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Evaluation of structural epoxy and cyanoacrylate adhesives on jointed 3D printed polymeric materials

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ABSTRACT

In this paper, comparisons of the adhesive strengths of two commercially available adhesives, epoxy and cyanoacrylate, on 3D printed plastic materials, Acrylonitrile Styrene Acrylate (ASA) and Nylon 12 Carbon Fiber (NCF) were carried out. The single lap shear test is used to determine the adhesive properties of the specimens with and without post-curing at elevated temperature. A comparison is made with fully printed, non-bonded specimens to give a relative gauge of the performance of the adhesives. It was found that for ASA and NCF, the adhesive strength for cyanoacrylate (CA) is much higher than that of epoxy. ASA and NCF bonded with CA had average failure load of 1810 kN and 2310 kN, respectively, as compared to those bonded with epoxy which had significantly lower failure load of 470 kN and 860 kN, respectively. It was observed that although heat treatment and surface treatment improve the adhesive strength of epoxy with both adherend materials, the improved adhesive strength of epoxy is still observed to be significantly weaker than that of CA.

1. Introduction

Rapid prototyping, or more commonly known as 3D printing, is an additive manufacturing method which has recently experienced a boom in terms of technological advancement and widespread adoption across industries such as biomaterials, aerospace and electronics. Various advantages of 3D printing include the ability to manufacture complex structures, short prototyping lead time, mass customization, waste minimization and freedom of design. However, despite the advantages that 3D printing might offer over conventional manufacturing methods, there are some potential downfalls. The anisotropic material properties, a result of the 3D printing process, and the size limitation of the machines are some disadvantages that require further in-depth studies to ensure that there is a wider adoption of the technology.

The Fused Deposition Modelling (FDM) technique is a 3D printing method that builds three-dimensional parts by drawing a filament through a layer by layer fashion to form the desired geometry. Review by Lee et al. [1] has shown that Acrylonitrile Butadiene Styrene (ABS), Acrylonitrile Styrene Acrylate (ASA), Polylactic Acid (PLA) and Polycarbonate (PC) are some of the typical materials used in FDM. Due to the limitations of 3D printers, there is often a trade-off between print resolution and part size. Yap et al. [2] have shown that large intricate parts often have to be printed in several separate components prior to being joined together to obtain the desired part. The joints, more often than not, become the weakest link in the entire structure if not done properly and could lead to catastrophic failure. Stokes [3] reviewed the jointing methods for plastics and plastic composites, and some of the commonly used joining methods include mechanical joints, such as dovetail joints and various woodworking joints, joints using screws and bolts, welding and adhesive joints, each of which is especially suited for specific materials and structures. With relatively low strength of these 3D printed plastics, mechanical joints are not recommended as they induce large amounts of stress concentration. Espalin et al. [4] investigated on various joining methods on 3D printed polymer and their results showed that welding of plastic materials, made possible through hot air welding and ultrasonic welding, allows very good adhesion between components. However, it is a technique that requires the labor of a skilled technician to achieve high joint quality. Alternatively, adhesives may provide an easier way for joining components without compromising on the mechanical performance of the structure.

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However, there exists a plethora of adhesives in the market which possess different adhesive strengths when used to bond different materials together. Using an unsuitable adhesive thus would lead to catastrophic failure of structures, which can and should be avoided. Furthermore, the study by Unuk et al. [5] has revealed that under elevated temperatures, the performance of adhesives may be altered and this becomes a point of consideration for particular applications which require operations under higher temperatures or are stored under elevated temperatures. To the best of the authors' knowledge, whilst adhesive tests have been extensively studied for polymers or composites fabricated by the traditional molding and subtractive manufacturing methods, for instance, Hall, et al. [6] investigated the adhesive bonding on polymers such as polyethylene, polypropylene, polystyrene and nylon 6 while Awaja et al. [7] reviewed the adhesive bonding for general polymers in terms of adhesion mechanisms, promoters and measurement techniques, there is very limited literature on recommendations for adhesives suitable for various FDM printed plastic materials, with the exception of a general study of various adhesive behaviors on the 3D printed material investigated by Espalin et al. [4].

