Performance Augmentation of Epoxy Adhesives with TiN Nanoparticles

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ABSTRACT: In the current study, nanoparticles (NPs) of titanium nitride (50−70 nm) in varying amounts (0−4 wt %) were uniformly suspended in an epoxy solution and then used to cast the films of nanocomposites. The same formulations were used to prepare the lap shear strength joints using stainless-steel coupons with the help of standard molds and then employing the compression molding technique. The nanocomposites films were characterized for their physical properties, thermal stability, friction performance, and scratch hardness, while the lap shear strength of joints prepared using nanocomposites as nanoadhesives was evaluated. The failed surfaces of joints were investigated using scanning electron microscopy (SEM) to understand the failure modes, that is, micro-failure mechanisms, while the cross-sectional surfaces of fractured nanocomposites were investigated using SEM to identify the distribution of NPs. The increase in the contents of NPs in the epoxy led to an almost linear increase in the selected performance properties. The highest (70%) improvement in the lap shear strength was observed with 4 wt % NPs, which was correlated with an increase in the hardness of composites.

1. INTRODUCTION

Joining two different or similar surfaces could be essential in building any structure, varying from high-speed machinery to load-supporting structural members. The process of joining two surfaces of various types, including metallic, ceramic, polymeric, fiber-reinforced composites, and so forth, can include riveting, nailing, welding, and adhesive application. Some techniques such as riveting or welding utilize a third dissimilar component, which may aggravate/corrosion, fretting, and fatigue; finally, as a combined effect, it can lead to premature joint failure with an accelerated rate. The technique of using adhesives, more precisely polymer-based adhesives, is free from these problems and has additional advantages. Such polymer-based adhesives are being used in common household appliances and industries for a long time and are generally based on cyanoacrylates, epoxy, an emulsion of polyvinyl acetate, and so forth. Such adhesives are widely commercialized because of the advantages of resistance to fretting due to the positive bonding vis-a-vis the absence of mechanical tolerance, viscoelastic properties, low-energy process (hence the reduced carbon footprints), corrosion resistance, and low weight.1,2

Instead of virgin polymers, composite adhesives, more specifically nanocomposite adhesives (NCAs), are more popular because of their excellent performance and are the focus of current research.3−15 The improvement in properties of NCAs mainly depends on the compatibility of a matrix with nanoparticles (NPs) used as fillers, their surface chemistry, energy, size, shape, amount, and so forth.5,16 The high surface area and aspect ratio are the common causes for a huge improvement in the performance at low loadings, generally around 1−4 wt %. The amount higher than this generally leads to more agglomeration problems and hence are restricted. NCAs based on high-performance polymers such as polyetherketoneketone, polyetheretherketone, polyaryletherketone, and nanofillers such as multiwalled carbon nanotubes (MWCNTs), titanium carbide (TiC), silicon carbide (SiC), boron carbide (B4C), and so forth have been reported with huge improvements in the past.16−18 The literature indicates that epoxy is the most popular matrix for adhesive development. Gupta et al.18 selected the NPs of alumina in varying amounts (0, 0.5, 1, 1.5, and 2 wt %) and shapes (nanospheres and nanorods, respectively). The improvement was around 4 wt % in the lap shear strength (LSS) to pristine epoxy for nanospheres and nanorods in epoxy and reported improvements of 52 and 56% in the lap shear strength (LSS) to pristine epoxy for nanospheres and nanorods, respectively. The improvement was attributed to the stiffening effect caused by the nanorods and spheres of alumina. Epoxy resin was again selected along with graphene, CNTs, and carbon nanofiber as fillers, reporting enhancements in the LSS of 30 and 33%, respectively, for carbon nanofiber and MWCNTs.11−14 Shin et al.15 used CNTs to improve the performance of epoxy-based adhesives in the air atmosphere (relatively low moisture), and the joints were...
cured in moist conditions to understand the effect of the presence of water molecules on curing vis-à-vis LSS. The addition of MWCNTs in epoxy led to the retention of the LSS of the adhesive. Apart from these, Ladani et al.\textsuperscript{19} explored the performance of carbon nanofiber-reinforced epoxy adhesives against carbon fiber-reinforced polymers-based surfaces. It was concluded that adding carbon nanofibers improved the performance under mode I cyclic fatigue with increased alignment and amount.

