, below which no significant FCG occurs.

As commented above, the aims of the present paper are to analyse cyclic-fatigue data that have been reported for different types of epoxy nanocomposite polymers employing the Hartman-Schijve methodology, as embodied in Equation (5).

3. Results and Discussion

3.1 Introduction

In this section of the paper results will be taken from the literature on the cyclic-fatigue behaviour of epoxy nanocomposite polymers and re-analysed using the ideas developed in the previous section.

3.2 Epoxy/anhydride nanocomposite polymers prepared using nanosilica

Kothmann et al. [21] have prepared nanocomposites which consist of nanosilica particles in an anhydride-cured epoxy polymeric matrix. The epoxy polymers possessed a glass transition temperature of about 150°C. The spherical nanosilica particles were very well dispersed and possessed a mean diameter of 20 nm with a narrow range of particle distribution [45]. The concentrations of the nanosilica filler employed were 0, 5, 10, 15 and 25 wt.%. The cyclic-fatigue tests were conducted under load control using a R -ratio of 0.1.

The fatigue behaviour of the neat (i.e. unmodified) epoxy polymer and the epoxy-nanosilica nanocomposite polymers from [21] is replotted in Figure 1 in the form of logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$. As may be seen, the fatigue resistance of the epoxy polymer increases significantly upon the inclusion of the spherical nanosilica particles. However, the fatigue resistance of the epoxy nanocomposites at relatively low values of da/dN , below about 10^{-6} m/cycle, is somewhat insensitive to the concentration of silica nanoparticles. Whilst at relatively high values of da/dN there is a steady increase in the fatigue resistance as the concentration of nanoparticles is increased.

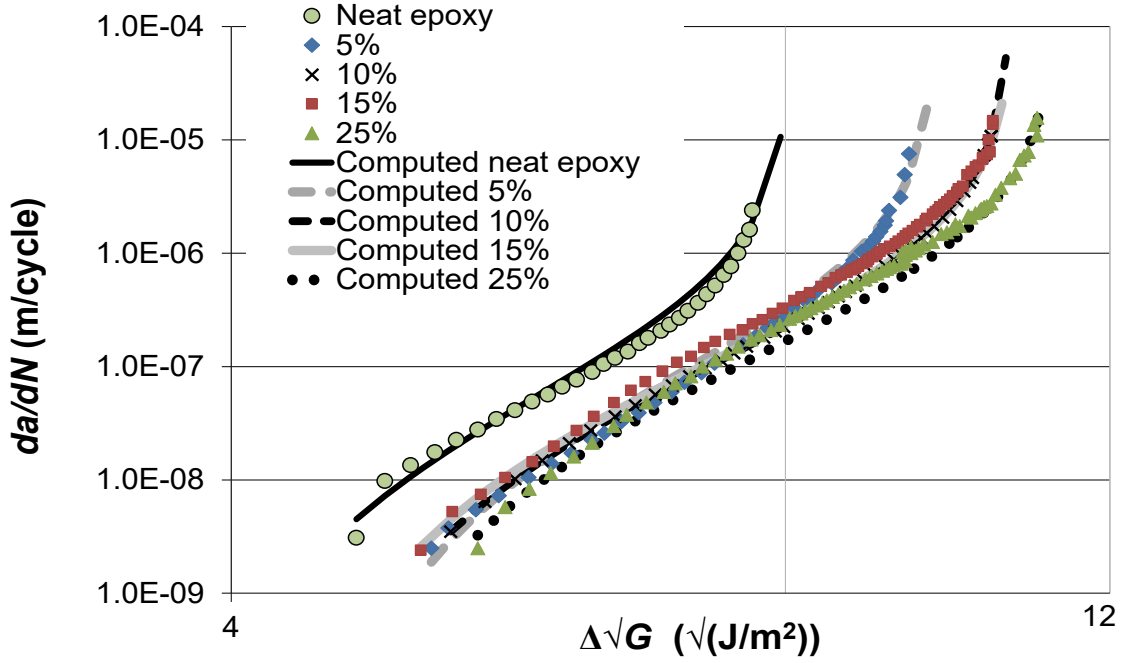


Figure 1. Logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$ showing the measured and computed FCG rate curves for the neat epoxy polymer and the epoxy nanocomposite polymers containing spherical nanosilica particles, replotted from [21]. The computed curves are from Equation (5) and the values employed are given in Table 1. (The concentrations are given as the wt.% of dispersed nanosilica filler particles.)

The results shown in Figure 1 for the neat epoxy and epoxy nanocomposite polymers may be plotted according to the Hartman-Schijve representation, see Equation (5). This is shown in Figure 2 where logarithmic da/dN is plotted against logarithmic $\left[\frac{\Delta\sqrt{G} - \Delta\sqrt{G_{thr}}}{\sqrt{1 - \sqrt{G_{max}}/\sqrt{A}}} \right]$ and the values of the various parameters derived are given in Table 1. As may be seen from Figure 2, the plot is indeed linear and gives a unique, ‘master’, linear relationship for the neat epoxy polymer and all the various concentrations of nanosilica in the epoxy nanocomposite polymers with constant values of D and n for all these different materials. Indeed, a relatively low degree of scatter is recorded, as indicated by the relatively very high value of the coefficient of determination, R^2 . Also, shown in Table 1 are the values of A , which may be thought of as the fatigue equivalent to the quasi-static value of the fracture energy, G_c , and the fatigue threshold value, $\Delta\sqrt{G_{thr}}$, below which no significant fatigue crack growth occurs, which were needed to obtain this unique, ‘master’, linear relationship.

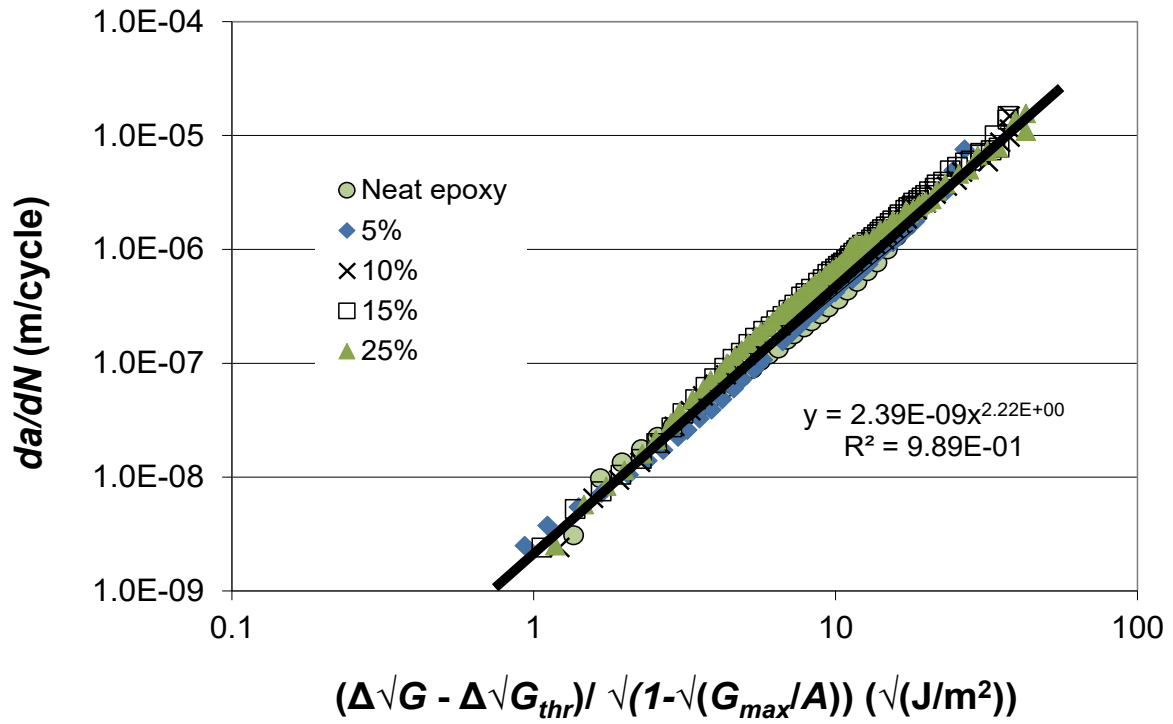


Figure 2. The Hartman-Schijve representation, see Equation (5), for the neat epoxy polymer and the epoxy nanocomposite polymers containing spherical nanosilica particles from the results shown in Figure 1. (The concentrations of the nanosilica filler are given in wt.%. The term R^2 is the coefficient of determination for the linear fit to the experimental data.)

