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Role of TiO₂ nanoparticles as particulate fillers in epoxy adhesives: Toughening mechanisms vs. agglomeration effects under fatigue loading

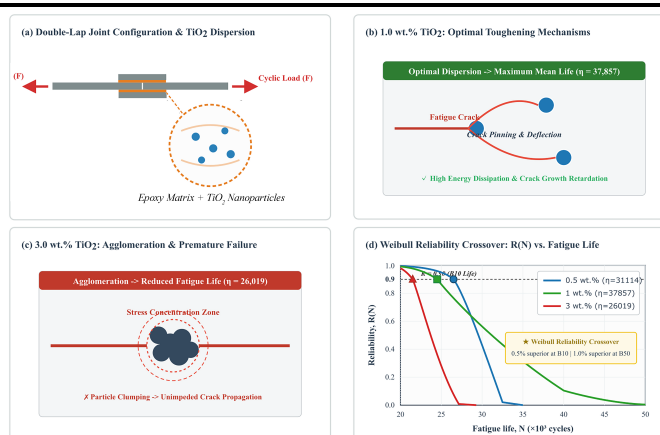
Pooria Akbarzadeh

Department of Mechanical Engineering, University of Sistan and Baluchestan, Zahedan, Iran

HIGHLIGHTS

- TiO₂ nanoparticles improved the static and fatigue performance of epoxy adhesives.
- Weibull analysis reveals a reliability crossover of 0.5 to 1.0 wt% TiO₂.
- While 1.0 wt% gave the highest mean life, 0.5 wt% showed the best B_{10} reliability.
- 3.0 wt% TiO₂ reduced life, likely due to agglomeration and stress concentration.
- Crack pinning and deflection are the main toughening mechanisms at 1.0 wt% TiO₂.

GRAPHICAL ABSTRACT



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ABSTRACT

Incorporating particulate metal-oxide nano-fillers into brittle epoxy matrices effectively modifies fracture toughness; however, structural endurance is fundamentally governed by the competition between effective nanoparticle dispersion and localized agglomeration. This study investigates the micro-mechanical behavior, toughening mechanisms, and agglomeration effects of TiO₂ nanoparticles incorporated into a structural epoxy adhesive at 0.50, 1.0, and 3.0 wt% loading fractions. Glass/epoxy double-lap joints were fabricated and subjected to quasi-static tensile and tension-tension cyclic fatigue testing ($R = 0.1$, 4 Hz) to evaluate these particulate systems. The results indicate that optimal dispersion at 1.0 wt% yields the best average performance, achieving the highest mean static failure load (8.44 kN) and maximum characteristic fatigue life ($\eta = 37,857$ cycles). Micro-mechanical analysis suggests this optimal fraction enhances fatigue resistance through energy-dissipating mechanisms, predominantly crack pinning and deflection. Conversely, 3.0 wt% loading severely degrades static and fatigue behavior, which is attributed to significant nanoparticle agglomeration, forming rigid clusters that act as localized stress concentrators and promote premature microcrack coalescence. Since direct microscopic characterization of the filler dispersion was not performed, these toughening and agglomeration mechanisms are inferred from the mechanical responses and fracture behavior. Furthermore, Weibull analysis exposed a crucial reliability crossover linked to filler distribution: while 1.0 wt% exhibited the highest average fatigue life, the more uniform distribution at 0.5 wt% minimized statistical scatter. This rendered it the safest conservative formulation at a 90 % reliability level (B_{10} life). These findings underscore that harnessing the full potential of particulate fillers requires balancing active micro-mechanical toughening with conservative statistical reliability.

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✉ Corresponding author: E-mail address: p.akbarzadeh@eng.usb.ac.ir ; Tel: +98-5431136465

1. Introduction

Adhesively bonded joints are increasingly used in lightweight engineering structures because they provide uniform stress transfer, reduce structural weight, avoid drilling-induced damage, and enable the joining of dissimilar materials [1–3]. These advantages are especially important in fibre-reinforced polymer composites, where mechanical fastening can cause fibre breakage, delamination, and severe stress concentrations around fastener holes [4,5]. Consequently, bonded composite joints are widely used in aerospace, automotive, marine, wind-energy, and other weight-sensitive applications requiring high structural efficiency and durability [6,7].

Reliable design of bonded composite joints remains challenging because their response depends on adhesive properties, adherend characteristics, interface quality, joint geometry, surface preparation, curing conditions, and loading mode [8,9]. This complexity is greater for composite adherends because their anisotropic and damage-sensitive nature can lead to competing failure mechanisms, including matrix cracking, delamination, fibre fracture, interfacial debonding, and cohesive or mixed-mode adhesive failure [10,11]. Therefore, joint-level testing under representative loading conditions is essential, since bonded-joint performance cannot be inferred solely from bulk adhesive properties.

Epoxy adhesives are widely used for structural bonding because of their high strength, chemical resistance, dimensional stability, and compatibility with composite adherends [12,13]. However, cured epoxies are generally brittle and have limited energy-dissipation capacity, which can facilitate crack initiation and unstable propagation under monotonic and cyclic loading [14–16]. Improving the fracture resistance and damage tolerance of the adhesive layer is therefore important for enhancing both static strength and fatigue durability.

The incorporation of micro- and nanoscale fillers is an established method for improving the mechanical and fracture properties of epoxy systems [17,18]. Well-dispersed nanoparticles can interact with advancing cracks through mechanisms such as crack deflection, pinning, particle debonding, plastic void growth, microcracking, and increased fracture-surface roughness [19,20]. However, the effectiveness of this modification depends strongly on particle type, size, surface characteristics, dispersion quality, and concentration [21].

Titanium dioxide TiO_2 nanoparticles are promising epoxy modifiers because of their stiffness, chemical and thermal stability, availability, and potential to improve mechanical

and fracture-related properties [22,23]. Previous studies have reported improvements in tensile response, fracture toughness, impact resistance, and fatigue behaviour of TiO_2 -modified epoxies when the particles are well dispersed and added at suitable concentrations [24–26]. In bonded joints, these improvements may delay crack initiation, restrict crack propagation, and increase cyclic-load resistance, although the benefits do not necessarily increase monotonically with nanoparticle content.