In the current study, epoxy resin was selected as a matrix for NCAs along with NPs of titanium nitride (TiN) as reinforcement to produce a series of nanocomposites (NCs) and NCAs. In addition to this, the developed nanosuspensions were used to prepare the films of NC castings and adhesive layers for lap shear joints. In the literature, hard NPs such as carbides of boron, silicon, titanium, and so forth\textsuperscript{\textsuperscript{21,22}} or their oxides\textsuperscript{\textsuperscript{21,22}} are explored in various matrices to enhance the LSS. Still, titanium nitride (TiN) NPs have not been explored for their potential to improve the performance of NCAs, though they also have very high hardness (31 GPa). The NCAs were assessed for their LSS to evaluate their efficiency as adhesives. Thus, the efforts were focused on formulating and fabricating NCs in the film form using the solution casting method based on TiN NPs and epoxy resin. The adhesive layer was designed to prepare joints using stainless-steel (SS) coupons and applying the compression molding technique based on identical formulation. Furthermore, the NCs were characterized for various performance properties such as microhardness, thermal stability, friction, and so forth. The details are given in the subsequent section.

2. RESULTS AND DISCUSSION

2.1. Physical Properties. Table 1 depicts the physical properties [density, void content, and critical interparticle distance (CID)] of composites. The addition of denser TiN NPs (density of 5400 kg/m\textsuperscript{3}) into the epoxy matrix (density of 1100 kg/m\textsuperscript{3}) led to the increase in the density of NCs. It was evident that the measured and calculated densities are in sync with the amount of NPs. The addition of TiN NPs resulted in a linear increase in the densities of NCs. Void content is a direct function of the efficiency of the processing technique used to develop composites, solution casting in this case. It might have led to the formation of solvent-based pores or entrapment of air while casting. The inclusion of TiN NPs in increasing amounts (0–4 wt %) resulted in a reduction of the dispersion of TiN NPs in the epoxy matrix. Since the composites were fractured by the impact, most of the NPs were debonded and removed from the fractured surface, leaving behind the circular cavities. The dimensions of cavities support the size of the NPs and their uniform dispersion in the matrix as NPs and not agglomerated particles. Moreover, Figure 1b shows a few particles still stuck (indicated by yellow circles) in the epoxy matrix. The field emission scanning electron microscopy (FE-SEM) micrographs show the well-dispersed and deagglomerated NPs. However, the interparticle distance was lower than the calculated CID.

2.2. Dispersion Analysis by Field Emission Scanning Electron Microscopy. Figure 1a depicts the evidence for the presence of TiN NPs in the epoxy matrix. Since the composites were fractured by the impact, most of the NPs were debonded and removed from the fractured surface, leaving behind the circular cavities. The dimensions of cavities support the size of the NPs and their uniform dispersion in the matrix as NPs and not agglomerated particles. Moreover, Figure 1b shows a few particles still stuck (indicated by yellow circles) in the epoxy matrix. The field emission scanning electron microscopy (FE-SEM) micrographs show the well-dispersed and deagglomerated NPs.

| Table 1. Physical Properties of the Developed Composites\textsuperscript{\textsuperscript{41}} |
|-----------------------------|---------|---------|---------|---------|---------|
| properties (standard/method) | ENC\textsubscript{0} | ENC\textsubscript{1} | ENC\textsubscript{2} | ENC\textsubscript{3} | ENC\textsubscript{4} |
| wt % (epoxy/TiN NPs)        | 100/0   | 99/1    | 98/2    | 97/3    | 96/4    |
| TiN NPs-vol %               | -       | 0.002   | 0.004   | 0.006   | 0.008   |
| measured density (kg/m\textsuperscript{3}) (ASTMD 792) | 1080    | 1130    | 1140    | 1160    | 1170    |
| calculated density (kg/m\textsuperscript{3}) (ROM\textsuperscript{b}) | 1100    | 1140    | 1180    | 1220    | 1260    |
| void content (%)\textsuperscript{c} | 1.18    | 0.21    | 3.53    | 5.24    | 7.31    |
| critical interparticle distance (nm)\textsuperscript{d} | 368.83  | 278.51  | 234.71  | 206.65  |

