S. Dizeci and A.Ç. Kandemir / Hacettepe J. Biol. & Chem., 2023, (2), 153-161

Research Article

Hacettepe Journal of Biology and Chemistry

journal homepage: www.hjbc.hacettepe.edu.tr

Effects of Silica/Clay Nanoparticles on Microstructural and Mechanical Properties of Epoxy Based Adhesives

Silika/Kil Nanoparçacıklarının Epoksi Esaslı Yapıştırıcıların Mikroyapısal ve Mekanik Özelliklerine Etkisi

Sehram Dizeci and Ayse Cağıl Kandemir*

Department of Mechanical Engineering, TED University, Ankara, Turkey.

ABSTRACT

Improving the mechanical properties of the epoxy-based adhesives with nanoparticles is one of the methods which justifies the use of adhesive joints. This work studies the strength of adhesively bonded single-lap joints (SLJs) considering the pure adhesive, the reinforced adhesive with nano-silica particles (NSPs), nano-clay particles (NCPs), and a combination of both nano particles. Uniaxial tensile testing of the SLJs was conducted to reveal the failure loads of the joints and their elongations at failure. Furthermore, Scanning electron microscope (SEM) images and X-ray Diffraction (XRD) Analyses were used to investigate dispersion quality. It was observed that the use of just 1 wt.% NCPs or 2 wt.% NSPs significantly improve the failure load by 48% and 44%, respectively; whereas the combination of both particles generally leads to large agglomerations. These agglomerations lead to 86.5% failure load reduction. It is also concluded that the dispersion quality is a key to improving the strength by shifting the failure mechanism from adhesion to cohesion type.

Key Words

Mechanical properties; adhesive; nanocomposite; nano-silica; nano-clay.

ÖZ

Epoksi esaslı yapıştırıcıların mekanik dayanımının nanoparçacıklarla iyileştirilmesi, güncel çalışmalarda yapıştırıcı temelli bağlantıların tasarımında araştırılmaktadır. Bu çalışmada, tek katmanlı bağlantıların mekanik dayanımının arttırılması hedeflenmiştir. Bu amaçla epoksi matris; nano-silika (NSP) ve nano-kil (NCP) ile güçlendirilerek nanokompozit yapıştırıcı üretilmiş ve söz konusu nanokompozitler kullanılarak paslanmaz çelik malzemeler yapıştırılmıştır. Üretilen nanokompozit yapıştırıcıların dağılım kalitesini incelemek için Taramalı Elektron Mikroskobu (SEM) görüntüleri ve X-ışını Kırınım (XRD) Analizleri kullanılmıştır. Akabinde yapıştırılan malzemelere, çekme testi uygulanarak, bağlantıların yetmezlik yükü ve kopmadaki uzama miktarı belirlenmiştir. Çalışmanın sonunda ağırlıkça %1 NCP veya ağırlıkça %2 NSP içeren nanokompozit kullanımının yetmezlik yükünü sırasıyla %48 ve %44 oranında iyileştirdiği ortaya çıkmıştır. Fakat, NCP-NSP parçacık kombinasyonunun büyük aglomerasyonlara yol açtığı ve yetmezlik yükünü %86.5 düşürdüğü gözlemlenmiştir. Sonuçlar değerlendirildiğinde, nanoparçacıkların epoksi içinde dağılım kalitesinin, kırılma mekanizmasını adheziyon tipinden kohezyon tipine çevirme hedefinde en önemli ölçüt olduğu ortaya çıkmıştır.

Anahtar Kelimeler

Mekanik özellikler; nanokompozit; yapıştırıcı, nanosilika, nanokil.

Article History: Received: Oct 21, 2022; Revised: Dec 26, 2022; Accepted: Jan 13, 2023; Available Online: Jan 13, 2023.

DOI: https://doi.org/10.15671/hjbc.1192751

Correspondence to: Ayse Cagil Kandemir cagil.kandemir@tedu.edu.tr TED University Ankara/ Turkey.

E-Mail: cagil.kandemir@tedu.edu.tr

INTRODUCTION

Adhesive bonding of materials is employed in several industries, including aeronautical, automotive, and maritime, due to their important characteristics. They possess several merits like good fatigue performance, lesser added weight, limited stress concentrations, and high loading capacity, which makes them a feasible method in attaching both similar and dissimilar materials [1-3].