In this paper, mechanical tests on two types of FDM materials, Acrylonitrile Styrene Acrylate (ASA) and Nylon 12 Carbon Fiber (NCF) and two types of commercially available adhesives, epoxy and cyanoacrylate, were performed to evaluate the adhesive performance of the various permutations of specimens and adhesives. ASA is chosen in this study because ASA, being UV resistant, is widely used for printing the outdoor end-use parts while the newly introduced NCF was selected as it possesses the highest strength-to-weight ratio and stiffness among FDM materials. As for the adhesives, epoxy and cyanoacrylate were used in this study because they are two of the most commonly used adhesives for polymer. This paper is written with an aim to provide a guideline for other FDM users to save time and costs on the selection of appropriate adhesives for their various purposes.

2. Experimental procedure

The single lap shear test, detailed by ASTM D3163-01 and ASTM D1002-10 [8,9], is used to test the lap shear strength of the adhesives for bonding the 3D printing polymers. According to the standards, dimensions for the single lap shear specimen is shown in Fig. 1(a) and it is printed and subsequently bonded with an overlap region of one-quarter of the specimen length. The specimen design was slightly modified to include the additional tab at the ends so that the specimens can be clamped using regular fixtures without introducing rotational moments. Each single lap shear joint specimen was printed in two parts and are bonded together with an overlapping length of 25.4 mm, as shown in Fig. 1(b) and (c).

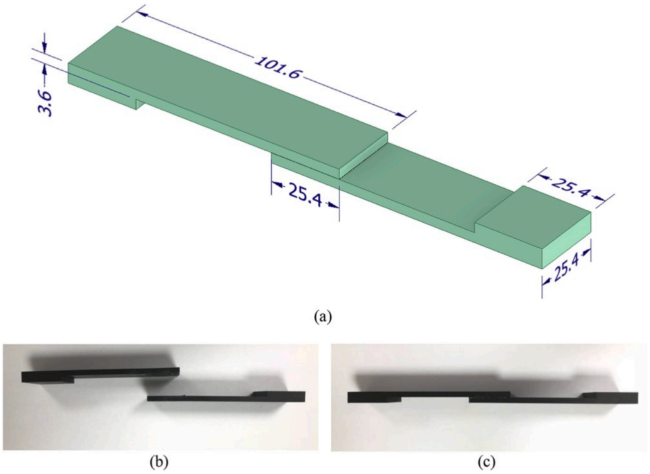


Fig. 1. (a) Dimensions of a single lap shear test specimen (unit in mm). (b) Unbonded half of single lap shear test specimen with extra tab printed. (c) Final geometry of specimen after bonding.

In addition to pairs of half-specimens, full specimens with the same geometry of the bonded specimens, printed as a single piece, were also printed to provide a comparison of the adhesive's shear strength relative to the interlayer shear strength of the printed materials.

A Stratasys Fortus 450mc industrial FDM printer (Stratasys, Ltd., Eden Prairie, MN, USA) was used to print the ASA and Nylon 12 Carbon Fiber (NCF) materials. T12 model tip and T12SR100 support tips were used for printing ASA while T20C model tip and T12SR100 support tip was used for NCF. Default FDM printing process parameters recommended by manufacturer were used and are listed in Table 1. The specimens were printed with the default 45°/-45° raster configuration in the X-orientation. The printed specimens were cooled to room temperature after printing. Upon removal from the build substrate, they were soaked in the diluted sodium hydroxide solution at 60 °C to dissolve residual support material. The specimens were washed using running tap water followed by drying in the ambient air for one day (see Table 2).

The material properties of ASA and NCF with 45°/-45° raster configuration were obtained through tensile and ultrasonic tests in our previous works and are given in Table 2 [10].

Two types of commonly used adhesives, Loctite E-20HP epoxy (Loctite Corporation, Dusseldorf, Germany) and ZAP slo-zap cyanoacrylate (Pacer Technology, California, USA), were used to join the specimens. The Loctite E-20HP is a two-part epoxy that cures at room temperature and its tensile strength, according to the manufacturer's datasheet, is 39 MPa. On the other hand, ZAP slo-zap is a cyanoacrylate (CA) with high viscosity and is able to cure within 60 s. Six pairs of half-specimens were prepared for every specimen material and adhesive combination. Before bonding, the specimen surfaces were cleaned with isopropyl alcohol. According to manufacturer recommendations, all the epoxy specimens as well as the CA specimens, which could be cured within 1 min, were allowed to cure for 24 h at room temperature after the application of adhesive for a more thorough curing. All the specimens were clamped together with spacers during curing to ensure alignment and uniform bondline thickness of 0.06 mm. Thereafter, three pairs of specimens using each adhesive were placed in an 80 °C heat chamber for 24 h to undergo heat treatment to investigate the effects of post-curing at elevated temperatures on the adhesives.