\textsuperscript{41}Density of TiN = 5400 (kg/m\textsuperscript{3}) and density of epoxy = 1100 (kg/m\textsuperscript{3}). \textsuperscript{4b}ROM: rule of the mixture. \textsuperscript{4c}Calculated using the standard formula given elsewhere.\textsuperscript{19}

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2.3. X-ray Diffraction Studies. Figure 2 shows the X-ray diffraction (XRD) patterns of pure epoxy and epoxy/TiN NCs. It is important to distinguish the peaks of the matrix and reinforcing phase. The major diffraction peaks at 21 and 48\textdegree{} are the signature peaks of pure epoxy, originating due to the cross-linking nature of pure epoxy.\textsuperscript{23} The peaks of pure epoxy are vastly broad, which indicates its amorphous behavior.\textsuperscript{24} The gradual addition of TiN NPs into the epoxy shows the appearance of new peaks. Adding 1 wt % NPs into the epoxy shows a new peak at 43.10\textdegree{} and can be indexed to the (200) plane of TiN (JCPDS no. 38-142). As the percentage of TiN NPs in the epoxy increased from 1 to 4 wt %, the intensity of the peak at 43.10\textdegree{} was significantly enhanced, which was well-anticipated. In addition, some more signature peaks of TiN at 37.17\textdegree{} (111), 62.38\textdegree{} (220), 74.86\textdegree{} (311), and 78.61\textdegree{} (420)
were observed. The lower intensity of TiN peaks was due to the lower loading of NPs in ENC1. Furthermore, increasing the weight % of TiN NPs into the epoxy matrix decreased the broad, amorphous band of the epoxy matrix and increased the intensity of the signature peak of TiN NPs. The addition of NPs into the epoxy altered the crystallinity and surface morphology of the matrix. The increasing weight percentage of NPs significantly increased the degree of crystallinity. The degrees of the crystallinity for ENC1, ENC2, ENC3, and ENC4 were 2.14, 6.42, 9.71, and 19.25%, respectively. This observation indicates that as the NP concentration in the epoxy matrix increased, the amorphous nature of the composites gradually decreased, and the crystallinity of the composites increased.

2.4. Thermogravimetric Analysis. Figure 3 shows the thermograms for the developed composites.

The addition of TiN NPs altered the thermal degradation mechanism and improved the thermal stability, which indicates the qualitative dispersion of the NPs. It suggests an enhanced interaction of the epoxy chain with TiN NPs and the extension to the 3D cross-linked epoxy structure. It is a well-known fact that NPs interact physically or chemically with the polymer chains. Any such interaction hinders the segmental or chain motion of the macromolecules. This restriction on motion sustains the thermal energy, resulting into the improved thermal performance. A similar kind of effect, generally termed as the stiffening effect, affects the mechanical/rheological performance of NCs. In the current case, the progressive addition of NPs increased the resistance to the movement of the polymeric chains, improving the thermal stability. The formation of inorganic or thermally resistive char on the surface also improved the thermal stability. $T_5$ and $T_{10}$ indicate the initial degradation behavior of the composites and are widely considered for the measurement of the relative degradation performance. The inclusion of NPs reduced the extent of degradation of NCs significantly. It was observed that amongst the selected compositions, ENC4 showed the highest thermal stability improvements in $T_5$ and $T_{10}$ by 81 and 20 °C, respectively, compared to that of the pristine epoxy resin (Table 2).