The results obtained from invoking the Hartman-Schijve methodology may be employed to further understand the fatigue behaviour of the materials. Firstly, using these values given in Table 1, together with Equation (5), the plots of logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$ given in Figure 1 may be computed and compared to the experimentally-measured values. As may be seen from Figure 1, the agreement between the computed and measured curves is excellent. Secondly, from examining the values of A and $\Delta\sqrt{G_{thr}}$, the effects of the concentration of the nanosilica in the epoxy polymeric matrix on the fatigue curves shown in Figure 1 may be readily interpreted. From Table 1 it may be seen that the value of A increases far more rapidly with an increase in the concentration of nanosilica filler in the epoxy polymer than the value of $\Delta\sqrt{G_{thr}}$. Indeed, the value of $\Delta\sqrt{G_{thr}}$ for the nanocomposites is clearly higher than that of the neat epoxy but does not then vary greatly with the actual concentration of nanosilica particles in the epoxy polymeric matrix. This may be more readily appreciated from Figure 3 where the normalised values of these terms are plotted against the concentration of nanosilica filler. (The normalised values represent values of A or $\Delta\sqrt{G_{thr}}$, as a function of the concentration of the nanosilica, which have been normalised with respect to the values of A or $\Delta\sqrt{G_{thr}}$ for the neat epoxy polymer, respectively, see Table 1.) The implication of these values is that, when the value of $\Delta\sqrt{G}$ approaches the threshold value, $\Delta\sqrt{G_{thr}}$, the FCG rate curve for

the epoxy nanocomposite polymers will demonstrate an improved fatigue resistance compared to that of the neat epoxy polymer. However, there will be little effect from the actual concentration of nanosilica particles that was employed. On the other hand, at relatively high values of $\Delta\sqrt{G}$, when the quasi-static toughness value is approached, then the epoxy nanocomposite polymers will again demonstrate an improved fatigue resistance compared to that of the neat epoxy polymer and, now, there will be a clear effect of the actual concentration of nanosilica particles in the polymer matrix. The computed curves from the values in Table 1, derived from the Hartman-Schijve approach, i.e. Equation (5), are clearly in accord with the experimental results shown in Figure 1. Thirdly, the reason for the results shown in Table 1 and Figure 3, namely that the value of A increases far more rapidly with the concentration of nanosilica particles in the epoxy polymer than the value of $\Delta\sqrt{G_{thr}}$, undoubtedly arises from the toughening mechanisms associated with the presence of the nanosilica particles in the epoxy polymer matrix. The silica nanoparticles induce various toughening mechanisms in the epoxy polymer matrix that have been identified [45] to be (a) localised plastic shear-band yielding in the epoxy around the particles and (b) debonding of the particles followed by subsequent plastic void growth of the epoxy. These are known as ‘intrinsic’ toughening mechanisms [46] that occur in the damage zone ahead of the crack tip. Now, at relatively low values of $\Delta\sqrt{G}$, the damage, or plastic, zone ahead of the crack tip, where these toughening mechanisms are active, will be relatively small in size. Hence, the nanosilica particles will be less effective in increasing the cyclic-fatigue performance of the epoxy nanocomposites compared to increasing the quasi-static toughness. This observation explains the form of the plots of logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$ as a function of the concentration of the nanosilica filler which are shown in Figure 1.

Table 1. Values of the parameters used in Figure 2 for the Hartman-Schijve representation, see Equation (5), for the neat epoxy and the epoxy nanocomposite polymers containing nanosilica filler. (The R -ratio used was 0.1.)

Polymer	D	n	A (J/m ²)	$\Delta\sqrt{G_{thr}}$ ($\sqrt{\text{J/m}^2}$)
Neat epoxy	2.39×10^{-9}	2.22	83	3.8
+ 5 wt.% nanosilica	2.39×10^{-9}	2.22	115	4.5
+ 10 wt.% nanosilica	2.39×10^{-9}	2.22	139	4.4
+ 15 wt.% nanosilica	2.39×10^{-9}	2.22	140	4.3
+ 25 wt.% nanosilica	2.39×10^{-9}	2.22	155	4.6

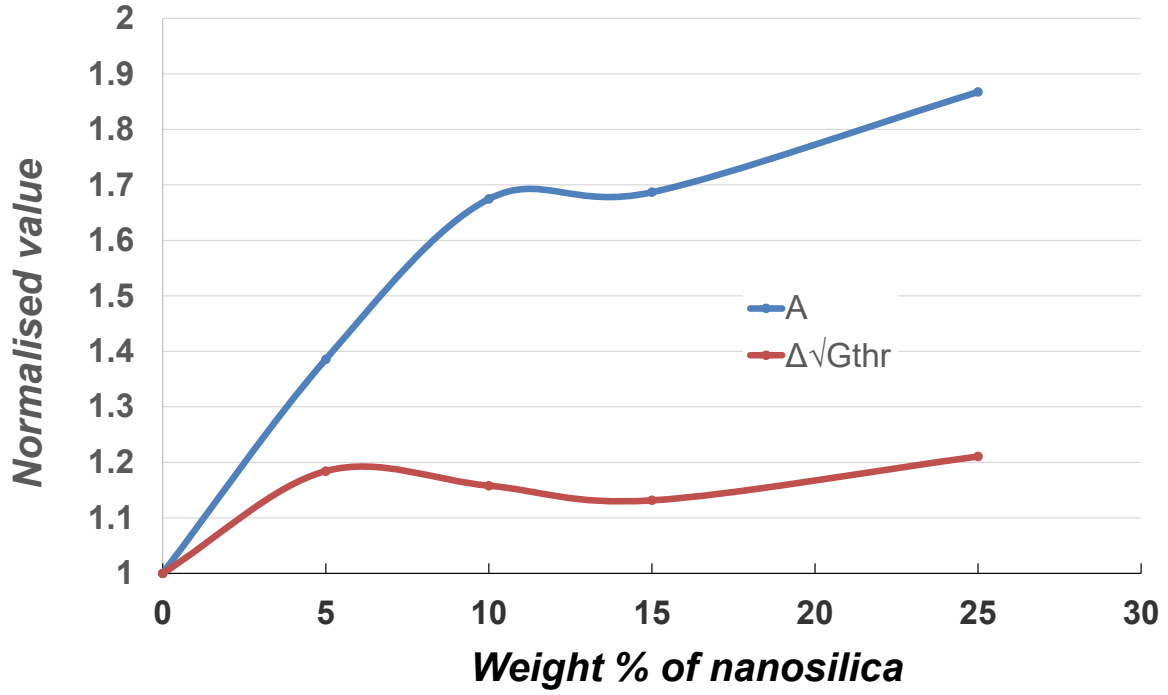


Figure 3. The effects of the concentration of nanosilica in the epoxy nanocomposite polymers on the values of A and $\Delta\sqrt{G_{thr}}$ given in Table 1, from Figure 2. (The normalised values represent values of A or $\Delta\sqrt{G_{thr}}$, as a function of the concentration of the nanosilica, which have been normalised with respect to the values of A or $\Delta\sqrt{G_{thr}}$ for the neat epoxy polymer, respectively, see Table 1.)