The single lap shear joint test was performed in a similar manner as tensile test (ASTM D638). The single lap shear joint was conducted at room temperature according to the ASTM D3163-01. Single lap shear specimens were subjected to a shearing stress by applying tensile load axially to the lapped substrates using the Shimadzu AGS-10kNX universal testing machine (Shimadzu Corporation, Japan) at a crosshead displacement rate of 1.3 mm/min.

3. Results and discussion

The lap shear test was first performed on the full specimens to determine the inherent material responses without the effects of any adhesion. Fig. 2 shows the load-displacement response of both types of specimens, each repeated twice. The right vertical axis depicts the corresponding shear stress from the quotient of force with the bonded area. The close agreement of both specimens for the same type of base material shows that the experiment was well-performed and reproducible. As expected, the NCF specimens exhibited larger stiffness and higher

Table 1
FDM printing process parameters for ASA and NCF.

Material	Raster width (mm)	Contour width (mm)	Slice height (mm)	Air gap (mm)
ASA	0.3556	0.3556	0.1778	0
NCF	0.5080	0.5080	0.2540	0

Table 2
Material properties of ASA and NCF.

Material	Young's modulus (GPa)	Yield strength (MPa)	Strain at yield	Ultimate tensile strength (MPa)
ASA	2.05	25	1.40	32
NCF	2.15	57	0.011	75

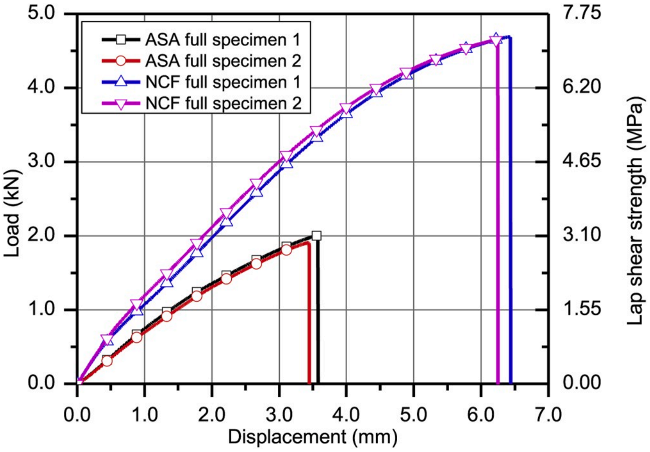


Fig. 2. Load-displacement curves of full specimens printed with ASA and NCF.

strength at failure. Comparisons between the full specimens and adhesive-bonded specimens would be helpful to better understand the effects of adhesion on the stiffness and strengths of the joints.

3.1. *Types of failure modes and effects of types of adhesive on the different materials*

Two types of failure modes were typically observed. Substrate failure was observed in all ASA specimens bonded with CA while adhesive failure occurred in all other specimens. The type of failure mode experienced depends on the relative strengths between the specimen material and adhesive. When the strength of the material is weaker than the shear strength of the adhesive used, the specimens fail by fracture in the region just adjacent to the adhesion region. Due to the symmetry of the specimens, it is expected that the specimens should break into 3 pieces in an ideal situation (Fig. 3(a), Specimen ASA CA2). However, in most specimens with adherend fracture, the fracture occurs in just one of the sides adjacent to the adhesion region (Fig. 3(b)) due to imperfections that might arise during the bonding and printing processes or due to misalignment during fixing of the specimens on the machine. Nevertheless, comparing the yield strength obtained by tensile test in previous study [10] and the failure stress of the single lap shear full specimens, there are only small differences of 16% and 10% for ASA and Nylon CF, respectively. The yield strength for the ASA tensile coupon, printed in the same configuration and printing parameters is 25 MPa while the stress at failure of the ASA single lap shear full specimen is 21 MPa. On the other hand, Nylon CF tensile specimen obtained yield strength of 57 MPa while the single lap shear full specimen experienced fracture at 51 MPa. The failure modes and fracture surfaces of the single lap shear specimens are also similar to those of the tensile specimens since they experienced fracture in the adherend outside the joint.

