

# Effect of zinc oxide nanoparticles on the mechanical properties of the recycle acrylonitrile butadiene styrene polymers

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## ABSTRACT

One of the primary issues with waste management and environmental preservation in recent years has been the recycling of plastic. Polymer materials are used in many aspects of daily life and business. In addition to their extended use, plastic waste became a problem since it was a persistent and dangerous after discarding. Reusing polymeric materials maximises waste utilisation to create consumable items and creates a path of valorisation, or a second life. The 3D printing sector is rapidly growing. A variety of thermoplastic materials, including recycled ones, can be used to make printable filaments. The article detailed a new application for material recovered from the recycling of acrylonitrile-butadiene-styrene (ABS): filaments that may be used in 3D printing were made by combining material gathered from 3D printing waste with machine filament waste. Using a universal testometer, samples of recycled ABS (rABS) and virgin ABS (vABS) from printing waste were mixed at seven distinct concentrations. The recycled polymer ABS was mixed with varying concentrations of zinc oxide nanoparticles (ZnO nano), and the impact of these particles on the mechanical characteristics of the polymer was investigated. After mixing the recycle polymer with nano filler ZnO at 3% concentration, fatigue tests were conducted on it.

**Keywords:** recycled polymer, 3D printing, filament production.

## INTRODUCTION

Using 3D printing technology, fused deposition modelling (FDM) is a quickly developing technique for creating small quantities and prototypes of polymer-based products [1]. Researchers and industry professionals are increasingly using this manufacturing technique, which falls under the category of additive manufacturing engineering, for research and development [2]. Fused filament fabrication (FFF), also known as FDM, uses filaments made from ABS or other polymers [3]. The fabrication of complex shapes and structures with effective material management is made possible by additive manufacturing processes, which reduce waste and gain appeal. The ability to design freely, customise on a large scale, reduce waste, build complex structures,

and quickly produce prototypes are the main benefits of additive manufacturing (AM), often known as 3D printing [4, 5]. Melting the raw material and then shaping it to create new shapes is the basic idea behind the FDM manufacturing method [6]. The most common kind of filament used in 3D printing is thermoplastic. Acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) are the two most often utilised materials [7]. Reusing post-consumer and post-print waste by turning them into feedstock for 3D printers is a practical way to combat the expanding issue of plastic waste. One of the most significant topics currently on national agendas is the energy transition, which is a component of the Paris Agreement, which calls for lowering carbon emissions and reaching net zero by 2050 [8]. Although there are benefits, 3D printing

produces significant quantities of waste due to unsuccessful prints or discarded support structures [9]. Furthermore, many prints are used as disposable prototypes, because they may be produced without the requirement for machining or other equipment [10]. Due to developments in additive technologies, thermoplastic prints are becoming more and more common, which presents a waste management concern. Making use of filaments made from recycled plastics could be one such choice. The extrusion procedure is usually utilised to create the filaments that are frequently used in 3D printing. In order to create a consistent material in the form of a line, granules or polymer powder are fed into an extruder, where they are heated. A standardised diameter that fits the size of the printer component is one of the unique features of filaments. Businesses are increasingly offering filaments produced from recycled ABS or PLA. Unfortunately, nothing is currently known regarding the mechanical properties of recycled filaments [11]. They have a significant effect on print quality. Therefore, the basic knowledge needed to enhance the 3D printing technology will be obtained by looking at these properties of recycled filaments and comparing them with unused material.

Previous studies on the secondary use of materials in additive technologies have largely concentrated on the effective use of filament to create three-dimensional objects [12, 13]. Because of the interactions at the nano scale, nano composite filaments for 3D printing are very popular these days. The mechanical stability and durability of the resulting materials may be enhanced by these interactions [14]. This study investigated the influence of recycling on the stress levels of ABS by including seven distinct quantities of the original ABS polymer and conducting experimental analyses on various mechanical properties of the recycled ABS material. An innovative experimental simulation was developed to assess the indoor recyclability of ABS filament. Furthermore, it examines and evaluates the mechanical properties of recycled ABS filament incorporating ZnO nano alongside the same recycled polymers. ZnO nano are of significant importance due to the features of zinc oxide, including its chemical stability, semiconductivity, and exceptional mechanical toughness [15]. The aim was to determine the impact of rABS treatment on the mechanical behaviour of the material.