At low concentrations, nanoparticles can remain sufficiently dispersed to reinforce the polymer matrix and interact with the crack front. Excessive concentrations, however, may increase adhesive viscosity, impair processing and wetting, and promote agglomeration [27,28]. Agglomerates and related voids can act as stress concentrators and crack-initiation sites, particularly within thin adhesive layers. Thus, an optimum concentration is expected: too little filler may provide limited reinforcement, while too much may introduce defects that offset the intended improvement.

Fatigue performance is critical because bonded structures often operate under repeated loads below their quasi-static capacity. Under these conditions, fatigue life is governed by the maximum load, load ratio, joint stress distribution, defects, and resistance of the adhesive and interfaces to progressive crack growth [11,16,29]. As demonstrated in recent probabilistic frameworks, the evolution of fatigue damage in composite lap joints — often manifested through progressive cyclic ratcheting strain — is inherently stochastic [30,31]. Consequently, conventional deterministic force–life (F – N) curves often fail to capture the true safe-life limits. Since improved static strength does not necessarily imply longer fatigue life, different nanoparticle concentrations must be compared under identical cyclic loading. Because fatigue results in adhesive joints are inherently scattered, reliability-based statistical measures are essential to support the interpretation of formulation-dependent differences at a common load level.

Although many studies have examined the bulk properties of nanoparticle-modified epoxies, fewer have addressed the joint-level fatigue behaviour and reliability of bonded composite joints with different TiO_2 contents. Bulk adhesive results cannot be directly transferred to bonded joints because the latter involve complex stress states, geometric constraints, interfaces, and possible composite-adherend damage [4,8,32]. A systematic approach is therefore needed, combining quasi-static screening, fatigue comparison at a common load level, reliability-based scatter analysis, additional load-level testing of the selected formulation, and fracture-surface evaluation.

Accordingly, this study experimentally investigates the effect of TiO₂ content on the quasi-static strength and fatigue performance of double-strap adhesively bonded composite joints. The epoxy adhesive was modified with 0.5, 1, and 3 wt% TiO₂, and all formulations were first assessed by quasi-static tensile tests. The 1 wt% joints showed the highest static load-carrying capacity, consistent with previous evidence that moderate nanoparticle concentrations can provide a favourable balance between reinforcement and dispersion [24,27,28]. Therefore, a larger number of specimens was assigned to this formulation for fatigue testing.

To directly compare fatigue performance, all three groups were tested at $F_{max} = 4800$ N and $R = 0.1$, corresponding to a cyclic load range of 480–4800 N. Fatigue-life scatter at this common load was further interpreted using Weibull-based reliability parameters. The 1 wt% joints showed the highest mean and characteristic fatigue lives, while the reliability analysis clarified scatter and safe-life implications. Based on the overall static and fatigue results, additional fatigue tests were conducted only on the selected 1 wt% formulation at $F_{max} = 4400$ and 5400 N, with $R = 0.1$. The results are evaluated in terms of quasi-static strength, load–displacement response, fatigue-life statistics and Weibull-based reliability at the common load level, force–life (F – N) behaviour of the selected formulation, and macroscopic and microscopic failure characteristics. The main objective is to determine how TiO₂ concentration affects joint performance, identify the most effective concentration, and characterize the fatigue response of the selected formulation at different load levels.

2. Materials and methods

2.1. Materials

The adherends used in this study were fabricated from glass/epoxy composite laminates consisting of 16 layers of bidirectional woven E-glass fabric. An epoxy-based adhesive system was used to bond the composite adherends, composed of a bisphenol epoxy resin cured with an HA-11 hardener and modified with titanium dioxide TiO₂ nanoparticles.

Commercial AEROXIDE® TiO₂ P25 nanoparticles, supplied from Evonik Corporation, were used as the

particulate modifier. According to the supplier's technical data, the material is characterized by an average primary particle size of approximately 21 nm and a high specific surface area. The key physico-chemical properties of the nanoparticles are summarized in Table 1. Because TiO₂ P25 possesses a high specific surface area and an inherent aggregate/agglomerate morphology, applying a robust dispersion procedure within the epoxy resin was considered essential to prevent defect formation.

Three nanoparticle contents — 0.5, 1, and 3 wt% — were selected to systematically investigate the concentration-dependent effects of TiO₂ nanoparticles on the static strength, fatigue life, and failure mechanisms of the bonded composite joints. For each formulation, the required TiO₂ mass was calculated relative to the total mass of the neat adhesive system (*i.e.*, the combined mass of the epoxy resin and HA-11 hardener prior to nanoparticle addition).

2.2. Preparation of TiO₂-modified adhesive

The required amount of TiO₂ nanoparticles, corresponding to 0.5, 1, and 3 wt% of the total adhesive mass, was accurately weighed using a precision balance. Although the nanoparticle weight fraction was calculated based on the final resin–hardener mass, the particles were initially introduced solely into the epoxy resin prior to the hardener addition (See Fig. 1). This sequential procedure was adopted to facilitate optimal nanoparticle dispersion and prevent premature curing (exothermic cross-linking) during the high-speed mixing stage.

The TiO₂ nanoparticles were dispersed within the epoxy resin via mechanical stirring at 2000 rpm for 1 h. Following this primary dispersion phase, the HA-11 hardener was added to the modified resin, and the blend was gently stirred at a lower speed of 400 rpm for 15 min. This reduced mixing speed was intentionally selected to ensure homogeneity while simultaneously minimizing air entrapment and preventing excessive heat generation. This identical preparation protocol was strictly followed for all adhesive formulations to isolate the effect of nanoparticle concentration and minimize the influence of processing variables on the mechanical response of the joints.

Table 1. Key physico-chemical properties of AEROXIDE® TiO₂ P25 nanoparticles.