2.5. Scratch Hardness. Figure 4 depicts the scratch hardness of the composites. With the progressive addition of TiN NPs to the epoxy resin, the scratch hardness improved by 18, 37, 62, and 81% for ENC1, ENC2, ENC3, and ENC4, respectively. This could be attributed to the significant hardness of NPs (31 GPa). Moreover, the improvement indicates the positive and enhanced interaction of NPs with the epoxy and the qualitative dispersion of NPs.

2.6. Friction Measurement. The coefficient of friction ($\mu$) of NCs is shown in Figure 5.

It seems that the highest $\mu$ for the epoxy was 0.08 and got reduced drastically to $\sim 0.01$. A similar trend was reported by Ayatollahi et al. with nanodiamond-reinforced epoxy. The

Table 2. $T_5$ and $T_{10}$ Temperatures for the Developed NCs

| Temperature/NCs | ENC0 | ENC1 | ENC2 | ENC3 | ENC4 |
|----------------|------|------|------|------|------|
| $T_5$ (°C)     | 222  | 257  | 298  | 302  | 303  |
| $T_{10}$ (°C)  | 318  | 330  | 333  | 336  | 338  |

$T_5$ and $T_{10}$: are the temperatures at which 5 and 10% of the weight loss were observed, respectively.
addition of the nanodiamond resulted in a 50−56% reduction in friction. It appears that the increased hardness is responsible for a drastic decrease in \( \mu \). The size, shape, amount, and hardness of filler particles affect the tribo-performance of composites apart from the tribo-configuration of a couple, sliding conditions (linear or reciprocating motion), sliding duration, and so forth. In this case, it was a single-pass forward motion by the ball. Hence, the interference of wear debris was not possible. Otherwise, the debris gets trapped and modifies the friction phenomenon. In the case debris contains sharp-edged hard particles, \( \mu \) increases. As TiN NPs are hard and spherical, their inclusion in the debris would not have deteriorated the \( \mu \). The ball against the composite film has again simplified the situation by nullifying the involvement of the debris during sliding. Thus, increased hardness is the only reason for the lowering of \( \mu \) of the composites.

2.7. Lap Shear Strength. Figure 6a depicts the LSS performance of adhesives, designated as ENA_0, ENA_1, ENA_2, ENA_3, and ENA_4 for 0, 1, 2, 3, and 4 wt % NPs, respectively. The addition of NPs resulted in a significant enhancement in the LSS of adhesives. ENA_4, ENA_3, ENA_2, and ENA_1 showed 69, 37, 36, and 20% improvements, respectively, compared to pure epoxy. NP-induced crystallinity and significant improvement in the quantity of the interface vis-à-vis the efficient transfer of the load could be the reason for such a significant improvement. Gupta et al.\(^\text{18}\) selected the NPs of alumina in varying amounts (0, 0.5, 1, 1.5, and 2 wt %) and shapes (nanorods and nanospheres) in the epoxy and reported improvements of 52 and 56% in the LSS to pristine epoxy for nanospheres and nanorods, respectively. In addition to this, it was found that the current LSS is sensitive to the loading of fillers, similar to the LSS performance of epoxy and TiN NPs. Sydlik et al.\(^\text{28}\) reported a similar trend for the LSS of CNT-reinforced epoxy-based LSS joints. Figure 6b depicts the load extension curve for the adhesive joints. The trend of the ultimate failure was found to be similar to that of the LSS of adhesive joints.

2.8. Failure Analysis. Figure 7 depicts the photographs and SEM micrographs of failed LSS joints, illustrating the failure mechanisms in macro- and microdomains. The photographs indicate the remnants of adhesives originally formed as films between two adherends. The films were stripped off in a complementary manner by both the coupons. For ENA_0, the nature of the failure was mostly adhesive failure since most of the part of the film was sticking to the upper coupon. Moreover, micro-plastic deformation (white patches in Figure 7a) is evident from the photograph. The micro-mechanisms in the failed joints could be observed using SEM micrographs. The ENA_4 micrograph Figure 7b depicts that the LSS joint failed dominantly due to the plastic deformation of epoxy resin. However, the failed surface did not show prominent features, except its shear flow. From the SEM micrograph of the failed joint, it could be articulated that the feature, which has the onset at 1 wt % loading of TiN, acts as a reinforcing phenomenon due to TiN NPs. As the wt % of TiN increased, the feature with pentagonal and hexagonal shear cups emerged dominantly. The observed topography could result from the deformation-resisting shear failure of a joint in the direction perpendicular to that of the lap shear force.