The increasing need to use adhesive joints and subsequently to enhance their features brings the idea of reinforcement to mind [4-6]. Nano-silica (SiO_2) is regarded as one of the most common types of nanomaterials in improving the mechanical properties of epoxy-based adhesives. Enhancing the debonding load and water-resistance of the silica-improved adhesives were studied by Wang et al. [7]. They revealed auspicious outcomes for the silica-reinforced adhesives utilized in both wet and dry media. Nasser et al. [8] used nanoparticles in two different weight percentages and sizes. They reported that in the same conditions, NSPs improve the mechanical properties of the adhesives more than alumina nanoparticles do. They also observed that increasing the concentration of NSPs from 2.5 to 5 wt. % reduces joint strength severely. The application of NSPs in the augmentation of the loading capacity in SLJs made of carbon fiber reinforced plastic (CFRP) adherands was investigated by Hasanifard et al. [9]. They reported a maximum improvement of 22% in debonding load for an epoxy-based adhesive, Araldite 2015, reinforced by NSPs with 30-50 nm size. The dependence of the debonding load on the nano-silica weight percentage was investigated by Paygozar and Saeimi [10]. They stated that the joint prepared by an epoxy adhesive with 2 wt.% of NSPs reflected the highest joint strength. Improving the characteristics of the adhesive joints using NSPs together with another type of nanoparticles was studied by Ayatollahi et al. [11]. They used tinier NSPs (10-15 nm) in addition to multi-walled carbon nanotubes in a lower concentration (0.8 wt.%) and stated 28% and 36% enhancements in the shear strength and elongation at failure, respectively.

Another suitable nanoparticle in improving the characteristics of the polymeric material is the nano-clay particle (NCP) which was investigated in several studies [12, 13]. For instance, Khalili et al. [14] investigated the mechanical properties of nano-clay-improved adhesive SLJ under tensile static loading. They attached Glass/epoxy composite adherends by an epoxy-based adhesive reinforced with three different concentrations of NCPs. They found out that the joint reinforced by 1wt.% concentration endured the maximum load before debonding. The use of NCPs in addition to other nanoparticles was investigated by Aliakbari et al. [15]. They observed that NCPs, waste rubber powder, and phenolic resin with weight percentages of 2, 15, and 30 wt.% respectively, improve the tensile strength up to 12.44%. Functionalized NCPs were utilized in a similar study [16] to improve the peel strength of the polyurethane adhesives. They reported 30% improvements using 1wt.% of hydroxyl-modified clay and 40% improvements by 1wt.% of aminosilane-modified clay in the peel strength.

This study investigates the effects of additive nanoparticles on the failure load and elongation at failure of the adhesively bonded SLJs. Three different concentrations of two different nanoparticles (silica, clay) as well as a combination of them, are utilized to reinforce the adhesive and monitor the aforementioned parameters of the joints. According to our knowledge, this is the only study investigating the mutual effects of silica and clay nanoparticles in a thermoset resin. SEM and X-ray Diffraction Analysis (XRD) images are utilized to investigate the quality of the nanoparticle dispersions.

Experimental work

The experimental works in this study include adhesive preparation, bonding processes, mechanical test, and microstructural analyses to check the dispersion quality of the utilized nanoparticles.

Materials

For the reinforcements, unmodified amorphous silica and organically surface-modified- nanoclay nanoparticles were chosen. Silica was purchased from Nanografi (Ankara, Turkey) while nanoclay was obtained from Sigma Aldrich. The details have been shown in Table 1. The adherends are stainless steel 304 with 350 MPa of yield strength and 615 MPa of UTS strength which are purchased from Ankara Bronz Dokum.

Table 1. Detailed properties of nanoparticles.

Material Name	Particle type	Surface modification	Size	Provider
Nanosilica	Silicon Dioxide	-	55-75 nm	Nanografi
Nanoclay	Montmorillonite	35-45 dimethly-dialkly (C14-C18) amine	thickness: 1 nm length: several hındred nm	Sigma Aldrich