Property	Value
Average primary particle size	~ 21 nm
Specific surface area (BET)	50 ± 15 m ² .g ⁻¹
Relative density	3.8 – 4.2 g.cm ⁻³
Crystal structure	Predominantly anatase with rutile fraction
Morphology	Aggregate/agglomerate structure

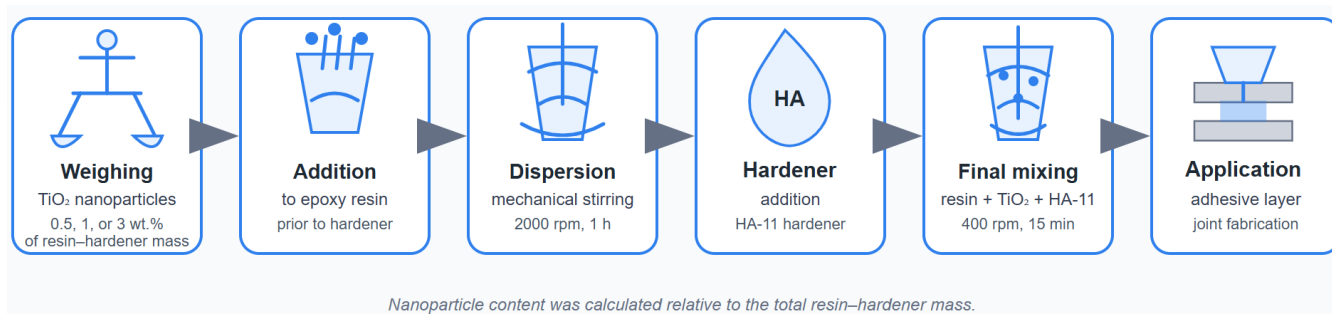


Fig. 1. Schematic illustration of the preparation procedure for the TiO₂-modified epoxy adhesive.

2.3. Specimen geometry and fabrication of double-lap joints

The mechanical performance of the TiO₂-modified adhesive systems was evaluated using adhesively bonded double-lap joints (DLJs) prepared according to the ASTM D3528 Type B configuration. This joint geometry was selected for both quasi-static tensile and tension-tension fatigue tests because it provides a symmetric load-transfer path and reduces bending effects compared with single-lap joints. The specimen geometry and main dimensions are shown in Fig. 2.

Before bonding, the adherend surfaces in the overlap region were prepared using the same surface-treatment procedure for all specimens to minimize fabrication-related variability. The prepared TiO₂/epoxy adhesive was then applied uniformly to the overlap region, and the joint components were carefully aligned to obtain a symmetric assembly and consistent bondline thickness.

All specimens were fabricated and cured under identical conditions for the different TiO₂ concentrations. Therefore, the observed differences in static strength and fatigue performance could be mainly attributed to the nanoparticle content rather than to variations in specimen geometry or fabrication procedure.

2.4. Mechanical testing

The mechanical performance of the double-lap joint

specimens was evaluated under quasi-static tensile and tension-tension fatigue loading conditions at room temperature using a universal testing machine (e.g., Zwick/Roell 100 kN). Quasi-static tests were conducted in displacement-controlled mode until complete failure, while the applied load and crosshead displacement were continuously recorded. The resulting load-displacement curves were used to characterize the static response and determine the ultimate load-bearing capacity of the 0.5, 1, and 3 wt% TiO₂-modified adhesive joints. A total of three, eight, and three specimens were tested for the 0.5, 1, and 3 wt% formulations, respectively.

Fatigue tests were performed in load-controlled mode using a sinusoidal waveform at a load ratio of $R = 0.1$ and a frequency of 4 Hz. A 4 Hz frequency was selected to minimize hysteretic heating. While periodic manual checks showed no noticeable temperature rise, the lack of continuous thermal recording remains an experimental limitation. The fatigue program was conducted in two stages. First, the influence of TiO₂ content was examined at a constant maximum load of $F_{max} = 4800$ N for all three modified formulations. This specific load level was selected as a common reference baseline to compare the cyclic behavior of the three nanoparticle concentrations under identical loading conditions. For this comparative analysis, five specimens were tested for the 0.5 and 3.0 wt% formulations, while seven specimens were tested for the 1.0 wt% group.

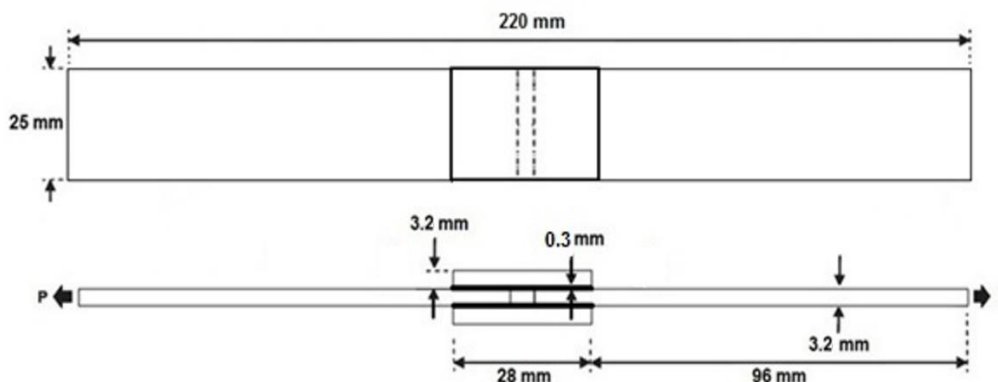


Fig. 2. Geometry and principal dimensions of the adhesively bonded double-lap joint specimen used for quasi-static tensile and fatigue tests.

In the second stage, the 1 wt% TiO₂-modified joints were tested at two other maximum load levels of $F_{max} = 4400$ and 5400 N to establish the load–life (F – N) relationship and provide the dataset required for subsequent Weibull-based probabilistic analysis.

After testing, the failed specimens were visually examined to identify the dominant failure modes, including adhesive failure, cohesive failure within the adhesive layer, and damage or delamination in the composite adherends. Representative fracture surfaces were further analyzed to correlate the observed failure mechanisms with the mechanical response under quasi-static and fatigue loading.