3. CONCLUSIONS

NCs and NCAs of epoxy filled with an increasing amount (1−4 wt %) of NPs of TiN were developed. The density and % crystallinity enhanced with the increase in the wt % of NPs. The thermal stability increased significantly (up to 303 °C by
40%) almost linearly with the increase in TiN NPs. The scratch hardness also increased substantially (by 81%) due to hard NPs. The coefficient of friction ($\mu$), on the other hand, decreased drastically due to the inclusion of NPs, which was in line with the increase in the hardness of NCs. The LSS also improved significantly. Among the selected composites, ENA4 showed the highest improvement by 69%, followed by ENA3, ENA2, ENA1, and ENA0 by 37, 36, and 20%, respectively.

The increase in LSS due to NPs was correlated with the reinforcing action of NPs based on the failure analysis of surfaces showing typical patterns of shear cups (hexagonal and pentagonal), thereby resisting the plastic deformation of the film in the joint. An increase in thermal stability could also be another reason for the increased LSS.

4. EXPERIMENTAL SECTION

4.1. Materials. Epoxy AREMCO BOND 2320 was purchased from AREMCO Products Inc. (USA) with a density of 1.10 g/cm$^3$ and the thermal resistance of 120 °C. TiN NPs (~20 nm: as per the supplier’s data) were from Nanostructured and Amorphous Materials Inc., USA with a nearly spherical shape and a surface area of 66 m$^2$/g. FE-SEM was used to verify the size and shape of TiN NPs, as shown in Figure 8. The NPs were spherical, with diameters in the range of 60–90 nm.

Figure 7. Failed surfaces of LSS joints: photographs (a,c,e,g,i) and SEM micrographs (b,d,f,h,j).

SS grade 316 was selected for the coupons with dimensions 65 mm $\times$ 15 mm $\times$ 1.5 mm (tolerance of $\pm$0.075) and surface roughness in the range of 0.15–0.20 $\mu$m. The roughness measurement was performed using a 3D profilometer (Nano-Map 1000 WLI). The coupons were procured from Parshwamani Metals, Mumbai, India. The lap shear joints were prepared using these coupons as per ASTM D 1002, as illustrated in Figure 9a.

4.2. Development of NCAs and NCs. TiN NPs were dispersed in acetone as the medium and probe-sonicated [Crome Tech Probe sonicator (UP 800 ultrasonic processor),...
parameters: 3 s pulse on, 3 s pulse off, and probe diameter: 8 mm] for various durations just to optimize the time required for proper dispersion.

For preparing the NCs, the total quantity of NPs to be added was divided into six equal parts and sonicated in acetone for 20 min in parallel. A measured amount of the hardener–resin premix was kept ready in six batches. The hardener-premixed epoxy resin was added to each acetone suspension at the precalculated amount to meet the NP loadings at 1, 2, 3, 4, and 5 wt %. The nanosuspension was further sonicated for 30 min for homogenization, and then, acetone was allowed to evaporate at ambient temperature. The measured quantity (0.10 g) of this viscous nanosuspension of TiN NPs in epoxy resin was spread on the coupon, and the mold was closed with the upper coupon, followed by a core half of the mold. The amounts of epoxy resin in EN0, EN1, EN2, EN3, and EN4 were 0.10, 0.099, 0.098, 0.097, and 0.096 g, respectively. The adhesive line/layer with the width of 15 mm, the length of 15 mm, and the thickness of ∼0.5 mm maintained was thus prepared. Subsequently, the mold was kept into a compression molding machine at 120 °C, and a pressure of 8 MPa was applied to allow the curing of NCAs. The mold was held under these processing conditions for 15 min and allowed to cool in ambient conditions [the samples were cooled for 8 h (naturally)]. For each composition, eight LSS joints were prepared.