## MATERIALS AND METHODS

The purpose of the study was to investigate the possibility of recycling waste from functioning parts and filament waste produced by 3D printers made of ABS polymer. ABS is a prevalent substance in material extrusion 3D printing [16]. ABS was chosen as the polymer matrix due to its extensive application across several industries, particularly in 3D printing, owing to its favourable physical and mechanical characteristics [17]. The primary mechanical characteristics of ABS are its impact resistance and toughness. The moulded pieces eligible for mechanical recycling were chosen based on their exterior dimensions, wall thickness, and the length of the flow route of the molten polymer during primary processing [18, 19] with its superior impact strength and many applications, constitutes a significant portion of WEEE. Although diverse approaches to recycling ABS have been developed, there remains an unmet need to enhance the mechanical properties of post-consumer recycled ABS with high recycling efficiency. The major hurdle to recycling ABS is caused by the thermo-oxidative degradation of the butadiene phase and phase separation between ABS and additives, which reduce the impact strength. Conventional methods employed compatibilizers and organic solvents to improve the compatibility between ABS and additives. Nevertheless, these approaches typically consume large amount of solvents, and thereby have limitations in terms of process feasibility, recycling efficiency, and environmental considerations. Here, we used plasma-assisted mechanochemistry (PMC). Making the right reinforcing choice is essential to enhancing the qualities of the matrix material. The technique, manufacturing cost, particle size and shape, and necessary composite qualities are taken into consideration while choosing reinforcement [20].

### Filament fabrication

Using filament extruders, which are plastic extrusion machines, thermoplastic filaments are produced for use in 3D printers. Raw plastic granules and any other additives, are combined in a mechanical mixer to run extrusion systems. Granules of ABS were mixed with powdered reinforcing material (ZnO) using a rolling mixer powered by electricity in a dry mixing mechanical method (ball mill) [21]. At a rotational speed

of 40 revolutions per minute, the mixing process took an average of one hour for each sample. After that, a screw shaft was used to move the composite grains via a feed hopper to the side of the heating nozzle [22].

### Preparation of 3D-printed samples

3D printer filaments with different concentrations of (rABS) ranging from 0% to 100% with (vABS) and a filament made from recycled ABS polymer with varying amounts of ZnO filler (1, 2, 3, 4, and 5% wt.) were fed into the printer to create 3D-printed specimens. All samples were printed using the following parameters: raster angle (45°), infill speed 40 mm/s, nozzle temperature 250 °C, nozzle diameter 0.40 mm, bed temperature 95 °C, and layer height 0.20 mm. The zigzag pattern was printed at a speed of 300 mm per minute.

### Scanning electron microscopy (SEM) test

Chemical elemental analysis of the sample was carried out using SEM test. To explain the organisation of the nano filler ZnO in the recycle polymer and the concentration of the same particle in the polymer from energy dispersive spectroscopy (EDS), the SEM samples were taken from the recycling polymer after the filament had been extruded by a machine extruder. EDS and SEM combine to produce semi-quantitative and qualitative findings. When combined, the two methods may reveal basic details on the material composition of scanned specimens that standard laboratory testing is unable to provide [23].

### Tension test

New ABS filament with a diameter of 1.75 mm was used to manufacture the testing specimens that were used initially. The subsequent specimens were made with varied amount of recycled ABS polymer and different amounts of ZnO

nano filler for each of the cases that were investigated. The tensile specimens that were manufactured in accordance with the standard D638 of the American Society of testing materials (ASTM) are displayed in (Fig. 1) [24]. The testometric device was used to conduct tensile tests. In order to obtain stress-strain curves for each sample, five specimens of each material were tested.