2.5. Statistical and reliability analysis

Fatigue life data of adhesively bonded composite joints inherently exhibit substantial statistical scatter. This dispersion is attributed to microstructural heterogeneities, fabrication-induced anomalies, and the complex nature of damage accumulation mechanisms under cyclic loading. To quantitatively evaluate this scatter, the experimental results were statistically analyzed. For each TiO₂ concentration, the quasi-static ultimate loads were summarized using the mean and standard deviation. The mean, standard deviation, and coefficient of variation (CV) were also calculated for the fatigue-life data. Because of the inherent scatter in fatigue life, a two-parameter Weibull distribution was used to characterize the fatigue-life datasets obtained at $F_{max} = 4800$ N and a load ratio of $R = 0.1$. The cumulative probability of failure was expressed as Eq. (1).

$$P_f(N) = 1 - \exp\left[-\left(\frac{N}{\eta}\right)^\beta\right] \quad (1)$$

where N is the number of cycles to failure, η is the characteristic life corresponding to a failure probability of 63.2 %, and β is the Weibull shape parameter. Within the Weibull model, a higher value of β indicates lower relative scatter and greater predictability of fatigue life.

For each experimental group, the fatigue lives were arranged in ascending order, and the probability of failure associated with the i^{th} observation was estimated using

Bernard's median-rank approximation as in Eq. (2).

$$P_{(f,i)} = (i - 0.3)/(n + 0.4) \quad (2)$$

where i is the failure rank and n is the number of tested specimens in the corresponding group. The Weibull parameters were estimated by linearizing the cumulative distribution function (Eq. (3)).

$$\ln[-\ln(1 - P_f)] = \beta \ln(N) - \beta \ln(\eta) \quad (3)$$

Linear regression of $\ln[-\ln(1 - P_f)]$ against $\ln(N)$ was then used to determine β from the slope and η from the intercept.

The corresponding reliability function was defined as Eq. (4).

$$R_s(N) = 1 - P_f(N) = \exp[-(N/\eta)^\beta] \quad (4)$$

The B_{10} life, representing the estimated fatigue life associated with 90 % reliability, was calculated as in Eq. (5).

$$B_{10} = \eta[-\ln(0.90)]^{1/\beta} \quad (5)$$

The resulting statistical and reliability indices were used to compare the fatigue-life performance and failure predictability of the different TiO₂-modified DLJ configurations.

3. Results and discussion

3.1. Quasi-static behavior

The quasi-static tensile response of the TiO₂-modified double-lap joints was evaluated to establish the baseline load-bearing capacity of the joints and to identify the most effective nanoparticle concentration for the subsequent fatigue study. Three TiO₂ contents, namely 0.5, 1.0, and 3.0 wt%, were examined under monotonic tensile loading. The statistical summary of the ultimate failure load and elongation at failure is presented in Table 2, while the corresponding mean load-displacement curves are shown in Fig. 3.

Table 2. Statistical summary of quasi-static tensile results for TiO₂-modified DLJs.

TiO ₂ Content (wt%)	Mean ultimate load (kN)	SD of Load (kN)	Mean elongation (mm)	SD of Elongation (mm)
0.5	7.75	0.17	1.31	0.04
1.0	8.44	0.61	1.35	0.09
3.0	6.85	0.13	1.17	0.03

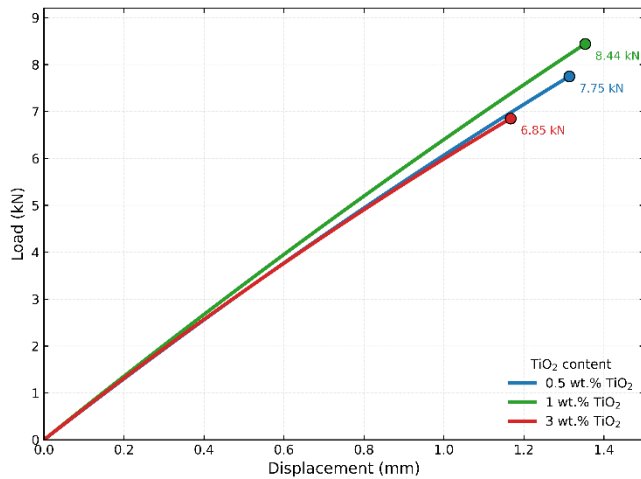


Fig. 3. Mean load-displacement curves for DLJ specimens modified with TiO₂ contents (0.5, 1.0, and 3.0 wt%).

As shown in Table 2 and Fig. 3, the 1.0 wt% TiO₂ formulation exhibited the highest quasi-static load-bearing capacity, with a mean ultimate load of 8.44 kN. Compared with the 0.5 wt% formulation, which reached 7.75 kN, this corresponds to an improvement of approximately 8.9 %. The same formulation also showed the highest mean elongation at failure, 1.35 mm, indicating that the improvement was not limited to strength but was also accompanied by a slight enhancement in deformation capacity before failure. The improved performance at 1.0 wt% can be attributed to a more effective reinforcing contribution of the TiO₂ nanoparticles within the adhesive matrix. At this concentration, the nanoparticles may promote better stress transfer and contribute to energy-dissipating mechanisms such as crack deflection, localized plastic deformation, and delayed damage propagation within the adhesive layer. In contrast, increasing the TiO₂ content to 3.0 wt% resulted in a clear reduction in mechanical performance. The mean ultimate load decreased to 6.85 kN, while the mean elongation at failure dropped to 1.17 mm. This reduction suggests that excessive nanoparticle loading may reduce the homogeneity of the adhesive matrix. At higher filler contents, particle agglomeration becomes more likely, and these agglomerates can act as local stress concentration sites, promoting premature damage initiation and limiting the load-bearing capacity of the joint. Overall, the quasi-static screening

results identify the 1.0 wt% formulation as the most effective configuration among the tested concentrations. Therefore, this formulation was selected for the extended fatigue testing program at different maximum force levels to further evaluate the durability and reliability of the DLJs under cyclic loading.

3.2. Fatigue performance

The fatigue performance of the TiO₂-modified double-lap joints was first evaluated under a constant-amplitude tension–tension loading condition with a maximum force of 4800 N and a minimum force of 480 N, corresponding to a load ratio of $R = 0.1$. This loading level was selected to compare the fatigue response of the three TiO₂ concentrations under identical cyclic loading conditions. The cycles to failure obtained for the 0.5, 1.0, and 3.0 wt% TiO₂-modified DLJs are summarized in Table 3.