Figure 9b depicts the process of solution casting for the NC film. NC films were developed by casting the nanosuspension on a mild steel substrate, as shown in Figure 10. The casted
coating/films were cured at 120 °C in a vacuum oven for 15–20 min, followed by natural cooling. The wt % of NPs was changed to 0, 1, 2, 3, and 4 wt %, and the resulting samples were denoted as per Table 1. It is well-established that generally beyond 4 wt %, NPs tend to agglomerate, and the benefits of NPs tend to reduce. Hence, the amount was restricted up to 4 wt %.

5. CHARACTERIZATION

5.1. Physical Properties. The density of epoxy/TiN composite films was measured using a Mettler Toledo ME155DU weighing balance following the ASTM D 792 standard (Archimedes principle). Eight specimens (casted NCs) were used to calculate the measured density. Void contents were calculated based on the density data (measured and calculated) using the equations reported elsewhere.

5.2. Dispersion by FE-SEM. The best performing composition (ENC4) was impact-fractured, and the cross-section was observed using FE-SEM (JEOL JSM 7800 F).

5.3. XRD Studies. XRD studies were conducted on a Philips XPERT-PRO; the 2 theta range was from 10 to 80° with a scanning rate of 5°/min. The analysis of the obtained XRD data was performed using OriginPro 2020b (64-bit) 9.7.5.184 (Academic) software.

5.4. Thermogravimetric Analysis. The thermal stability of the composites was measured in an air atmosphere on a Linseis 1000 PT instrument with a ramp rate of 10 °C from room temperature to 900 °C. Origin 2020 and Linseis evaluation software packages were used for the data analysis. T5 and T10 are the temperatures at which 5 and 10% of the weight loss were observed, respectively. Moreover, it is an indication of the onset of degradation.

5.5. Scratch Hardness. The scratch hardness of the composites was measured on a CETR UMT (Bruker) tribometer. The analysis was carried out using the ASTM G 171-03 standard under a 50 N load. A 0.02 m/s speed was maintained to scratch the composites by keeping the scratch distance of 15 mm as a constant. A Meiji optical microscope (10× objective) was used for the analysis of the scratch. The scratch hardness value was calculated using the standard equation in the literature. For each sample, five film specimens were used, and an average value was considered.

5.6. Friction Measurement. The influence of TiN NPs on the frictional behavior of NCs was studied using the ball on flat configuration on a CETR/Brucker UMT 3MT tribometer. The experiment was conducted in a single pass condition. The friction was recorded under a normal load of 50 N, at a speed of 0.002 m/s, and for a sliding distance of 15 mm. For each sample, five casted NCs specimens were used, and an average value was considered.

5.7. Lap Shear Strength. A Zwick Roell universal testing machine was used to measure the LSS of the NCA joints with a load of 250 kN capacity following ASTM D 1002 in the lab shear mode with a constant crosshead speed at 1.3 mm/min. Eight samples of each lap shear joint were tested. The average value was considered to be the LSS of the particular composite. The LSS measurement was performed using the formula mentioned in the ASTM standard and the literature. For each sample, eight specimens were used, and an average value was considered.

5.8. Failure Analysis. Failed portions of samples (15 mm × 15 mm) were cut from each coupon and were gold-coated as per general practice to avoid charging problems during SEM investigations. The samples were placed in an SEM chamber on double-sided carbon tape and then investigated using a Zeiss Evo 10 scanning electron microscope. The secondary electron detector/mode at a high vacuum setting was selected. The working distance between the samples and the electron gun was maintained at 8–8.5 mm, whereas 20 kV voltage was used to produce the electron beam. The best performing composition (ENC4) was fractured, and the cross-section was observed using FE-SEM (JEOL JSM 7800 F).

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Notes
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