Adhesive preparation method

Two different nanoparticles were added into an epoxy-based two-component adhesive, Araldite 2011 in orderto prepare the reinforced adhesives. The improved adhesives with nanoparticles in three different concentrations (i.e. 1, 2, and 5 wt.%) were prepared in three sets containing NSPs, NCPs, and a combination of both (50 wt.% of each). To prepare the specimens, the adhesive was diluted by acetone to lessen its viscosity and to make it a suitable medium for nanoparticle addition and dispersion [10]. Then, the nanoparticles were added to the diluted resin, and the mixtures were blended with magnetic stirrers (700 RPM) for about 30 minutes. The process is followed by putting them into a sonication bath for another 30 minutes. The vacuum pump apparatus was utilized to distill the acetone of the resin and in the next step, the hardener part of the adhesive was added to the obtained resin and they got blended with a glass stirring rod inside a flat bottomed flask for around 5 minutes to be mixed appropriately. Eventually, the reinforced adhesives were used to bond the degreased adherends and got cured for about 3 hours at room temperature followed by curing at 60˚C for 30 minutes inside an oven.

Bonding processes

To achieve high-quality bonding, the adhernad surfaces should be prepared initially. For this purpose, roughening of the surfaces and degreasing them should be conducted in several steps as follows [17-19]:

- Immerse the adherends in trichloroethylene and subsequently in isopropyl alcohol to degrease them.
- Wash the surfaces with tap water.
- Use a P120 silicon carbide grinding paper to roughen the adherend surfaces
- Repeat step 1 (each section takes about 30 min).
- Wash with distilled water.

After the surface preparation step, two SS304 adherends were attached with a 0.2 mm layer of reinforced adhesives. A specific mold was utilized to obtain an accurate thickness of the layers. Fig. 1 shows the general configuration of the produced joints and a set of reinforced joints as examples. The properties of the specimens are clearly shown in Table2.

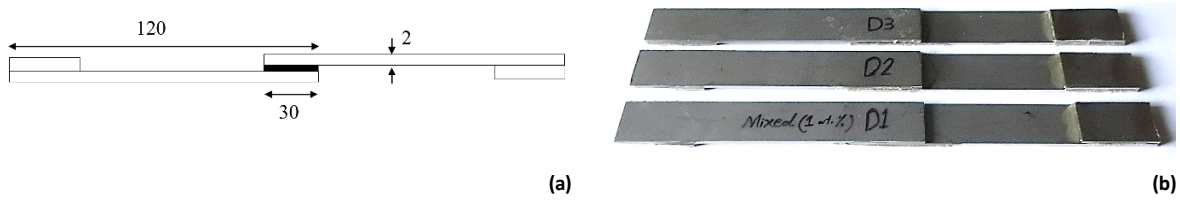

Figure 1. The joints: (a) general configuration (out of plane thickness is 20 mm), (b) different specimens reinforced with nanoclay particles.

Mechanical tests

All the specimens with three repetitions were tested using a universal tensile testing machine (MTS, Model 45) to obtain the failure load of the joints. The samples were loaded under a cross-head speed of 1mm/min.

Microstructural analyses

The dispersion quality of the nanoparticles was analyzed by different microstructural analyses. Several SEM images were taken from all specimens using the scanning electron microscope, FEI Quanta 400F, The Netherland. Besides, the intercalation /exfoliation level of NCP particles was tested by XRD via Rigaku Ultima-IV, CuKa 40 kV, 40 mA under a continuous scanning range of 1–10º.

Results and Discussion

The load-displacement curves obtained from tensile tests were utilized to compare the failure loads and the elongation at failure of the joints. Furthermore, several SEM and XRD image results were employed to correlate the increase or decrease in the failure loads and ductility levels with the dispersion quality of the specimens.

3.1 NSP Nanocomposites

The load-displacement responses of the reinforced joints were plotted against the joint with neat adhesive (Fig.2) to compare the effects of the nanoparticles with different concentrations. From the curves, it can be observed that there is a particular concentration in which the failure load of the joint is higher than the others showing the maximum improvement. In other words, a lower or higher amount of the weight percentage leads to lower failure loads.

For NSPs, the most proper concentration was found to be 2 wt.%. On any amount above or below this concentration, both failure load and failure elongation dropped. However, for the adhesives reinforced by NCPs, the suitable concentration was 1 wt.% and above this concentration, the failure load was reduced severely. For the combination of the nanoparticles, there is a contradictory behavior in the failure load and the elongation at failure. Increasing the weight percentage of nanoclay decreases the failure load and intriguingly improves the elongation at failure considerably.

From Fig.2 and Table 2 data, it is obvious that the addition of 1wt.% NSPs has improved the joint failure load slightly, whereas the addition of 2wt.% NSP increased the failure load by 44%. In the same concentration, the maximum improvement in the elongation at failure (31%) was also achieved.