As shown in Table 3 and Fig. 4, the 1.0 wt% TiO₂ formulation exhibited the longest fatigue life among the tested configurations, with a mean life of 34,860 cycles. In comparison, the 0.5 wt% formulation reached an average fatigue life of 29,955 cycles, corresponding to a reduction of approximately 14 % relative to the 1.0 wt% specimens. The 3.0 wt% formulation showed the lowest fatigue resistance, with a mean life of 24,966 cycles, representing a decrease of approximately 28 % compared with the 1.0 wt% configuration. The scatter plot in Fig. 4 provides a direct visual comparison of the individual fatigue lives, along with the mean and standard deviation for each formulation under the same loading condition, highlighting the scatter in the experimental data.

The superior fatigue response of the 1.0 wt% TiO₂-modified DLJs is consistent with the quasi-static results presented in Section 3.1, where the same formulation exhibited the highest ultimate load and elongation at failure. This agreement suggests that the 1.0 wt% nanoparticle content provides a favorable balance between reinforcement and matrix continuity. Under cyclic loading, such a balance can improve fatigue resistance by promoting more effective stress transfer, delaying crack initiation, and increasing the energy required for crack propagation within the adhesive layer.

Table 3. Fatigue life of TiO₂-modified DLJs tested at $F_{max} = 4800$ N and $R = 0.1$.

TiO ₂ Content (wt%)	Number of specimens	$F_{max} - F_{min}$ (N)	Mean cycles to failure	Fatigue life change relative to 1 wt% (%)
0.5	5	4800 – 480	29,955	–14
1.0	7	4800 – 480	34,860	Reference
3.0	5	4800 – 480	24,966	–28

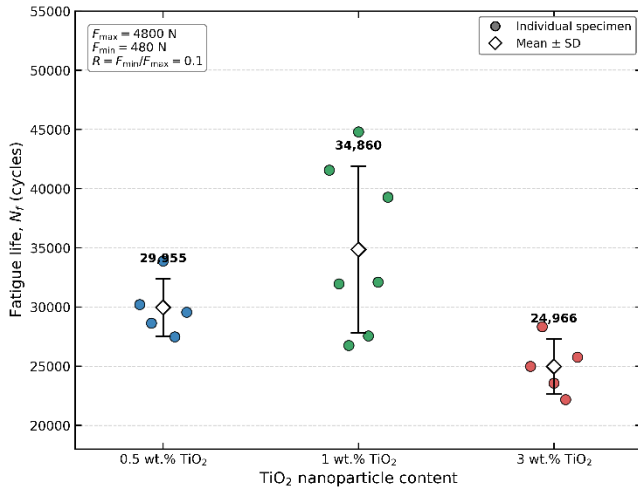


Fig. 4. Individual fatigue lives and mean $\pm$ standard deviation for TiO₂-modified DLJs with different nanoparticle contents tested at $F_{max} = 4800$ N and $R = 0.1$.

In contrast, the lower fatigue life observed for the 0.5 wt% formulation indicates that this nanoparticle content may be insufficient to provide the maximum reinforcing effect under cyclic loading. Although the 0.5 wt% joints showed acceptable quasi-static performance, their lower fatigue life suggests that the extent of crack-arresting and energy-dissipating mechanisms was less effective than that of the 1.0 wt% formulation. The reduction in fatigue life at 3.0 wt% is more pronounced and may be associated with a higher tendency for nanoparticle agglomeration at elevated filler contents. Such agglomerates can act as local stress concentration sites within the adhesive layer, thereby accelerating damage initiation and promoting premature crack growth under repeated loading. Therefore, excessive

TiO₂ loading may reduce the fatigue durability of the joint despite the presence of a larger amount of reinforcing particles.

Overall, the fatigue screening results identify the 1.0 wt% TiO₂ formulation as providing the most effective fatigue performance among the tested nanoparticle concentrations. Based on this result, the 1.0 wt% formulation was selected for an extended fatigue testing program. Additional specimens were tested at $F_{max} = 4400$ and 5400 N, and the resulting data were combined with those obtained at the initial screening level of $F_{max} = 4800$ N. All tests were conducted at $R = 0.1$ and a frequency of 4 Hz. The resulting load-life response for the selected formulation is presented in Fig. 5.

As shown in Fig. 5, the fatigue life of the 1.0 wt% TiO₂-modified DLJs decreased markedly with increasing maximum cyclic force. A linear relationship was obtained between F_{max} and the logarithm of fatigue life, expressed as $\log_{10}(N_f) = 10.139 - 0.001157F_{max}$, where N_f is the number of cycles to failure and F_{max} is expressed in newtons. The regression model exhibited a coefficient of determination of $R^2 = 0.949$, indicating that the maximum cyclic force accounted for a substantial proportion of the observed variation in logarithmic fatigue life. The 95 % confidence interval represents the uncertainty associated with the estimated mean load-life response, whereas the wider 95 % prediction interval reflects the expected variability of individual fatigue-life observations. These results establish the F – N relationship for the selected 1.0 wt% formulation and provide the experimental basis for the probabilistic analysis presented in the following section.

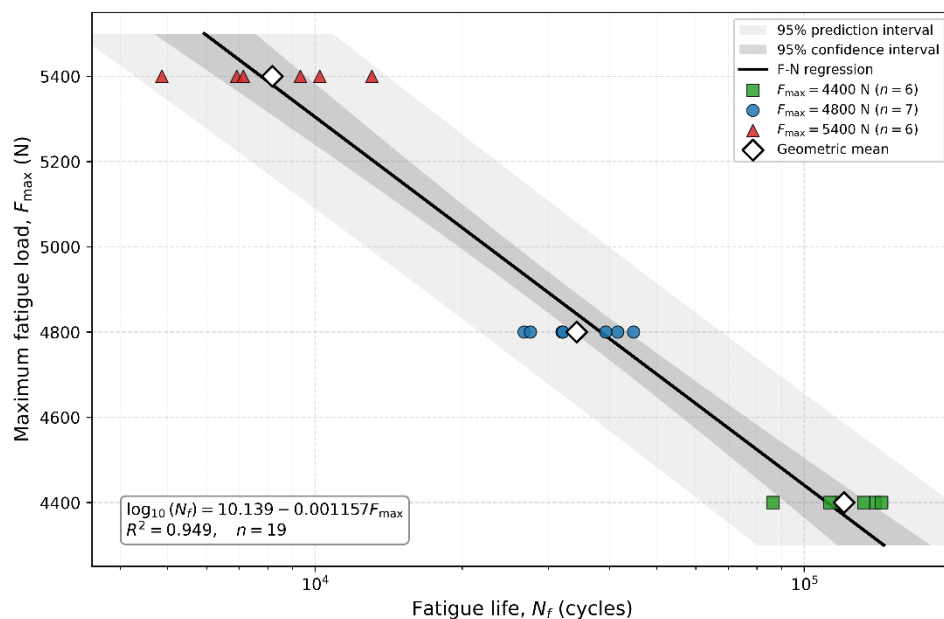


Fig. 5. Load-life (F – N) relationship for 1.0 wt% TiO₂-modified DLJs tested under tension-tension fatigue loading at $R = 0.1$ and $f = 4$ Hz.