Samples were placed in the universal tester used in the mechanics laboratory according to ASTM D638 test to assess the tensile strength of specimens (Fig. 2)

The samples were positioned in the tester with the grips set at a certain distance apart, and then subjected to tension until they break. The test speed of the material was established according to the specifications of ASTM D638 and is equivalent to 2 millimetres per minute. The testometer is used to determine the elongation and tensile modulus. The ASTM D638 test technique aims to produce precise tensile property data that may be used to specify and regulate plastic materials. In addition to being useful for qualitative characterisation, these data are also advantageous for research and development.

### Bending tests

In accordance with ASTM D790, bending test specimens were 3D printed with dimensions of 125 mm in length, 12.7 mm in breadth, and 3.2 mm in thickness [25]. For every case, five specimens must be tested. A microcomputer-controlled electric universal testing equipment with a 75 mm support span that was compliant with the three points test was used to conduct the bending tests. For testing, the machine chuck speed was set to 5 mm/min. Experimental data of force (Newton) versus displacement (mm) are recorded at a sampling rate of 2000 Hz and stored in a file. The experiments were carried out at 22 °C, or room temperature. In these investigations, the flexural strength and flexural modulus of elasticity of

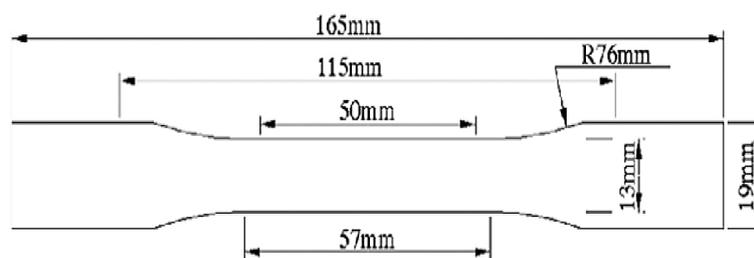


Figure 1. Tensile test specimen according to ASTM with thickness of ( $t = 3.2$  mm)



Figure 2. Testometric instrument

## RESULT AND DISCUSSION

### SEM and EDS test result

The energy dispersive spectroscopy analysis revealed the arrangement of ZnO nano fillers at concentrations ranging from 1% to 5% by weight within recycled ABS polymer, as illustrated in Figure 3 (a to e).

The EDS analysis of the samples demonstrated a significant concentration of zinc (Zn) and oxygen (O), suggesting the formation of zinc oxide (ZnO). Figure 4 illustrates the peak analysis of recycled polymer ABS with the nano filler ZnO, while Table 1 presents the concentration levels of various elements in the polymer with ZnO filler across all samples, as detailed by the EDS test. The carbon and oxygen elements shown in the peak chart represent the component of polymer material.