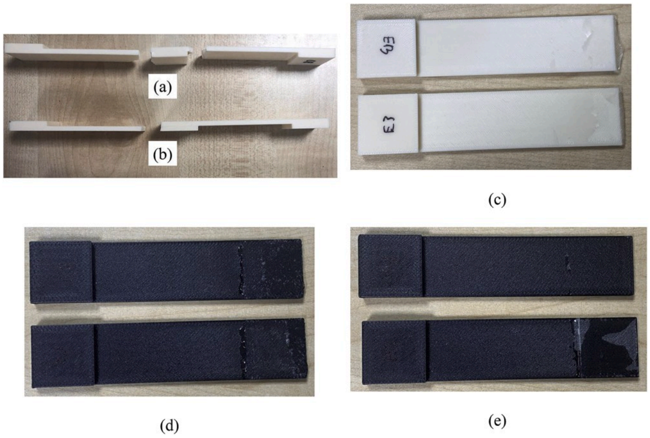


Fig. 3. Types of failure modes observed in single lap shear test specimens. (a) Substrate failure at both adherends, (b) substrate fracture at one adherend, (c) fracture surface of ASA adherend with epoxy exhibiting adhesive failure, (d) fracture surface of NCF adherend with CA, (e) fracture surface of NCF adherend with epoxy.

Comparing the maximum load experienced with the case of a full specimen, the specimens which fracture at one adherend (Specimens ASA CA1 and ASA CA3) possess significantly lower maximum load than the specimen that failed at both the adherends (Specimen ASA CA2). This is because for the energy required for two cracks to grow and fail is twice of that for failure at one side, leading to a necessary higher load.

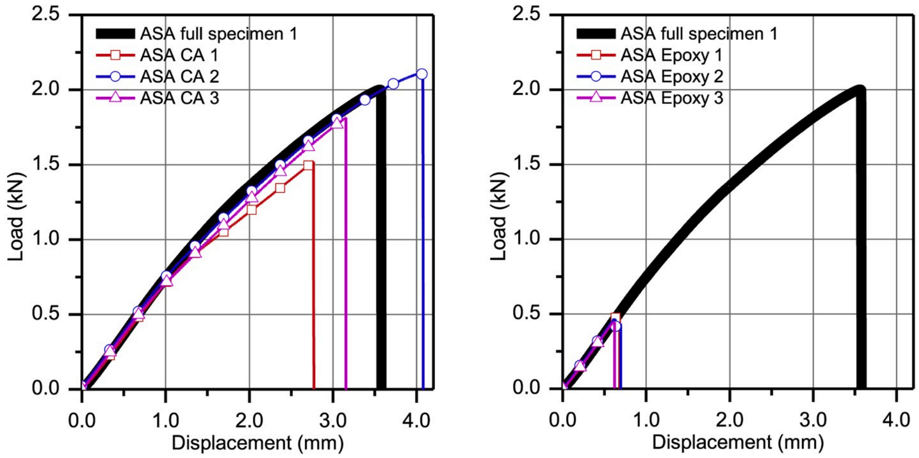
On the other hand, the adhesive failure mode suggests poor bondability between the substrate surface and adhesive. Hence, the shear strength of the adhesive is weaker than the material strength, and failure occurs by adhesive failure, as shown in Fig. 3(c)–(e).

Fig. 4 shows the load-displacement curves of both bonded using both adhesives, together with the load-displacement curves of the full specimens as a comparison. Fig. 5 shows the failure loads for various configurations of specimens. Based on the change in slope among the specimens, it can be observed that the CA joints started to deform plastically at 1 mm displacement (Fig. 4(a) and (c)). Observing from the failure load of ASA bonded with CA (1810 N), ASA bonded with CA possesses about the same strength as the full specimen with failure load of 1950 N, and both exhibited cohesive failure mode. On the contrary, epoxy bonded specimens experienced adhesive failure at a significantly lower load. This shows that ASA has a lower material strength as compared to the adhesion strength of CA but it is significantly stronger than the bonding strength of the epoxy. On the other hand, the strength of NCF is much higher than both CA and epoxy, which is observed by the significantly lower failure load of 2310 N for CA and 860 N for epoxy compared with the full specimen with 4670 N failure load. The NCF single lap shear specimens also exhibited adhesive failure modes for both types of adhesive.

For epoxy bonded specimens, both ASA and NCF failed at significantly smaller loads than the corresponding full specimens, indicating poor lap shear strength between epoxy and the adherend materials. This result is similar to the work by Espalin et al. [4] where most of the epoxy-bonded FDM polymers have much lower ultimate tensile strengths than those bonded with other adhesives and using other methods. Nevertheless, the CA bonded lap joint was able to withstand up to half of the failure load of the full specimen.