3.3. Statistical reliability and Weibull analysis of fatigue life

Given the intrinsic macroscopic scatter in the fatigue behavior of adhesive joints, relying solely on average fatigue life is insufficient for engineering design, particularly in critical applications such as aerospace structures. To establish a robust design envelope, a two-parameter Weibull statistical model was applied to evaluate the reliability of the -modified double-lap joints. The fatigue life distribution was analyzed at a constant maximum cyclic load of 4800 N ($R = 0.1$) across three different nanoparticle concentrations (0.5, 1.0, and 3.0 wt%). Due to the limited sample sizes, the mechanical and fatigue comparisons are

evaluated based on descriptive statistical trends (mean, standard deviation, and Weibull parameters) rather than formal inferential significance tests (e.g., ANOVA).

The extracted Weibull parameters directly from the probability plots, including the shape parameter (β) and characteristic life (η), along with the calculated median life (B_{50}) and safe life (B_{10} for 90 % reliability), are summarized in Table 4. It must be acknowledged that estimating 90 % reliability (B_{10} life) from small sample sizes ($n = 5$ to 7) inherently carries statistical uncertainty. Therefore, these values are presented as conservative engineering estimates rather than absolute statistical boundaries.

Table 4. Statistical fatigue data and Weibull parameters for double-lap joints with various TiO₂ weight percentages at a maximum load of 4800 N.

Nanoparticle concentration (wt%)	Shape parameter (β)	Coefficient of determination (R^2)	Scale parameter (η)	Median life (B_{50})	Safe life (B_{10})
0.5	12.13	0.851	31,114	30,187	25,792
1.0	5.08	0.909	37,857	35,222	24,179
3.0	10.96	0.957	26,019	25,163	21,142

According to Table 4, the 1.0 wt% joints exhibit the highest characteristic life ($\eta = 37,857$ cycles) and median life ($B_{50} = 35,222$ cycles), confirming that this specific concentration provides the optimal toughening mechanism on average. Conversely, increasing the nanoparticle content to 3.0 wt% results in a significant degradation of fatigue performance (η drops to 26,019 cycles). This premature failure is primarily attributed to nanoparticle agglomeration at higher concentrations, which acts as internal stress concentrators and initiates early fatigue

crack growth in the adhesive layer.

However, an in-depth reliability analysis reveals a more complex scenario when considering the data scatter. The shape parameter (β), which inversely correlates with the dispersion of fatigue data, is significantly lower for the 1.0 wt% concentration ($\beta = 5.08$) compared to the 0.5 wt% ($\beta = 12.13$) and 3.0 wt% ($\beta = 10.96$) configurations. This indicates a much wider scatter in the fatigue life of the 1.0 wt% specimens. The practical consequence of this scatter is best observed in the reliability curves (Fig. 6).

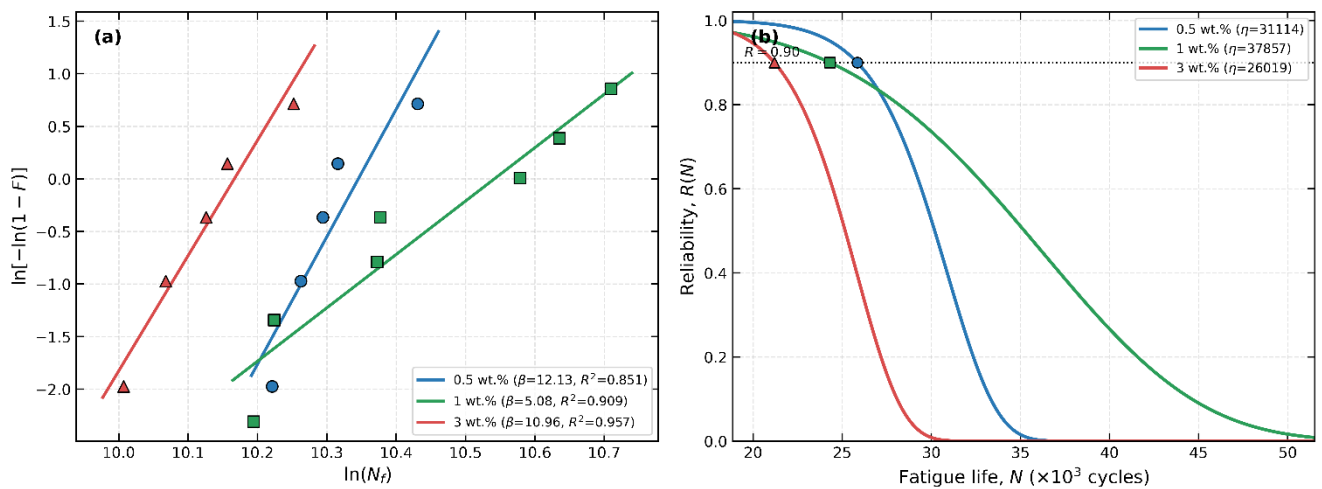


Fig. 6. (a) Weibull probability plot and (b) fatigue reliability curves for double-lap joints modified with 0.5, 1.0, and 3.0 wt% TiO₂ nanoparticles under a cyclic load of 4800 N, $R = 0.1$.