3.3 Epoxy/amine polymer nanocomposite polymers prepared using CNFs

Ladani et al. [22] have dispersed, using a three-roll mill, CNFs in an epoxy resin which was cured at room temperature using a blend of aliphatic amines and aliphatic amine adducts based on diethylenetriamine and triethylenetetramine. The epoxy polymers possessed a glass transition temperature of about 70°C. The CNFs had a diameter in the range of about 70 to 300 nm and a length in the range of 30 to 200 μm . The concentrations of the CNF filler employed were 0, 0.4, 0.7 and 1.0 wt.%. The effects of the concentration of the CNFs and their orientation, i.e. randomly-dispersed versus aligned normal to the direction of crack propagation, were investigated with the alignment induced via the use of an electric field which was applied prior to gelation of the epoxy resin. The cyclic-fatigue tests were conducted under displacement control using a R -ratio of 0.5.

The fatigue behaviour of such epoxy nanocomposites from [22] is replotted in Figure 4 in the form of logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$. As may be seen, the fatigue resistance of the materials steadily increases as the concentration of CNFs increases from 0.4 wt.% to 1.0 wt.%, and the aligned CNFs impart slightly superior fatigue properties at concentrations of 0.4 and 0.7 wt.%, compared to the randomly-dispersed CNFs. However, the

effect of alignment of the CNFs in the epoxy nanocomposite on the level of improvement diminishes as the concentration of CNFs in the epoxy polymeric matrix is increased. This is because, at relatively high concentrations of the CNFs, the very close packing of the CNFs limits the free space available for them to rotate and align when subjected to the applied electric field. Thus, the degree of alignment decreases as the concentration of the CNFs is increased.

The improvement observed in the fatigue performance of the epoxy-CNF nanocomposite polymers was found to be due to the additional toughening mechanisms induced by the presence of the CNFs in the epoxy. In these types of nanocomposites both ‘intrinsic’ toughening mechanisms, as described above, as well as ‘extrinsic’ [46] toughening mechanisms, which occur behind the advancing crack tip, were observed. These ‘extrinsic’ toughening mechanisms involved crack bridging, pull-out and eventually rupture of the CNFs, and these mechanisms were more effective when the CNFs were aligned normal to the direction of the advancing crack tip. Therefore, when the CNFs were so aligned, these types of epoxy-CNF nanocomposites polymers demonstrated a slightly enhanced fatigue behaviour compared to the nanocomposites containing randomly-dispersed CNFs.

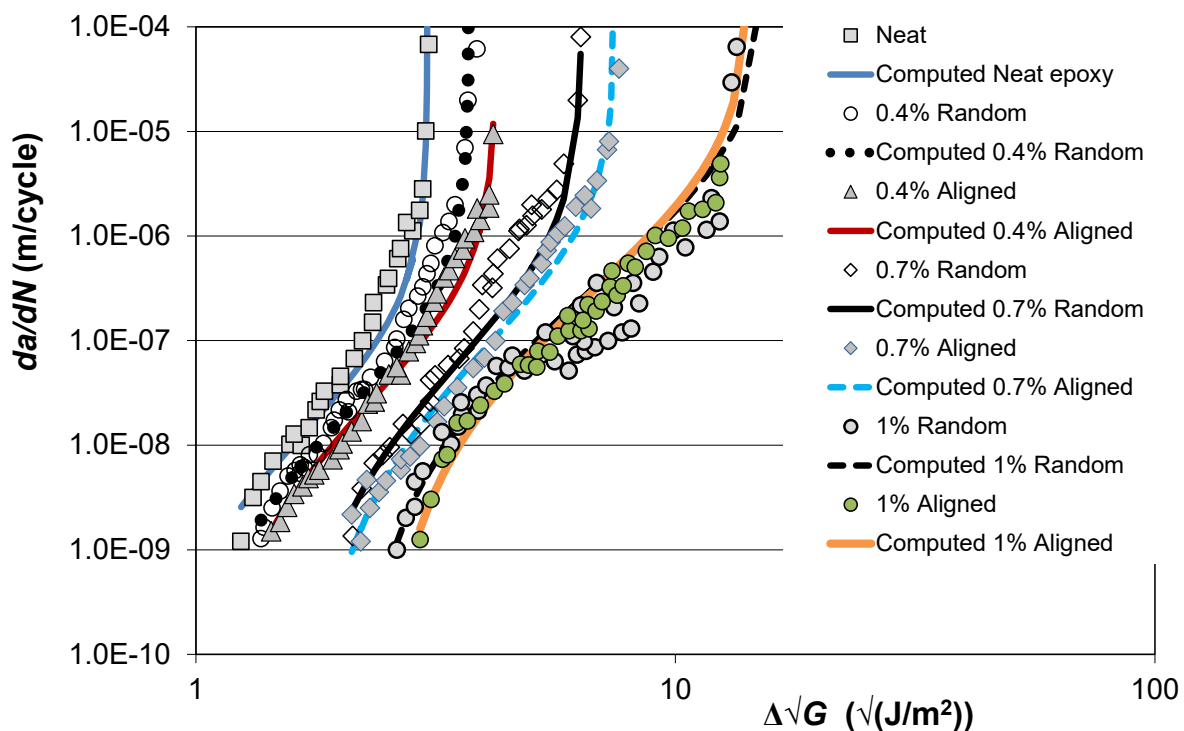


Figure 4. Logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$ showing the measured and computed FCG rate curves for the neat epoxy polymer and epoxy nanocomposite polymers containing randomly-dispersed and aligned CNFs, replotted from [22]. (The computed curves are from using Equation (5) and the values employed are given in Table 2. The concentrations are given as the wt.% of CNFs.)

Again the results shown in Figure 4 for the neat epoxy and epoxy-CNF nanocomposite polymers maybe be plotted according to the the Hartman-Schijve representation, see Equation (5). This is shown in Figure 5 where logarithmic da/dN is plotted against logarithmic $\left[\frac{\Delta\sqrt{G} - \Delta\sqrt{G_{thr}}}{\sqrt{\{1 - \sqrt{G_{max}/\sqrt{A}}\}}} \right]$ and the values of the various parameters deduced are given in Table 2. As may be seen from Figure 5, the plot is indeed linear and gives a unique, ‘master’, linear relationship with constant values of D and n for all these different materials. Indeed, a relatively low degree of scatter is recorded, as indicated by the relatively high value of the coefficient of determination, R^2 . This is especially noteworthy when the relatively large number of individual data points included in Figure 5, for a very wide range of materials, is considered. Also, shown in Table 2 are the values of A and $\Delta\sqrt{G_{thr}}$ which were needed to obtain this ‘master’ relationship. From the significant increases observed in the values of $\Delta\sqrt{G_{thr}}$ with increasing concentration of the CNFs, the very dramatic effect that adding the CNF nanofiller to the epoxy polymeric matrix has upon improving the cyclic-fatigue behaviour may be readily appreciated. The results obtained from invoking the Hartman-Schijve methodology may again be employed to further understand the fatigue behaviour of the materials. Using these values given in Table 2, together with Equation (5), the plots of logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$ given in Figure 4 may be computed and compared to the experimentally-measured values. As may be seen from Figure 4, the agreement between the computed and measured curves for the neat epoxy and the epoxy-CNF nanocomposite polymers is excellent.