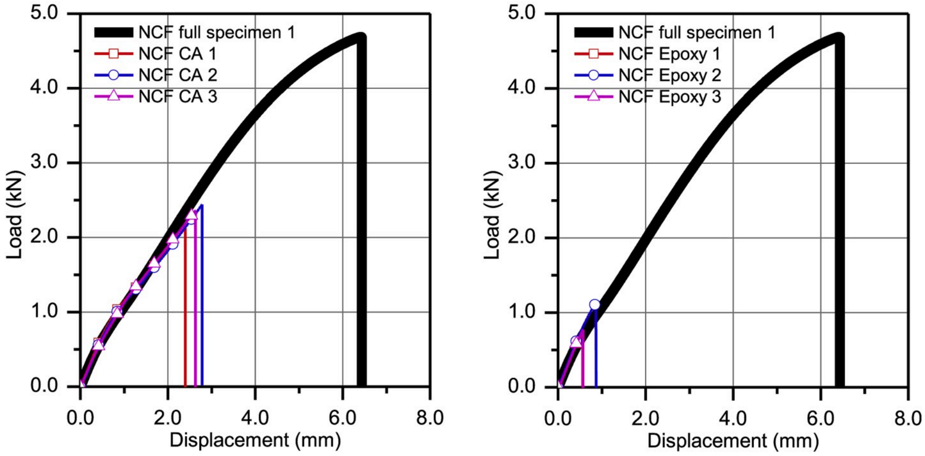
3.2. *Effects of temperature on each material*

Fig. 6 shows a comparison of the failure load of the bonded specimens with and without heat treatment. From the studies of Moniruzzaman et al. [11] and Budhe et al. [12], it is evident that heat treatment improves the strength of epoxy, due to better curing of the adhesive under heat, which increases the crosslink density of the epoxy polymer chains. However, there is no mixed observations observed from the heat treatment of cyanoacrylate specimens, evident from the reduction in the failure load of ASA and increase in failure load of NCF. As general-purpose cyanoacrylate could withstand temperatures up to about 82 °C, the strength of the adhesive joints might be affected as a result of degradation of CA adhesive. The difference in observation may be due to slight difference in the degradation transition temperatures of



(a) ASA with CA adhesive

(b) ASA with epoxy adhesive



(c) NCF with CA adhesive

(d) NCF with epoxy adhesive

Fig. 4. Load-displacement curves of adhesive bonded specimens as compared with the full specimen.

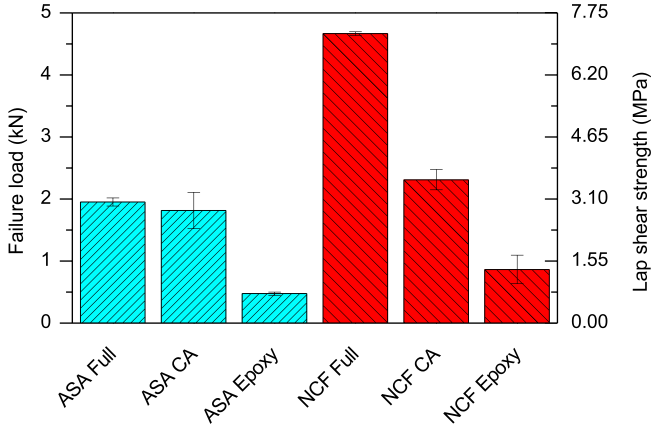


Fig. 5. Failure load and lap shear strength of specimens under different adhesive bonds.