As depicted in Fig. 6(b), a distinct crossover phenomenon occurs between the reliability curves of the 0.5 and 1.0 wt% joints. While the 1.0 wt% adhesive offers superior life at a 50 % reliability level, the situation reverses at higher reliability demands. For a stringent safe-life design requiring 90 % reliability ($R = 0.90$), the B_{10} value of the 1.0 wt% joints (24,179 cycles) dips below that of the 0.5 wt% joints (25,792 cycles).

This finding emphasizes a critical design principle: an adhesive composition yielding the highest average fatigue life does not necessarily guarantee the highest reliability in fail-safe designs. The pronounced scatter at 1.0 wt% diminishes its safe-life advantage, demonstrating that statistical reliability analysis is an indispensable tool for optimizing nano-reinforced double-lap joints for structural applications.

3.4. Failure mechanisms and crack propagation behavior

To elucidate the physical phenomena governing the fatigue behavior and to explain the statistical variations observed in the Weibull analysis, the failure mechanisms of the TiO₂-modified joints were evaluated. Rather than relying solely on microscopic fractography — which often struggles to capture the dynamic interactions between the propagating crack front and the nanoscale reinforcement — a conceptual micro-mechanical model was developed based on the macroscopic observations and fatigue life trends.

3.4.1. Macroscopic fracture surface analysis

The macroscopic evaluation of all tested specimens was conducted to identify the overall failure modes, offering fundamental insights into the predominant failure modes of the composite double-lap joints subjected to cyclic loading. The fracture surfaces suggest a predominantly cohesive failure within the adhesive layer, accompanied by local light fiber tear from the composite adherends.

Fig. 7 illustrates representative fracture surfaces exhibiting these generalized features. This observation demonstrates highly effective interfacial adhesion between the epoxy matrix and the substrate, most likely resulting from proper surface preparation and adhesive wetting. The dispersed TiO₂ nanoparticles may have further contributed to energy dissipation within the adhesive bulk rather than directly governing the interfacial bonding. Consequently, the primary fatigue crack was constrained to propagate through the bulk of the nano-modified adhesive, which maximized energy dissipation and delayed ultimate failure.

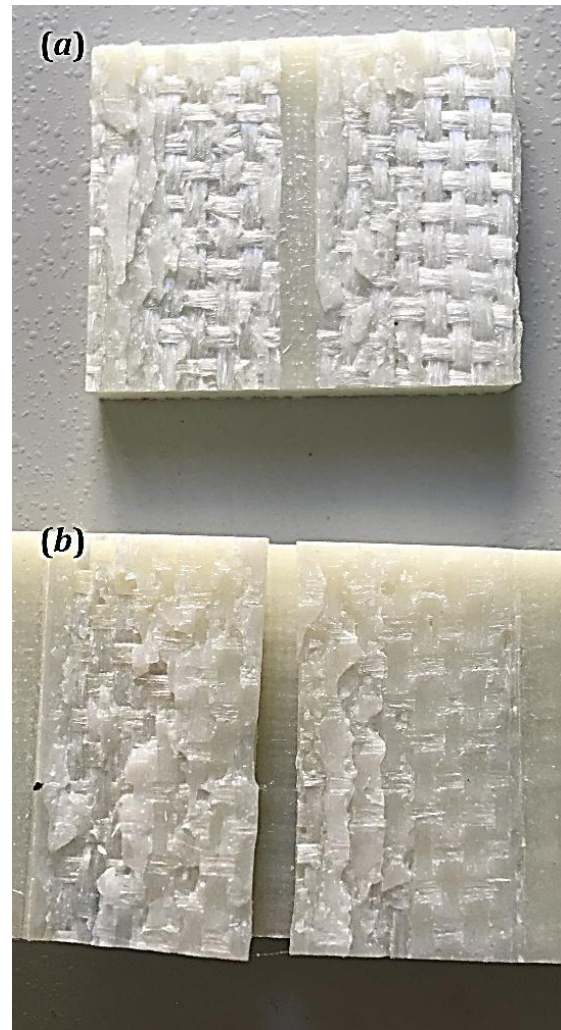


Fig. 7. Representative macroscopic fracture surfaces of the composite double-lap joints under fatigue loading. The strong interfacial bonding forces the fracture path near the substrate interface, resulting in a mixed failure mode: (a) the fiber-rich surface (inner adherend) exhibiting light fiber-tear and exposed woven fibers, and (b) the corresponding resin-rich mating surfaces (outer adherends) retaining the bulk of the adhesive layer.

3.4.2. Conceptual model of nanoparticle-crack interaction

To physically justify the statistical data—specifically, why the 1.0 wt% concentration yielded the highest characteristic life ($\eta = 37,857$ cycles) while the 3.0 wt% concentration suffered a severe degradation ($\eta = 26,019$ cycles) — a schematic representation of the crack propagation paths is illustrated in Fig. 8. This model highlights the critical role of nanoparticle dispersion and concentration on the fatigue crack trajectory.

As depicted in Fig. 8, the fatigue behavior is governed by the interplay between the advancing crack and the TiO₂ nanoparticles:

- **Low TiO₂ content (0.5 wt%):** At lower concentrations (Fig. 8(a)), the nanoparticles are relatively sparse. While