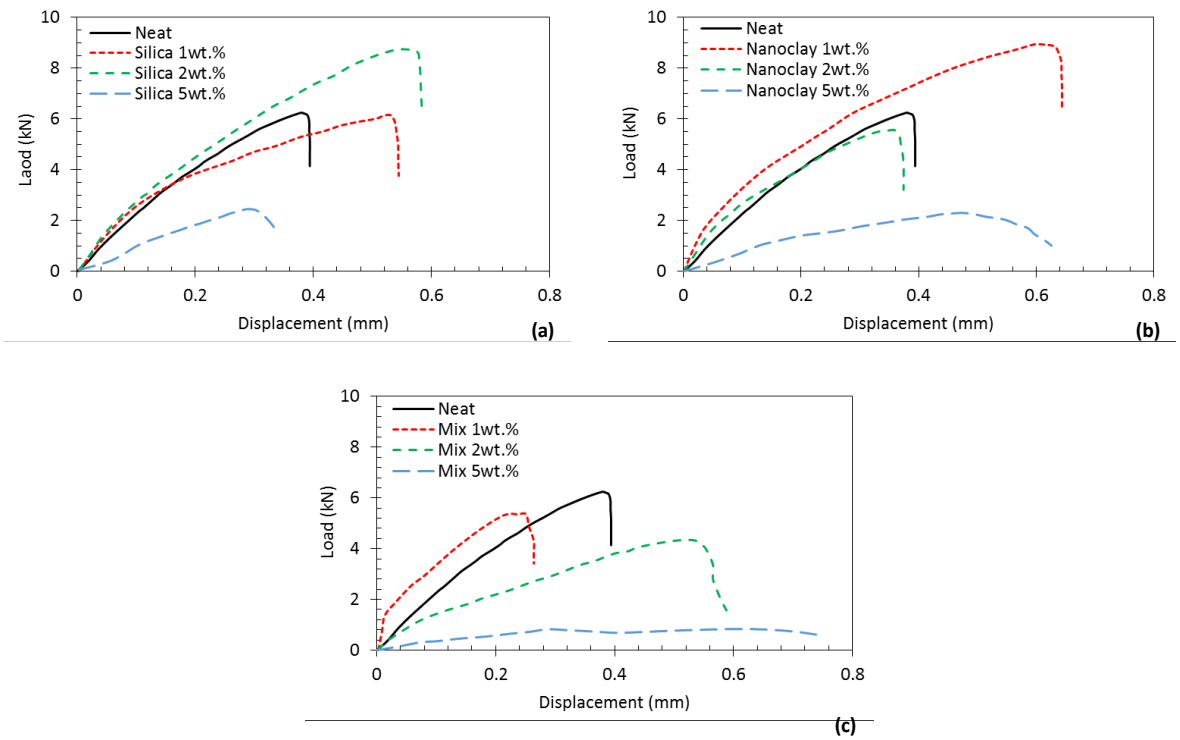

Figure 2. comparison between the failure load of SLJ prepared by neat adhesive and reinforced adhesives including, (a) nano-silica, (b) nano-clay, and (c) a mixture of both nanoparticles.

The relevant data including the failure load of the joints and the values of elongation at failure were collected in Table2 as follows,

Table 2. Failure load and elongation at failure for different samples.

Sample No.	Nano type & percentage	Failure load (kN)	Elongation at failure (mm)
A1	none	6088	0.37
B1	1 wt. % Silica	6128	0.53
B2	2 wt. % Silica	8789	0.56
B3	5 wt. % Silica	2455	0.29
C1	1 wt. % Nanoclay	8991	0.61
C2	2 wt. % Nanoclay	5616	0.35
C3	5 wt. % Nanoclay	2330	0.47
D1	1 wt. % Mixed *	5474	0.25
D2	2 wt. % Mixed	4352	0.52
D3	5 wt. % Mixed	822	0.76

* The values shown in bold, demonstrate the failure loads higher than that of a joint with neat adhesive.