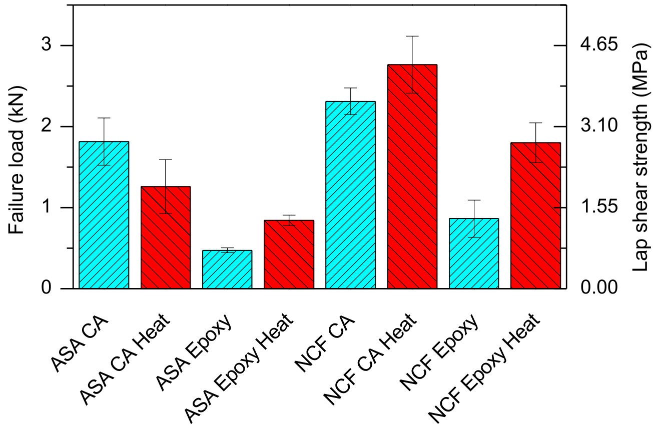


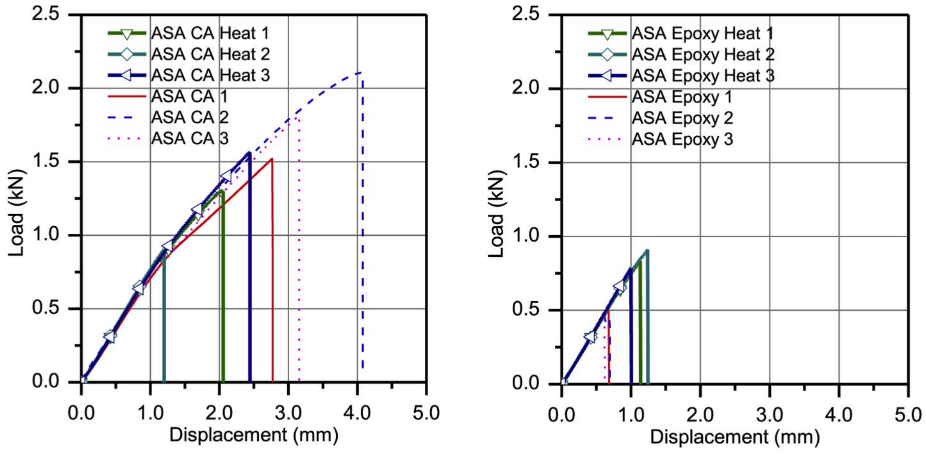
Fig. 6. Failure load and lap shear strength of specimens under different adhesive bonds and heat-treatment conditions.

CA when applied to different materials, where degradation was observed in ASA specimens and improvement was observed in NCF specimens. This shows that under the critical temperature of about 82 °C, heat treatment does improve the strength of CA, but care has to be taken not to approach the critical temperature in order to avoid degradation of the adhesive strength.

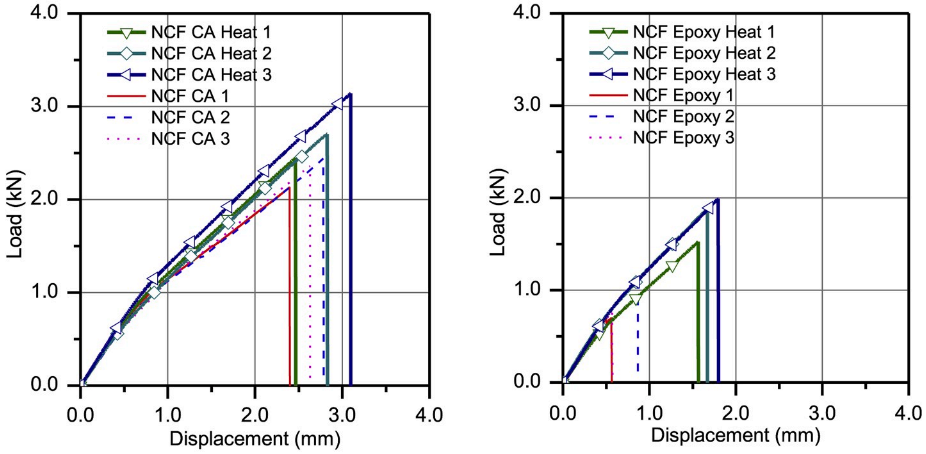
From the graphs in Fig. 7, the initial gradients of all curves remain the same despite heat treatment, indicating that stiffness of both the adhesive and adherend are not affected by heat treatment. The independence of adherend stiffness on heat treatment is to be expected as the specimens were exposed to similar temperatures during the printing process.