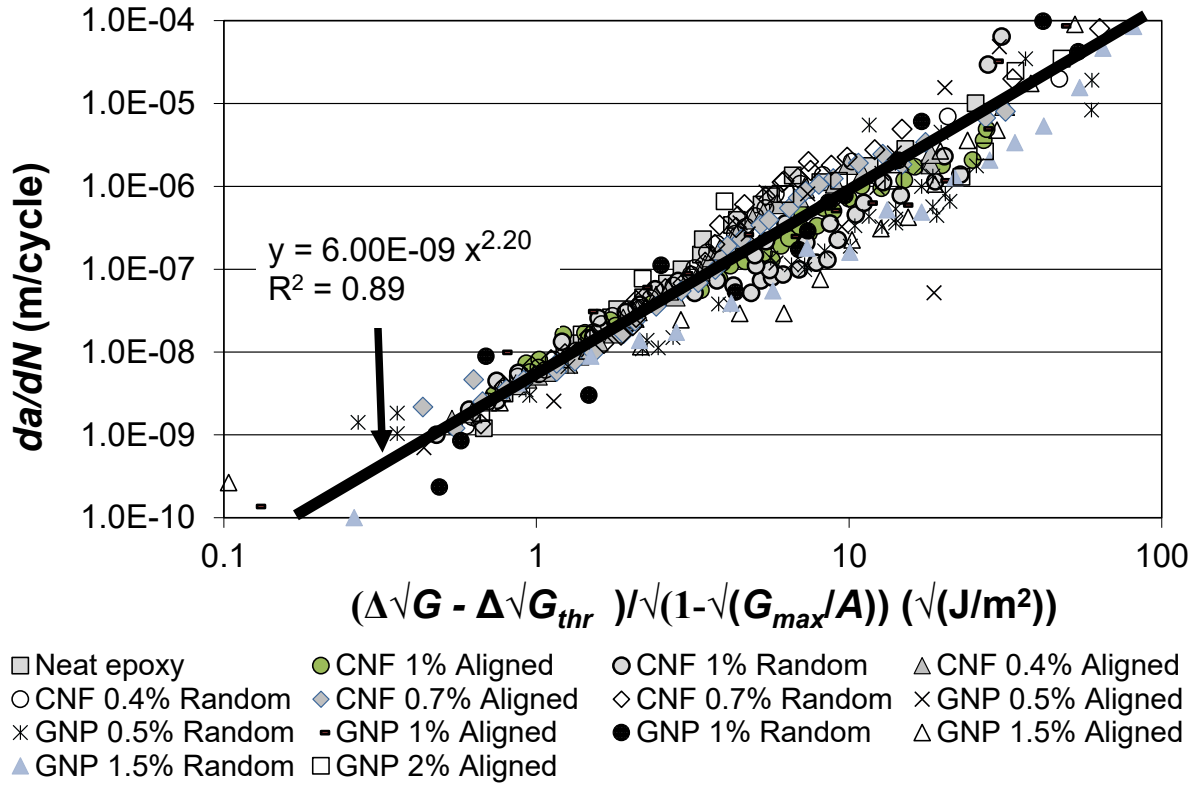


Figure 5. The Hartman-Schijve representation, see Equation (5), for the neat epoxy and the epoxy nanocomposite polymers containing CNFs and GNPs from the results shown in Figures 4 and 6, respectively. (The concentrations of the nanofiller are given in wt.%. The term R^2 is the coefficient of determination for the linear fit to the experimental data.)

Table 2. Values of the parameters used in Figure 5 for the Hartman-Schijve representation, see Equation (5), for the neat epoxy and the epoxy nanocomposite polymers containing CNFs. (The R -ratio used was 0.5.)

Polymer	D	n	A (J/m ²)	$\Delta\sqrt{G_{thr}}$ (√(J/m ²))
Neat epoxy	6.0×10^{-9}	2.20	37	0.72
+ 0.4 wt.% random	6.0×10^{-9}	2.20	55	0.89
+ 0.4 wt.% aligned	6.0×10^{-9}	2.20	71	1.00
+ 0.7 wt.% random	6.0×10^{-9}	2.20	163	1.58
+ 0.7 wt.% aligned	6.0×10^{-9}	2.20	225	1.75
+ 1.0 wt.% random	6.0×10^{-9}	2.20	960	2.19
+ 1.0 wt.% aligned	6.0×10^{-9}	2.20	880	2.49

In Figure 6 the normalised values of the terms A and $\Delta\sqrt{G_{thr}}$, which were needed to obtain the Hartman-Schijve ‘master’ relationship, see Table 2, are plotted against the concentration of CNFs. (The normalised values represent values of A or $\Delta\sqrt{G_{thr}}$, as a function of the concentration of the CNFs, which have been normalised with respect to the values of A or $\Delta\sqrt{G_{thr}}$ for the neat epoxy polymer, respectively, see Table 2.) The main observation from the results shown in Figure 6 is that clearly the effect of adding the CNFs is far more marked on the value of A , compared to that of $\Delta\sqrt{G_{thr}}$.

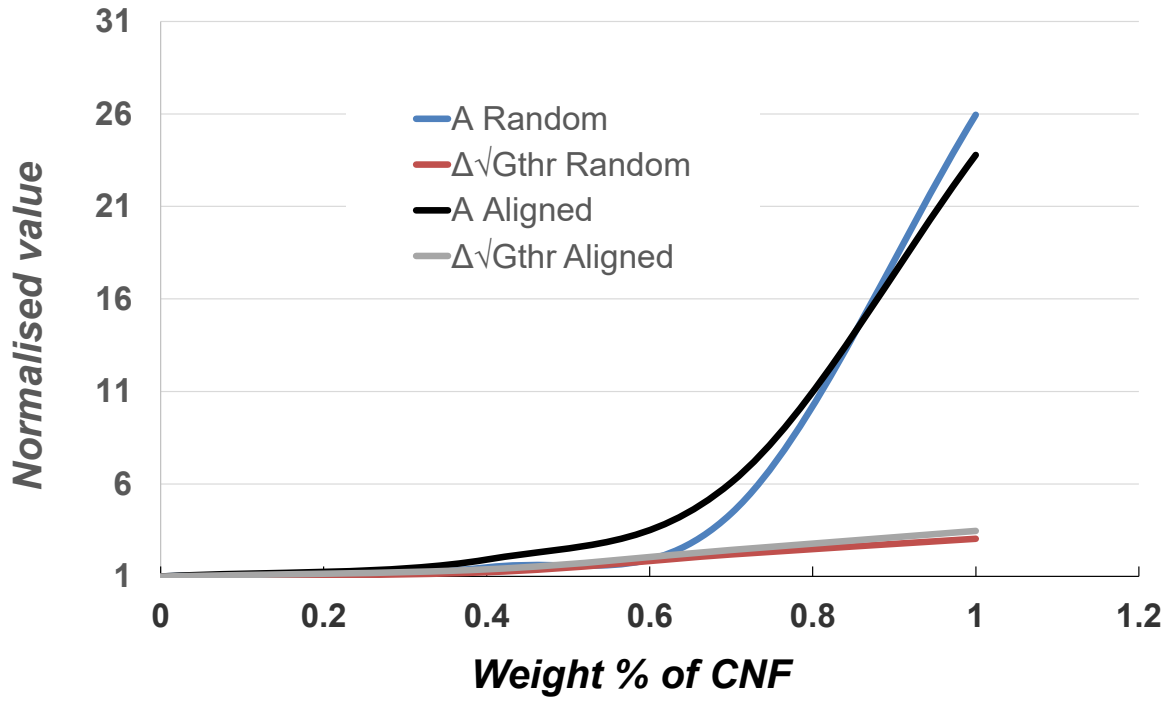


Figure 6. The effects of the concentration of CNFs in the epoxy nanocomposite polymers on the values of A and $\Delta\sqrt{G_{thr}}$ given in Table 2, from Figure 5. (The normalised values represent values of A or $\Delta\sqrt{G_{thr}}$, as a function of the concentration of the CNFs, which have been normalised with respect to the values of A or $\Delta\sqrt{G_{thr}}$ for the neat epoxy polymer, respectively, see Table 2.)