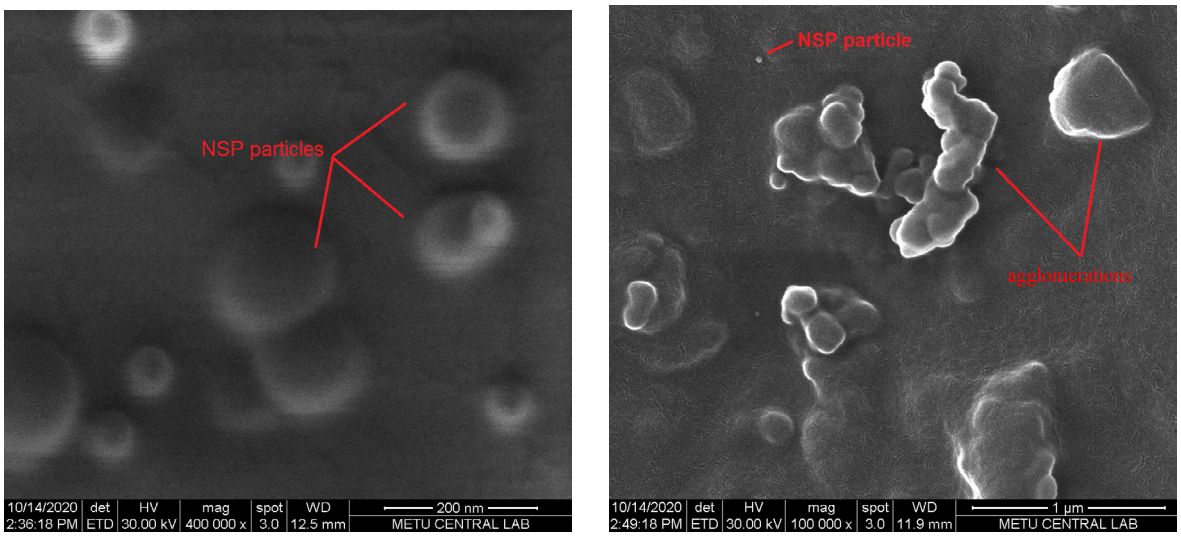

Figure 3. SEM images of reinforced adhesives with NSPs, (a) no visible agglomeration at 2wt.% and (b) huge agglomerations at 5wt.%.

SEM images were utilized to investigate the dispersion quality and to monitor the possible agglomerations of the nanoparticles inside the polymer. Two samples were prepared from the specimens reflecting the greatest improvement in the failure load and subsequently examined by SEM. Fig. 3a demonstrates the representative SEM image for 2wt % NSP reinforcement revealing that there is no visible agglomeration for this particular composition which supports the well dispersion quality and improved mechanical properties accordingly. It is known that nanoparticles would improve the strength of the polymers as long as they have optimal bonding strength. Since the unmodified NSPs utilized in this study have hydrophilic characteristics, their surfaces are compatible with the hydrophilic polymer matrix.. Therefore, with no agglomerations, efficient stress transfer from the matrix to high surface area bounded-NSPs led to highly improved failure load. In Fig. 3b it is observed that huge agglomerations lead to microvoids which dropped the failure load and the elongation at failure.

Figure 4. Mixed failure mechanism on debonding surface of specimen reinforced with 2wt.% NSPs.

In Fig.4, the debonding surfaces of 2wt % NSP specimen are shown where the failure mechanism is mostly cohesive type. On the other hand, considering that the neat adhesive showed pure adhesion type failure, it can be understood that the NSP particles have probably improved the adhesion properties by increasing the wettability of the adherend surfaces. Consequently, this has altered the failure mechanism from adhesion to adhesion/cohesive failure resulting in higher failure loads.