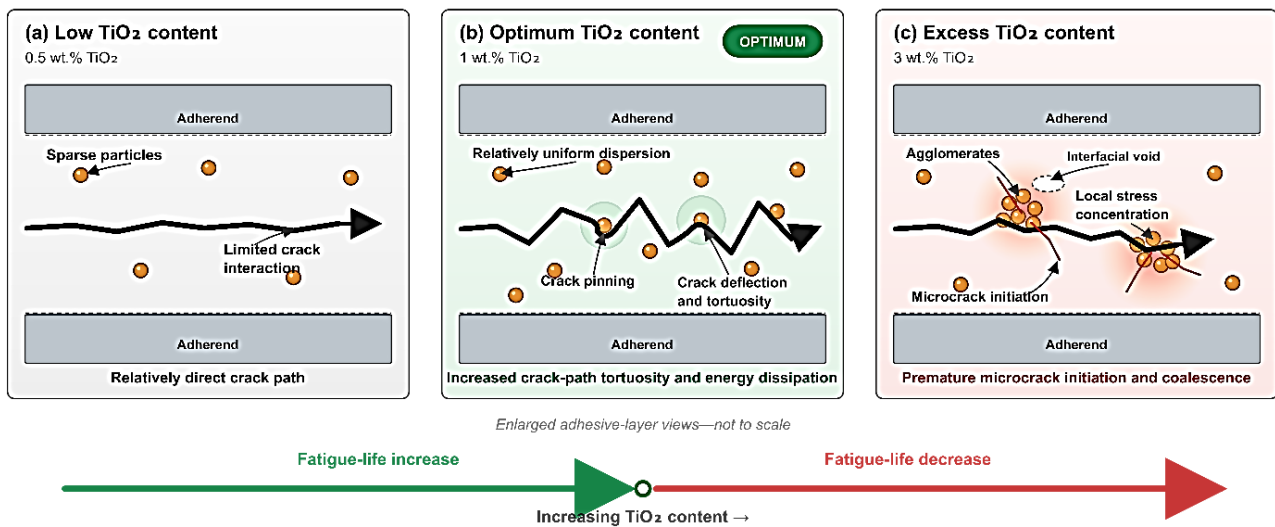


Fig. 8. Schematic illustration of fatigue crack propagation mechanisms in the adhesive layer at different nanoparticle contents: (a) 0.5 wt% with limited interaction, (b) optimum 1.0 wt% exhibiting crack pinning and tortuosity, and (c) excess 3.0 wt% showing agglomeration-induced microcrack initiation.

dispersion is generally good, the large distances between particles result in limited crack interaction. The fatigue crack propagates through the epoxy matrix via a relatively direct path, dissipating less fracture energy. This explains the moderate fatigue life observed in the statistical analysis.

- **Optimum TiO₂ content (1.0 wt%):** The 1.0 wt% concentration (Fig. 8(b)) represents a critical threshold where relatively uniform dispersion is achieved alongside sufficient particle density. As the fatigue crack advances, it continuously interacts with the rigid TiO₂ nanoparticles. The primary toughening mechanisms activated are crack pinning and crack deflection. These interactions force the crack to bow and deviate from its planar trajectory, significantly increasing the crack-path tortuosity. This highly tortuous path demands substantially more energy for crack propagation, effectively retarding the crack growth rate and resulting in the highest fatigue life.
- **Excess TiO₂ content (3.0 wt%):** Beyond the optimum threshold, the high surface energy of the nanoparticles overcomes the shear forces during the mixing process, leading to the formation of agglomerates (Fig. 8(c)). These agglomerates are detrimental to fatigue performance. They not only create interfacial voids due to poor matrix wettability but also act as severe local stress concentrators. Under repetitive cyclic loading, premature microcracks initiate at these weak interfaces. The rapid coalescence of these microcracks provides a path of least resistance for the main fatigue crack, entirely overshadowing any potential crack deflection

mechanisms. This premature microcrack initiation directly causes the severe drop in fatigue life and reliability for the 3.0 wt% joints.

4. Conclusions

The current research explored the influence of TiO₂ nanoparticle weight fractions on the cyclic fatigue behavior, statistical reliability, and governing failure mechanisms of composite double-lap joints. Synthesizing the experimental data, Weibull statistical evaluation, and conceptual micro-mechanical modeling yields the following principal conclusions:

- **Peak Average Fatigue Performance:** Incorporating TiO₂ nanoparticles enhanced the cyclic resistance of the adhesive joints up to a specific optimal threshold. The 1.0 wt% configuration achieved the maximum characteristic fatigue life ($\eta = 37,857$ cycles) and median life ($B_{50} = 35,222$ cycles), clearly outperforming both the lower (0.5 wt%) and higher (3.0 wt%) nanoparticle loadings in terms of mean structural performance. It should be explicitly noted that this fatigue life ranking applies specifically to the selected maximum load level of 4800 N and should not be interpreted as a universal ranking across all possible stress levels.
- **The Reliability Crossover Phenomenon:** The Weibull analysis exposed a crucial disparity between average fatigue life and engineering safety. While the 1.0 wt% joints provided the highest mean life, the 0.5 wt% joints exhibited markedly lower statistical scatter (maximizing the shape parameter to $\beta = 12.13$ compared to $\beta = 5.08$ for 1.0 wt%).

Consequently, for highly conservative design limits targeting a 90 % survival rate, the 0.5 wt% concentration emerged as the safest formulation, yielding a higher B_{10} life (25,846 cycles) than the 1.0 wt% optimum (24,307 cycles). However, considering the limited sample sizes ($n = 5$ to 7), these Weibull parameters should be interpreted as conservative engineering estimates rather than absolute statistical boundaries, and the observed crossover phenomenon should be regarded as a dataset-specific trend requiring confirmation with larger sample sizes.

- *Performance Degradation at Elevated Concentrations:* Raising the nanoparticle content to 3.0 wt% resulted in a severe deterioration of both fatigue longevity and statistical reliability ($\beta = 10.96$). Based on the macroscopic mechanical responses and statistical scatter, this detrimental effect is inferred to be primarily attributed to nanoparticle agglomeration, which introduces severe localized stress concentrations within the adhesive layer and accelerates fatigue damage.
- *Micro-Mechanical Toughening vs. Defect Generation:* A conceptual micro-mechanical model was introduced to explain the statistical observations. Since direct microscopic characterization of the filler dispersion (e.g., SEM or TEM) was not performed in this study, these toughening and agglomeration mechanisms are inferred from the mechanical behavior and existing literature. At the presumably well-dispersed 1.0 wt% loading, toughening mechanisms such as crack pinning and crack deflection are hypothesized to have increased the tortuosity of the crack path, effectively retarding fatigue crack propagation. In contrast, at the 3.0 wt% loading, the agglomerates acted as crack initiation sites, promoting rapid microcrack coalescence and premature joint fracture.

Ultimately, this study underscores that designing nano-modified adhesive joints based purely on maximum average fatigue life can compromise structural safety. A comprehensive statistical reliability assessment is essential for successfully deploying these joints in fatigue-critical applications.

Conflict of interest

The authors declare no conflicts of interest regarding this manuscript.

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Additional information

Correspondence and requests for materials should be addressed to P. Akbarzadeh.

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