3.4 Epoxy/amine polymer nanocomposites prepared using GNPs

Bhasin et al. [23] have dispersed, using a three-roll mill, GNPs in an epoxy resin which was cured at room temperature using an amine hardener. The epoxy polymers possessed a glass transition temperature of about 90°C. The multi-layer GNPs were in the form of platelets with an average thickness of 6 to 8 nm, i.e. being composed of approximately eighteen layers, and with a mean diameter of 25 μm . The concentrations of the GNPs employed were 0, 0.5, 1.0, 1.5 and 2.0 wt.%. The effects of the concentration of the GNPs and their orientation, i.e. randomly-dispersed versus aligned normal to the direction of crack propagation, were investigated with the alignment induced via the use of an electric field which was applied prior to gelation of the epoxy resin. The cyclic-fatigue tests were conducted under displacement control using a R -ratio of 0.5.

The fatigue behaviour of such epoxy-GNP nanocomposite polymers from [23] is replotted in Figures 7 and 8 in the form of logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$. (Two figures have been used for clarity due to the relatively large number of different formulations studied.) As may be seen, the fatigue resistance of the materials steadily increases as the

concentration of GNPs increases from 0.5 wt.% to 1.5 wt.%. However, at the highest concentration of 2.0 wt.% of GNPs the fatigue behaviour is now inferior to that at a concentration of 1.5 wt.%, see Figure 8. The reason suggested in [23] for this observation was the significant agglomeration of the GNPs in the epoxy polymer matrix which was observed at this relatively high concentration. Further, at this highest concentration of 2.0 wt.% of GNPs, there is no significant further improvement in the fatigue behaviour arising from the alignment of the GNPs. As for the epoxy-CNF composite polymers, the very close packing of the GNPs at this relatively high concentration limits the free space available for them to rotate and align when subjected to the electric field.

The improvement observed in the fatigue performance of the epoxy-GNP nanocomposite polymers was found to be due to the additional toughening mechanisms resulting from the presence of the GNPs in the epoxy. As for the epoxy-CNF nanocomposite polymers, these were due to both ‘intrinsic’ and ‘extrinsic’ toughening mechanisms being induced by the presence of the GNPs. These included the ‘intrinsic’ mechanisms of (a) debonding of the GNPs and (b) microcracking leading to crack deflection and branching ahead of the main fatigue crack; and the ‘extrinsic’ mechanisms of (a) pull-out, crack-bridging and rupture of the GNPs, and (b) the formation of debris inside the advancing fatigue crack which promoted a crack tip shielding effect behind the crack front. These ‘extrinsic’ toughening mechanisms operated more effectively when the GNPs were aligned normal to the direction of the advancing crack and were hindered if the GNPs formed agglomerates, thereby explaining the above observations.

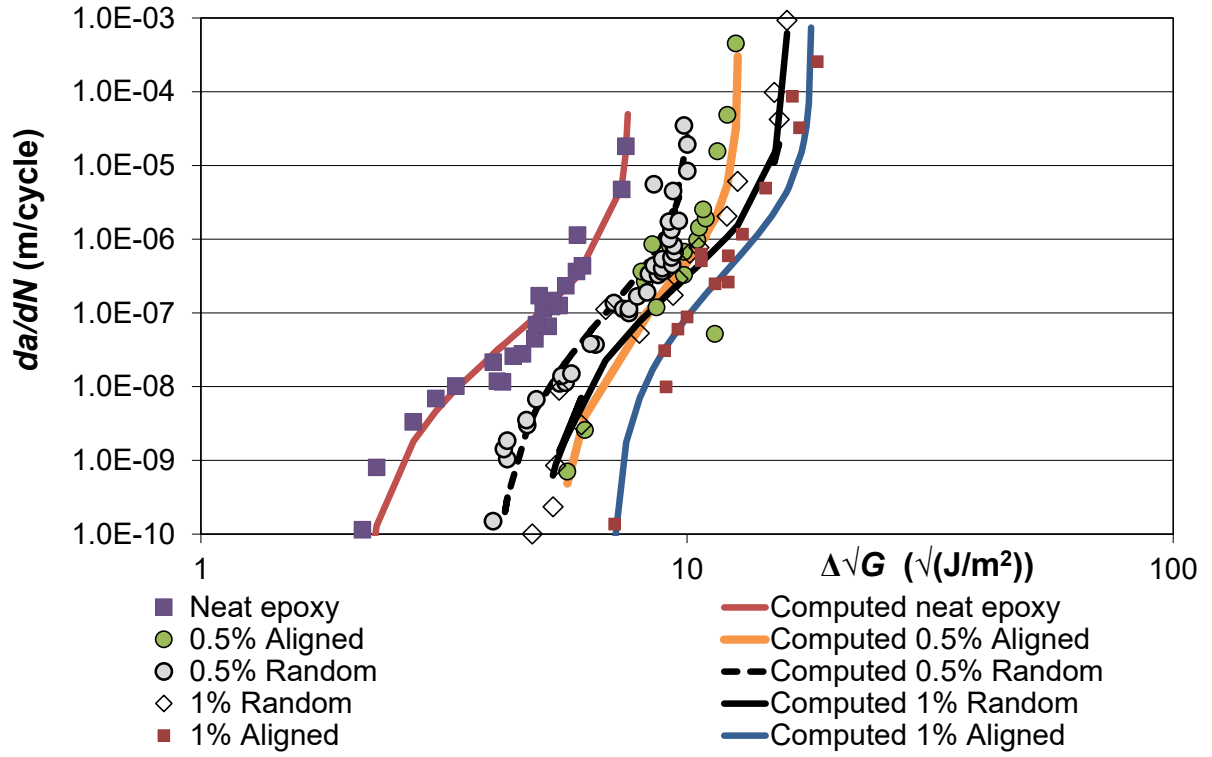


Figure 7. Logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$ showing the measured and computed FCG rate curves for the neat epoxy and epoxy nanocomposite polymers containing randomly-dispersed and aligned GNPs, replotted from [23]. The concentrations are given as the wt.% of GNPs and data for 0, 0.5 and 1.0 wt.% are shown. (The computed curves are from using Equation (5) and the values employed are given in Table 3.)