NCP Nanocomposites

In the case of a nanocaly set of joints, the concentration of 1wt.% has shown a considerable improvement in failure load by 48%. The same failure mechanism explained for NSPs in Fig. 4 was also observed for 1wt.% NCPs as well resulting in mixed failure where neat adhesive had a pure adhesion failure. Similar to NSPs, adding more NCPs diminished the failure load to levels lower than the neat adhesive because of huge agglomerations (Fig 5b). The elongation at failure also peaks at 1wt.% concentration similarly and reaches 39% improvement. These outcomes can be attributed to the dispersion level of silicate layers in NCPs. XRD results for NCP-reinforced composites are shown in Fig. 6 where the calculated value of the initial interlayer spacing of NCP is 2.658 nm. As the first peak of the nanocomposites points out, this value was increased to 3.790 nm for 5wt% NCP addition and the intensity of this peak was reduced for 1 wt% NCP reinforcement. This outcome indicates intercalated (possibly with limited exfoliation) and intercalated/exfoliated morphologies for 5 wt% and 1 wt% reinforced nanocomposites, respectively. The results reveal, on the one hand, only intercalated morphology is not enough for efficient stress transfer to silicate layers of NCPs rather resulting in stress concentration effect which is confirmed by diminished mechanical properties of 5 wt% reinforced NCP-nanocomposite (Table 2). On the other hand, intercalated/exfoliated morphology achieves significantly improved mechanical properties revealing the necessity of exfoliation. SEM image (Fig. 5b) also supports the XRD outcomes that there is no noticeable agglomeration for 1 wt% NCP reinforced nanocomposite. In addition to it, the area under load-displacements curves of Figure 2 becomes maximum with the addition of either 2 wt% NSP or 1 wt% NCP . These particular nanocomposites leading to maximum failure load, also absorb the highest energy until rupturing. This could be attributed to their optimal amount leading to agglomeration-free distribution.

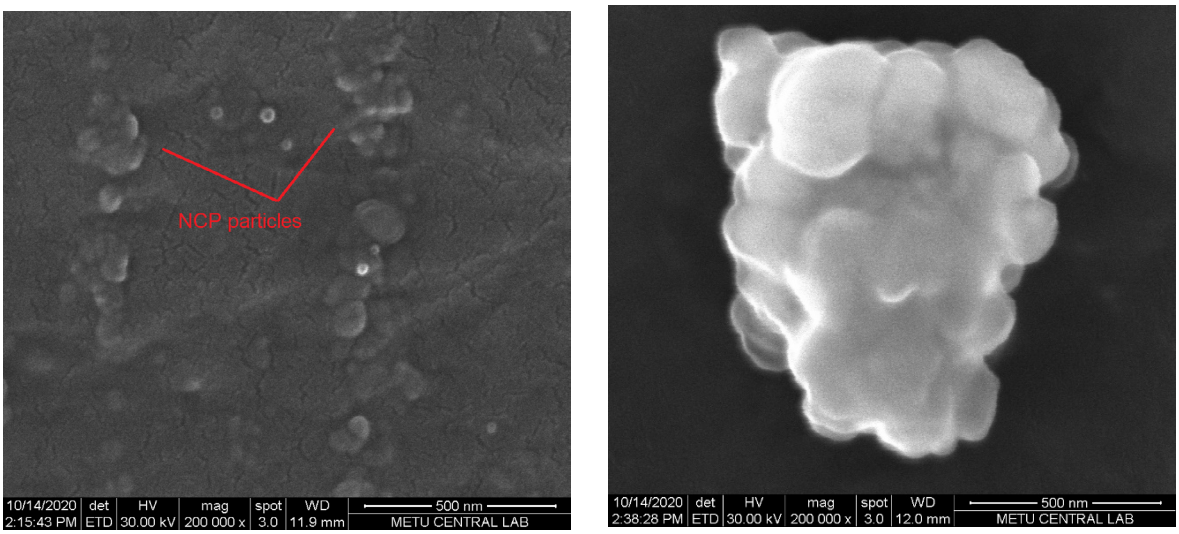

Figure 5. SEM images of reinforced adhesives with NCPs, (a) no visible agglomeration at 1wt.% and (b) huge agglomerations at 5wt.%.

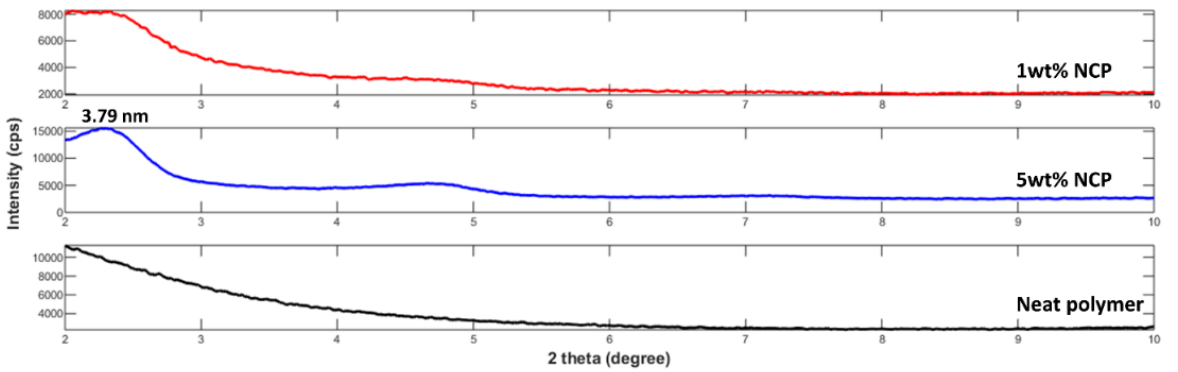

Figure 4. Mixed failure mechanism on debonding surface of specimen reinforced with 2wt.% NSPs.