3.3. Effects of adherend surface conditions

In addition to cleaning procedures described earlier, additional



(a) ASA with CA adhesive (b) ASA with epoxy adhesive

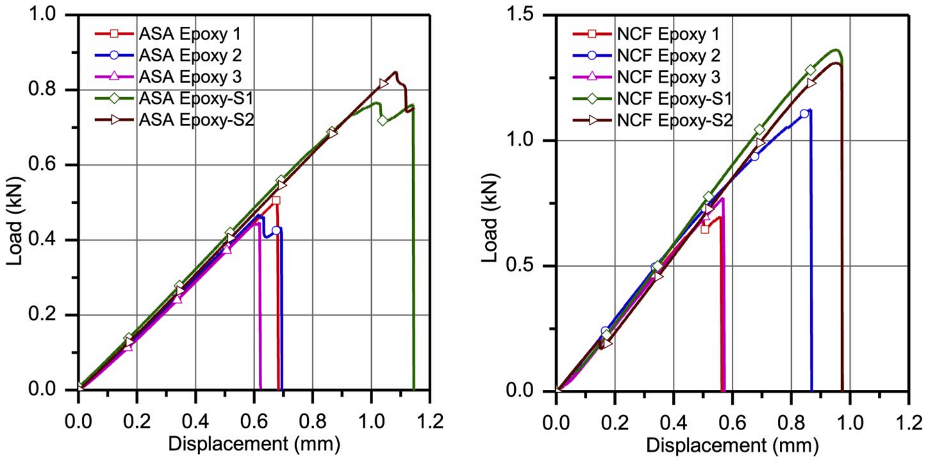


(c) NCF with CA adhesive (d) NCF with epoxy adhesive

Fig. 7. Load-displacement curves of heat-treated bonded specimens with untreated bonded specimens.

surface treatments including solvent wiping and sanding were carried out to compare the effects of adherend surface condition to epoxy bonding of both materials. In this study, ethanol and acetone are used as solvent for cleaning the surface of ASA and NCF, respectively. After solvent wiping, the bonding surface was sanded using a 320 grit silicon carbide sandpaper. Finally, the adherends were wiped with solvent and were allowed for evaporation of solvent for 20 min before bonding.

The surface roughness of both ASA and NCF were analysed before and after surface treatment using Keyence 3D laser confocal microscope, VK-X250. The Ra values for ASA are 13 μm before surface treatment and 5 μm after surface treatment while NCF has Ra values of 19 μm and 13 μm before and after surface treatment, respectively. After surface



(a) ASA with epoxy adhesive (b) NCF with epoxy adhesive

Fig. 8. Load-displacement curves of specimens before and after surface treatment (the specimens after surface treatment are indicated by S1 and S2).

treatment, Rz value for ASA reduces from 120 μm to 75 μm while Rz value for NCF reduces from 178 μm to 140 μm. The difference in the surface conditions before surface treatment is mainly due to the different printing parameters as shown in Table 1.

Additional 2 specimens were prepared and tested to analyse the effects of surface treatment on the epoxy bonding on ASA and NCF. Fig. 8 shows the load-displacement curves of ASA and NCF before and after surface treatment. For ASA, there is a significant improvement on the adhesive shear strength after surface treatment which can be attributed to the improved surface conditions of the ASA after sanding. The average failure load increases about 70% from 473 N to 808 N after surface treatment. On the other hand, the load at failure for NCF also improves approximately 54% from 864 N to 1335 N after surface treatment. Despite the improvement in the lap shear strength of the epoxy bond after surface treatment, the loads at failure are still much inferior as compared to the full specimens or to the CA bonded specimens. Nevertheless, this analysis shows that the surface conditions of the 3D printed adherends do have a significant effect on the adhesive bonding of lap shear joints. It is, therefore, recommended to carry out surface treatment such as solvent wiping and sanding to enhance bonding between 3D printed surfaces and epoxy.

4. Conclusion

Single lap shear tests were performed on 3D printed ASA and Nylon 12 Carbon Fiber specimens, which were bonded using epoxy and cyanoacrylate adhesives. Heat treatment at about 80 °C was also performed to compare and determine whether post-curing at elevated temperature has effects on the adhesive properties. The tests performed show conclusively that epoxy is not a suitable adhesive for the adherend materials tested, namely ASA and NCF. On the other hand, cyanoacrylate has shown varied changes with elevated temperature, which is likely due to the heat treatment temperature being close to its glass transition temperature that causes degradation in adhesive strength. While CA possesses significantly higher adhesive strength than epoxy, it was observed that the adhesive strength of CA with particularly the ASA adherend was significantly higher, evident from the adherend exhibited cohesive failure at high strains as compared to the adhesive failure in all other cases. In addition, it was observed that CA strength remains relatively invariant under heat treatment whereas epoxy shows a significant increase in strength after heat treatment. Although heat treatment and surface treatment improve the adhesive strength of epoxy with both adherend materials, the improved adhesive strength of epoxy is still significantly weaker than that of CA.

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