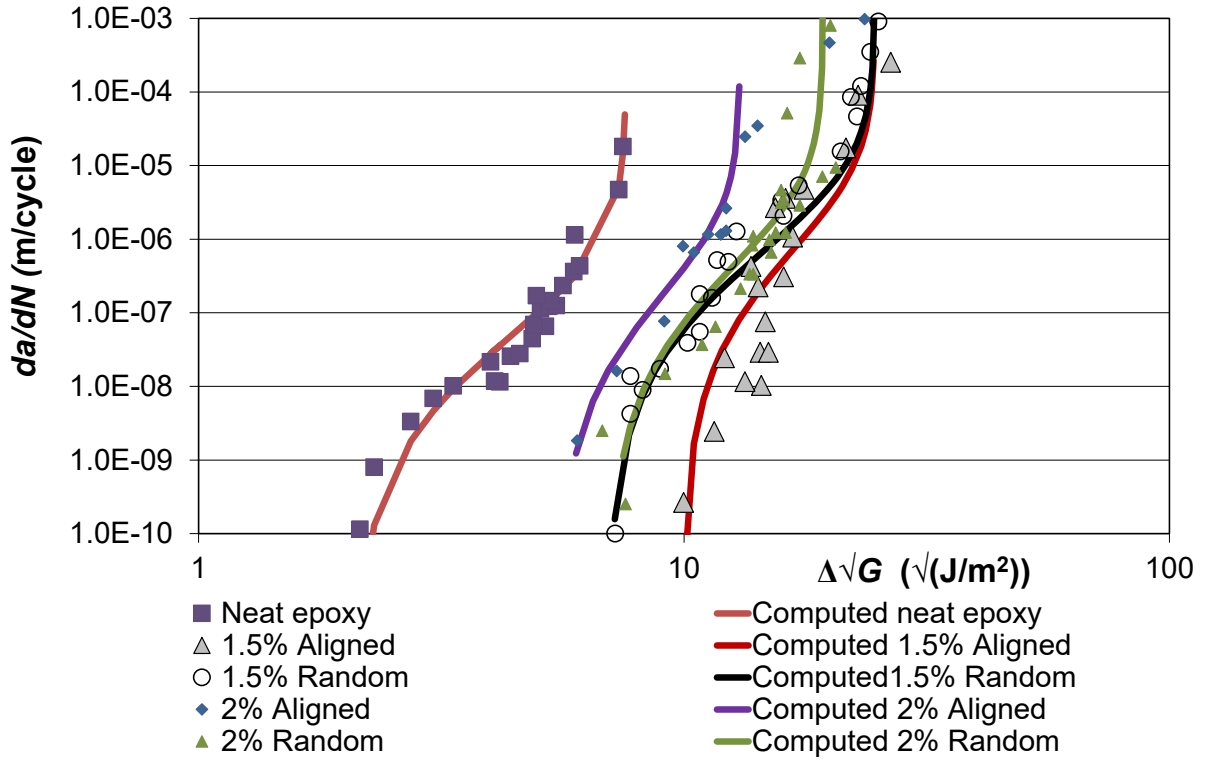


Figure 8. Logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$ showing the measured and computed FCG rate curves for the neat epoxy and epoxy nanocomposite polymers containing randomly-dispersed and aligned GNPs, replotted from [23]. The concentrations are given as the wt.% of GNPs and data for 0, 1.5 and 2.0 wt.% are shown. (The computed curves are from using Equation (5) and the values employed are given in Table 3.)

Again the results shown in Figure 7 and 8 for the epoxy and epoxy-GNP nanocomposite polymers may be plotted according to the the Hartman-Schijve representation, see Equation (5), where the results for the epoxy-CNF nanocomposites discussed above are also plotted. This is shown in Figure 5 where logarithmic da/dN is plotted against logarithmic $\left[\frac{\Delta\sqrt{G} - \Delta\sqrt{G_{thr}}}{\sqrt{1 - \sqrt{G_{max}/\sqrt{A}}}} \right]$ and the values of the various parameters employed are given in Table 3 for the epoxy-GNP nanocomposite polymers. As may be seen from Figure 5, the plot is indeed linear and gives a unique, ‘master’, linear relationship with the values of D and n independent of the type of material, with a relatively low degree of scatter, for the neat epoxy polymer and all the various types of epoxy-GNP nanocomposite polymers. Thus, the values of the coefficient of determination, R^2 , of 0.89 (see Figure 5) and 0.989 (see Figure 2) indicate that the respective experimental results for these various epoxy nanocomposites may both be fitted to linear relationships with a high degree of confidence. Interestingly, from Figure 5 and Tables 2 and 3, the values of the constants D and n are independent of the exact type and formulation for all these neat epoxy polymers and epoxy-CNF and -GNP nanocomposite polymers. This is

suggested to arise from the very similar nature of both types of the carbon-based nanofillers and of the epoxy polymeric matrices. Unfortunately, as may be seen by comparing the data shown in Table 1 to that in Tables 2 and 3, and as discussed in more detail below, the values of D and n have not been found, in general, to be constant material parameters for the many very different types of epoxy nanocomposite and microcomposite polymers reported in the literature.

The values of $\Delta\sqrt{G_{thr}}$ given in Table 3 are the threshold values and represent the values of $\Delta\sqrt{G}$ below which no significant FCG is observed. From the increases observed in these values with an increasing concentration of the GNP nanofiller, the very dramatic effect that adding the GNPs to the epoxy polymeric matrix has upon improving the cyclic-fatigue behaviour may be readily appreciated. However, it should be noted for a concentration of 2.0 wt.% of GNPs the values of A and $\Delta\sqrt{G_{thr}}$ do not increase compared to the values for 1.5 wt.% of GNPs. This is in qualitative agreement with the observations made from Figures 7 and 8. Further, using the values given in Table 3, together with Equation (5), the plots of logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$ given in Figure 7 and 8 may be computed and compared to the experimentally-measured values. As may be seen, the quantitative agreement between the computed and measured curves for the neat epoxy and the epoxy-GNP nanocomposites is excellent.

Table 3. Values of the parameters used in Figure 5 for the Hartman-Schijve representation, see Equation (5), for the neat epoxy and the epoxy nanocomposite polymers containing GNPs. (The R -ratio used was 0.5.)

Polymer	D	n	A (J/m ²)	$\Delta\sqrt{G_{thr}}$ ($\sqrt{\text{J/m}^2}$)
Neat epoxy	6.0×10^{-9}	2.20	260	2.10
+ 0.5 wt.% random	6.0×10^{-9}	2.20	500	4.00
+ 0.5 wt.% aligned	6.0×10^{-9}	2.20	650	5.35
+ 1.0 wt.% random	6.0×10^{-9}	2.20	1035	5.10
+ 1.0 wt.% aligned	6.0×10^{-9}	2.20	1300	6.90
+ 1.5 wt.% random	6.0×10^{-9}	2.20	2450	6.98
+ 1.5 wt.% aligned	6.0×10^{-9}	2.20	2304	10.90
+ 2.0% wt.% random	6.0×10^{-9}	2.20	1585	7.80
+ 2.0% wt.% aligned	6.0×10^{-9}	2.20	850	5.80

In Figure 9 the normalised values of the terms A and $\Delta\sqrt{G_{thr}}$ which were needed to obtain the Hartman-Schijve ‘master’ relationship, see Table 3, are plotted against the concentration of GNPs. (The normalised values represent values of A or $\Delta\sqrt{G_{thr}}$, as a function of the concentration of the GNPs, that have been normalised with respect to the values of A or

$\Delta\sqrt{G_{thr}}$ for the neat epoxy polymer, respectively, see Table 3.) From the results shown in Figure 9, firstly, as shown in Figure 6 for the addition of CNF nanofillers, it may be clearly seen that the effect of adding the GNPs is far more marked on the value of A compared to that of $\Delta\sqrt{G_{thr}}$. Secondly, unlike in Figure 6 for the epoxy-CNF nanocomposite polymers, the values of A or $\Delta\sqrt{G_{thr}}$ as a function of the concentration of GNPs in the epoxy-GNP nanocomposite polymers shown in Figure 9 either attain a plateau value or pass through a peak value. As discussed above, this is suggested to arise from the significant agglomeration of the GNPs in the epoxy polymer matrix that was observed at relatively high concentrations of GNPs. Thirdly, the effect of aligning the GNPs in the epoxy nanocomposites is relatively more marked for the GNPs than for the CNFs, see Figure 6. This is especially the case when considering the threshold fatigue value, $\Delta\sqrt{G_{thr}}$. Fourthly, it is of interest to compare the effect of the different nanofillers on the value of the threshold fatigue value, $\Delta\sqrt{G_{thr}}$. It is evident, from Tables 1 to 3 and Figures 3, 6 and 9, that the CNF and GNP fillers are significantly more effective in increasing the value of $\Delta\sqrt{G_{thr}}$ than the nanosilica. Whether this is because only the CNF and GNP nanofillers are able to induce ‘extrinsic’ toughening mechanisms that operate behind the tip of the advancing fatigue crack is an intriguing question that will need further work to resolve.