Co-addition of NSP and NCP

The failure loads of all the joints in the third set (mixed composition) have been decreased to values much lower than the neat adhesive (maximum 86.5% reduction). However, the elongation at failure for a concentration of 5wt.% has been improved by nearly 90%. This intriguing outcome should have resulted from the large agglomerations of NCP and NSP combinations. It is well-known that microvoids could be formed around the agglomerations which absorb the energy for crack propagation and enable plastic deformation. The low failure loads are also attributed to the formation of these agglomerations observed in all concentrations (Fig 7). Having diverse shapes and aspect ratios, NCP and NSP inhibit the interaction of each other with the polymer chains. For instance, NSP acts as a barrier for polymer chains to penetrate the NCP silicate layers restricting intercalation and exfoliation. Similarly, NCP limits the surface attraction of NSP with the polymer chains resulting in agglomerations rather than well-dispersion.

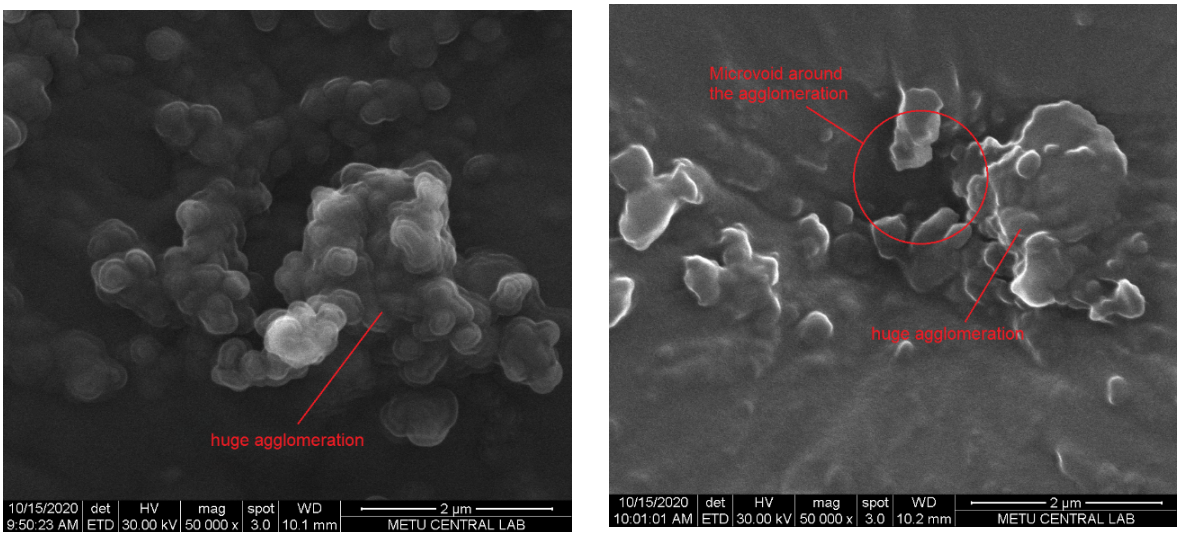

Figure 7. SEM images of reinforced adhesives with mixed NSP/NCP, (a) agglomeration at 1wt.% and (b) microvoids around huge agglomerations at 5wt.%.

Conclusion

In this study, two different nanoparticles, and mixtures of them were utilized to modify an epoxy-based structural adhesive, in three different weight percentages.

- It was observed that the adhesives reinforced by 1wt.% nanoclay and 2wt.% nanosilica reflected the greatest improvement in the failure load of the joints compared with neat adhesive due to good dispersion quality and shifting the failure mechanism from the adhesion type to the adhesion/cohesion type.
- The higher concentrations or even the mixture of both nanoparticles have reduced the failure load considerably, resulting from the poor dispersion quality due to huge agglomerations.
- The addition of different nanoparticles should be applied carefully where both nanoclay and nanosilica improved the failure loads individually but the mixing of them lead to huge agglomerations in all concentrations.
- It was observed that the increase in the concentration of mixed particles (NCP and NSP) improved the elongation at failure tremendously. The dispersion quality of the nanoparticles and the formation of the large clusters inside the reinforced adhesives were reasoned for the noticeable alternations in the parameter.