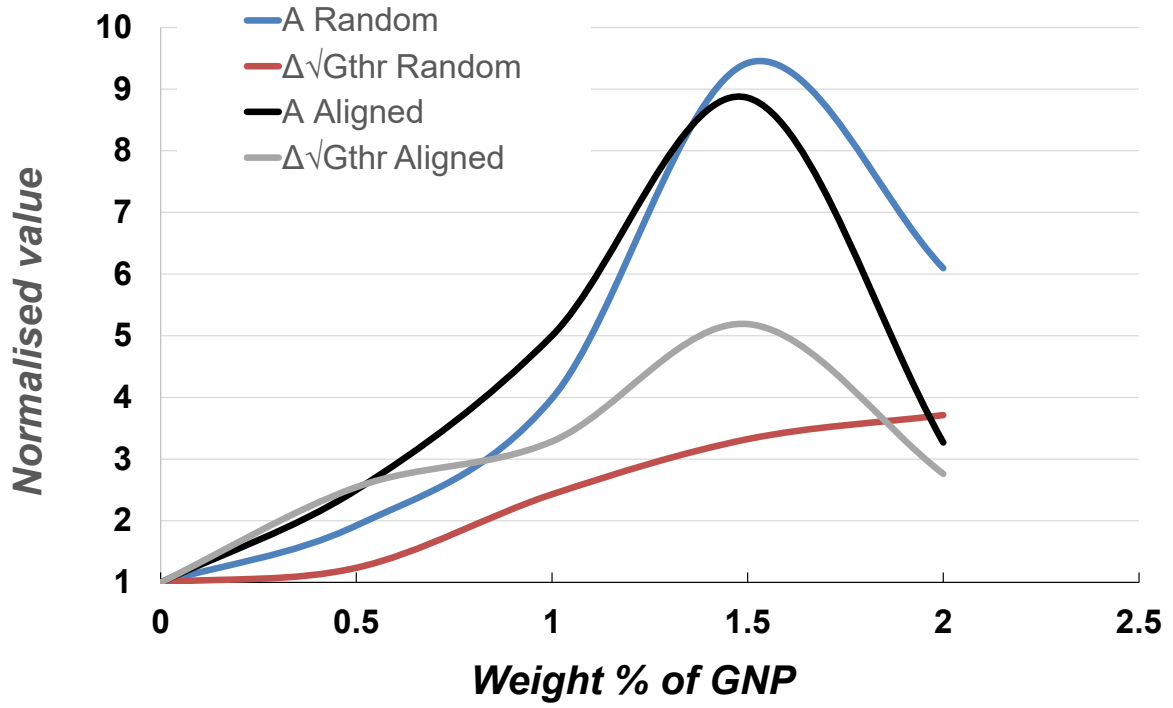


Figure 9. The effects of the concentration of GNPs in the epoxy nanocomposite polymers on the values of A and $\Delta\sqrt{G_{thr}}$ given in Table 3, from Figure 5. (The normalised values represent values of A or $\Delta\sqrt{G_{thr}}$, as a function of the concentration of the GNPs, which have been normalised with respect to the values of A or $\Delta\sqrt{G_{thr}}$ for the neat epoxy polymer, respectively, see Table 3.)

3.5 Comparison of the epoxy nanocomposite and other epoxy microcomposite polymers

From the ‘master’, linear Hartman-Schijve plots shown in Figures 2 and 5, and from the values given in Tables 1, 2 and 3, it is evident that the values of n are essentially independent of whether nanosilica particles, CNFs or GNPs are present in the epoxy nanocomposite polymer. However, for the epoxy nanosilica polymers, which possess both a very different type of nanofiller and epoxy polymeric matrix, whilst the value of the slope, n , has a very similar value to that of the epoxy-CNF and -GNP nanocomposite polymers, the value of D , i.e. the intercept, is significantly different. Further, the values of A and $\Delta\sqrt{G_{thr}}$ deduced from the Hartman-Schijve relationships reveal that the three different neat epoxy polymers employed for the three different types of epoxy nanocomposites possess very different values of these parameters. The values of A and $\Delta\sqrt{G_{thr}}$ are then subsequently dependent on the type, concentration and alignment of nanofiller used in a given nanocomposite.

It is therefore of interest to compare the different forms of the Hartman-Schijve representation for various types of epoxy nanocomposite and, also, for epoxy microcomposite polymers. This comparison is shown in Figure 10, where logarithmic da/dN is plotted against

logarithmic $\left[\frac{\Delta\sqrt{G} - \Delta\sqrt{G_{thr}}}{\sqrt{\{1 - \sqrt{G_{max}/\sqrt{A}}\}}} \right]$ for a range of epoxy nanocomposite polymers and for two epoxy microcomposite polymers. The microcomposite polymers are commercially-available structural adhesives, namely ‘FM73’ and ‘FM300’ which are both from Cytec, USA. Both of these epoxy microcomposite polymers are rubber-toughened structural adhesives containing a dispersed phase of spherical rubber particles of a few micrometres in diameter [26,27,47]. Furthermore, the epoxy polymeric matrices for these two structural adhesives have very different chemistries to each other, and also compared to the epoxy nanocomposite polymers studied in the present paper. The glass transition temperatures of the epoxy matrix phases for these two rubber-toughened microcomposite polymers are about 100°C and 175°C for ‘FM73’ and ‘FM300’, respectively [48,49].

From the results shown in Figure 10, it may be seen that the individual plots are all linear for the many different types of materials and, therefore, give a unique, ‘master’, linear relationship from which the values of D and n may be calculated. (Work in the present paper, and previously [24-27,44], has revealed that a relatively low degree of scatter is recorded for these linear plots, as indicated by the relatively high values of the coefficients of determination, R^2 , associated with them.) However, whilst the various linear relations from the Hartman-Schijve equation for the many different types of materials shown in Figure 8 do have somewhat similar values of slope, n , the values of the intercept, D , are significantly different.

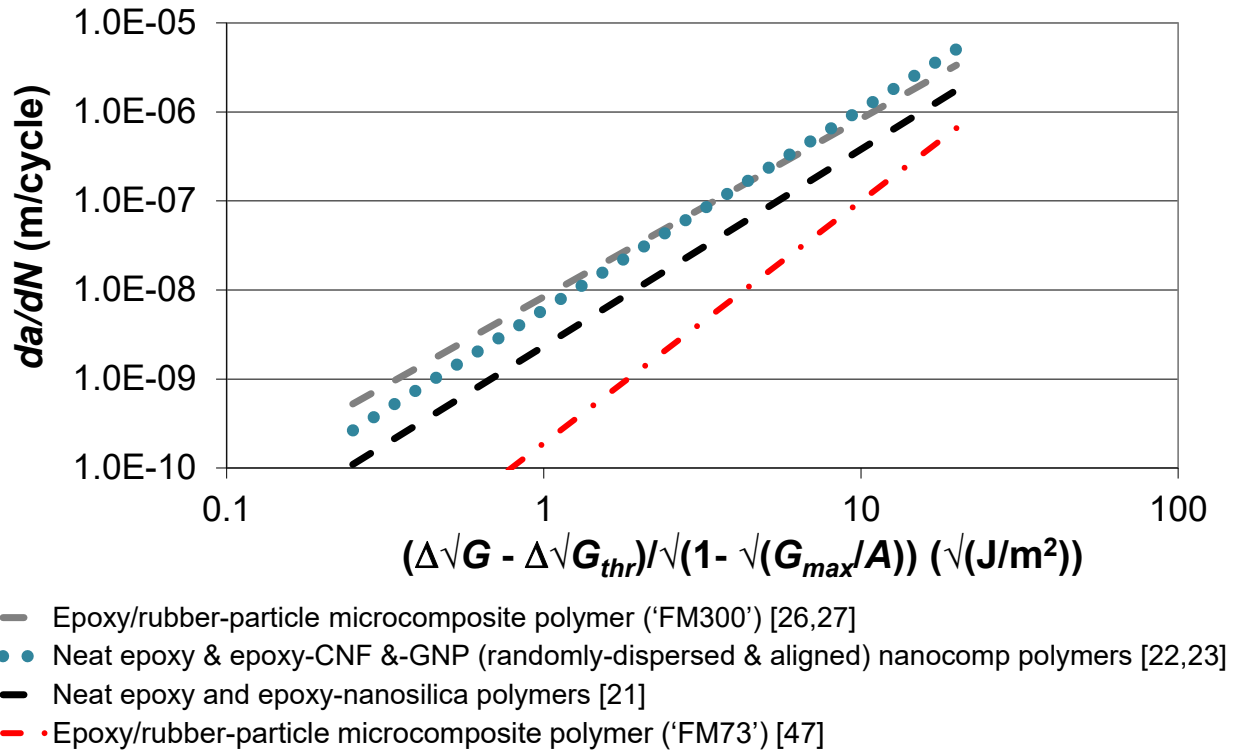


Figure 10. Comparison of the Hartman-Schijve representations, see Equation (5), for the various epoxy nanocomposites. Note that the linear relationship for [22,23] encompasses all the various types of CNF and GNP epoxy nanocomposite polymers which have identical values of slope, n , and intercept, D , see Tables 2 and 3. The Hartman-Schijve plots for the results [26,27,47] from two rubber-toughened epoxy microcomposites are also shown for comparative purposes. (The references are given for the sources of the original fatigue results.)

Notwithstanding, for each material, the values of A , which may be thought of as the fatigue equivalent to the quasi-static value of the fracture energy, G_c , and the fatigue threshold value, $\Delta\sqrt{G_{thr}}$, below which no significant fatigue crack growth occurs, may be deduced with a high degree of accuracy from calculating these unique, ‘master’, linear Hartman-Schijve relationships. Thereby, these parameters, i.e. D , n , A and $\Delta\sqrt{G_{thr}}$ deduced from the Hartman-Schijve relationship, may be used to compute the respective da/dN versus $\Delta\sqrt{G}$ curves. In the present study, as in previous work [26,27], there is invariably a good agreement between the computed and experimentally-measured FCG rate curves. These parameters have also been employed to further understand the form of such FCG relationships between da/dN versus $\Delta\sqrt{G}$, with respect to the structures of the epoxy nanocomposite polymers. Furthermore, in other work [24,25,44], it has been shown how these parameters may also be used to establish a methodology for estimating an ‘upper-bound’ FCG curve, which takes into account experimental scatter and allows for any retardation of the FCG rate due to such factors as extensive fibre-bridging that may occur in polymer-matrix fibre-composites. This ‘upper-bound’ FCG rate curve, which may be thought of as a material-allowable property, provides a

‘worst-case’ FCG rate curve for both (a) material development and comparative studies, and (b) design and sustainment studies in industries such as aerospace and wind-energy.

Finally, the types of epoxy nanocomposite polymers studied in the present paper would appear to offer the possibility of leading to improved formulations for both structural adhesives [e.g. 50] and for matrices for carbon-fibre and glass-fibre composites [e.g. 51]. Since they may increase both the toughness and the cyclic-fatigue threshold, and may offer other advantages such as increased electrical conductivity leading to improved lightning strike resistance, for example. In this context, a recent paper by Jones et al. [52] predicted the effect of relatively small changes in value of the fatigue threshold of an adhesive on the fatigue life of bonded joints used for repairing metallic aircraft fuselages and wings. This study revealed that going from a fatigue threshold, $\Delta\sqrt{G_{thr}}$, value of 5.6 to 7.1 $\sqrt{\text{J/m}^2}$ resulted in a significant increase in the fatigue life of the adhesively-bonded repair. Now, for the epoxy nanocomposite polymers listed in Table 3, the value of the fatigue threshold, $\Delta\sqrt{G_{thr}}$, is shown to increase from approximately 2 to 10 $\sqrt{\text{J/m}^2}$, depending on the concentration and alignment of the nanofiller employed. Thus, it would appear that, when taken together with the large increase in toughness that is frequently associated with presence of the nanofillers, an appropriate choice of epoxy polymer and nanofiller may indeed offer a major enhancement in the damage tolerance of adhesively-bonded repairs and polymeric-matrix fibre composites.

4. Conclusions

The present paper has undertaken detailed analyses of experimental data for the cyclic-fatigue behaviour of epoxy nanocomposite polymers. It has been shown that the data may be accurately interpreted using the Hartman-Schijve relationship to yield a unique, ‘master’, linear relationship from which the values of n , i.e. the slope, and D , i.e. the intercept, may be calculated. Further, a relatively low degree of scatter is recorded for these linear plots, as indicated by the relatively high values of the coefficients of determination, R^2 . Thus, for each material, the values of A , which may be thought of as the fatigue equivalent to the quasi-static value of the fracture energy, G_c , and the fatigue threshold value, $\Delta\sqrt{G_{thr}}$, below which no significant fatigue crack growth occurs, may be deduced with a high degree of accuracy from obtaining these unique, ‘master’, linear Hartman-Schijve relationships. It is evident that the values of n are essentially independent of whether nanosilica particles, CNFs or GNPs are present in the epoxy nanocomposite polymer. However, for the epoxy nanosilica polymers, which possess both a very different type of nanofiller and epoxy polymeric matrix, whilst the

value of the slope, n , has a very similar value to that of the epoxy-CNF and -GNP nanocomposite polymers, the value of D , i.e. the intercept, is significantly different. Further, the values of A and $\Delta\sqrt{G_{thr}}$ deduced from the Hartman-Schijve relationships reveal that the three different neat epoxy polymers employed for the three different types of epoxy nanocomposites possess very different values of A and $\Delta\sqrt{G_{thr}}$, which are then subsequently dependent on the type, concentration and alignment of nanofiller used in a given nanocomposite.

It has then been shown how the values of these parameters obtained from these ‘master’, Hartman-Schijve plots may be used (a) to compute the logarithmic da/dN versus logarithmic $\Delta\sqrt{G}$ curves, which are found to be in very good agreement with the experimentally-measured values, and (b) to understand the observed cyclic-fatigue behaviour with respect to the structure of the epoxy nanocomposite polymers. Finally, the Hartman-Schijve methodology has been shown to be a valid approach in analysing the cyclic-fatigue behaviour of both structural adhesives [26,27,47] and polymer-matrix fibre composites [24,25,44,52]. Therefore, it will most likely be readily applicable to these classes of materials which employ relatively small concentrations of nanofillers. This will enable an ‘upper-bound’, i.e. ‘worst-case’, fatigue crack growth (FCG) rate curve to be deduced that can be used by industry to aid material development and selection, and as a design and service-life prediction tool, for such advanced nanomaterials. This is the subject of current work.

Competing Interests

The authors state that they have no competing interests.

Authors’ Contributions

All the authors contributed to the conception and planning of the project, and to the analysis and interpretation of the data. All the authors gave their final approval for the published version of the paper.

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