Declarations

- Partial financial support was received from [TED University] under grant agreement No [T-18-B2010-33021]
- The authors have no other financial or proprietary interests in any material discussed in this article.

References

1. L.F.M da Silva, A. Öchsner, and R.D. Adams, Handbook of Adhesion Technology, Springer International Publishing. (2018).
2. R.D Adams, N.A. Peppiatt, Stress analysis of adhesive-bonded lap joints. J. Strain Anal., 31 (1974) 185-196.
3. B. Paygozar., S.A. Dizaji, L.F.M. da Silva, Bonding dissimilar materials via adhesively bonded spot-welded joints: cohesive zone model technique. J. Adhes. Sci. Technol., 34(21) (2020) 2352-2363.
4. P. Jojibabu, Y.X. Zhang, B.G. Prusty, A review of research advances in epoxy-based nanocomposites as adhesive materials. Int. J. Adhes. Adhes., 96 (2020) 102-454.
5. S.M.R., Khalili, Numerical study of lap joints with composite adhesives and composite adherends subjected to in-plane and transverse loads. Int. J. Adhes. Adhes.,. 28(8) (2008) 411-418.
6. G. A. Nemati , Effect of reinforcements at different scales on mechanical properties of epoxy adhesives and adhesive joints: a review. The Journal of Adhesion, 94(13) (2018) 1082-1121.
7. Z. Wang, Bonding strength and water resistance of starch-based wood adhesive improved by silica nanoparticles. Carbohydr. Polym., 86(1) (2011) 72-76.
8. S. A. Nassar, Effect of Adhesive Nanoparticle Enrichment on Static Load Transfer Capacity and Failure Mode of Bonded Steel–Magnesium Single Lap Joints. J. Manuf. Sci. Eng., 137(5) (2015).
9. S. Hassanifard, B. Paygozar, Investigation of an Optimum Concentration for Nano-Silica Used as an Adhesive Bonding Strength Enhancer. J. Fail. Anal. Prev., 18(2) (2018) 315-321.

10. 10. B. Paygozar, M.A. Saeimi Sadigh, Adhesively Bonded Aluminum Double-Strap Joints Improved by Nano-silica. Trans. Indian Inst. Met., 73(5) (2020) 1401-1406.
11. M. R. Ayatollahi, Mechanical properties of adhesively single lap-bonded joints reinforced with multi-walled carbon nanotubes and silica nanoparticles. J. Adhes Sci Technol., 93(11) (2017) 896-913.
12. M. Shettar, Experimental investigation on mechanical and wear properties of nano clay–epoxy composites. J. Mater. Res. Technol., 9(4) (2020) 9108-9116.
13. Z. Ahmadi, Nanostructured epoxy adhesives: A review. Prog. Org. Coat., 135 (2019). 449-453.
14. S. M. R. Khalili, M. Tavakolian, A. Sarabi, Mechanical Properties of Nanoclay Reinforced Epoxy Adhesive Bonded Joints Made with Composite Materials. Journal of Adhesion Science and Technology, 24(11-12) (2010) 1917-1928.
15. M. Aliakbari, O. M. Jazani, M. Sohrabian, Epoxy adhesives toughened with waste tire powder, nano clay, and phenolic resin for metal-polymer lap-joint applications. Prog. Org. Coat., 136 (2019) 105-291.
16. H. Dodiuk, I. Bellinski, A. Dotan, S. Kenig, Polyurethane adhesives containing functionalized nanoclays. J. Adhes Sci Technol., 20(12) (2006)1345-1355.
17. S. G. Semerdzhiev, Metal-to-metal Adhesive Bonding, Business Books (1970).
18. L. Kozma, I. Olefjord, Basic processes of surface preparation and bond formation of adhesively joined aluminum. Mater. Sci. Technol., 3(10) (1987) 860-874.
19. R. Prakash, V. K. Srivastava, G. S. R. Gupta, Behavior of adhesive joints in a corrosive environment. Exp. Mech, 27(4) (1987) 346-351.