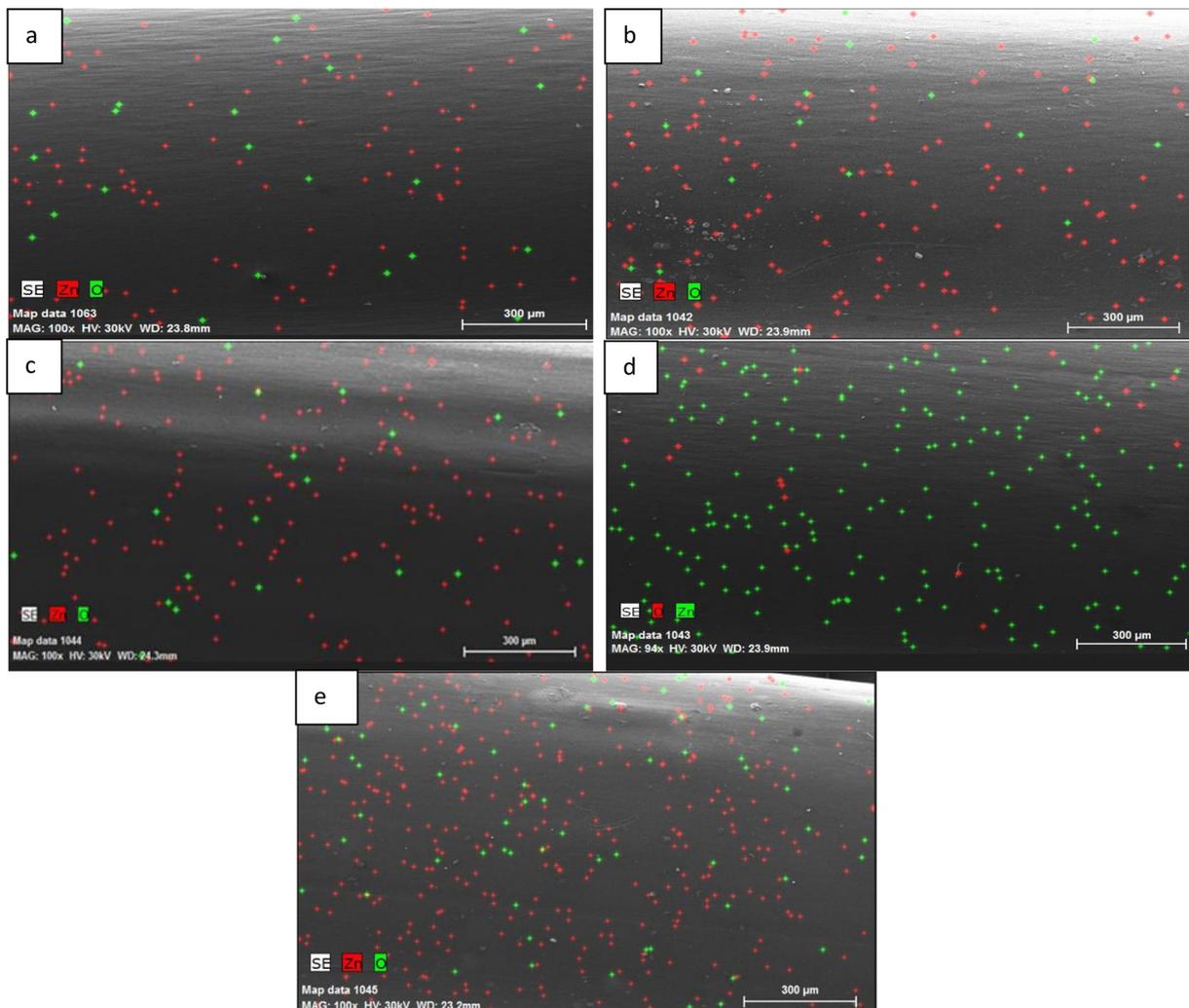


Figure 3. EDS analysis for recycle polymer ABS with ZnO filler arrangement

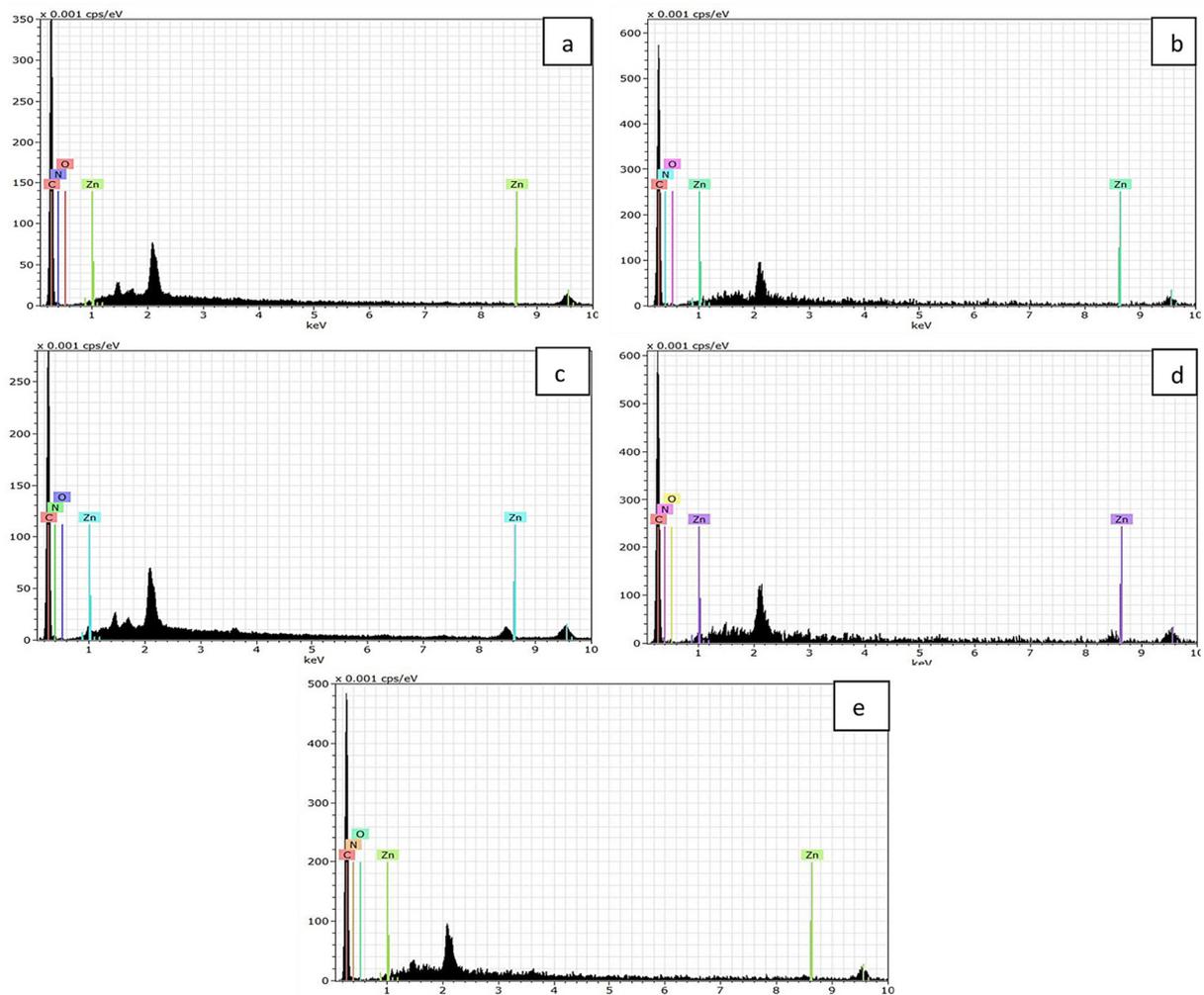


Figure 4. EDS analysis for recycle polymer ABS with ZnO concentration

Table 1. Concentration of element in polymer

Samples	ZnO% wt	Elements %			
		Nitrogen (N)	Carbon (C)	Oxygen (O)	Zinc (Zn)
a	1	14.148	84.712	0.539	0.601
b	2	14.063	83.881	1.011	1.045
c	3	13.976	83.011	1.501	1.512
d	4	13.546	82.502	2.001	1.951
e	5	13.017	82.001	2.471	2.511

### Tensile test result for recycle abs

The 35 specimens of the tensile test were examined using a testometric device for tensile testing, and the FDM samples were manufactured using a 3D printing device in compliance with the ASTM D638 requirements. The stress-strain curves for each sample were obtained by testing five specimens of each

material. Following the drawing of the stress-strain curve in (Fig. 5), the average value of the mechanical characteristics (ultimate stresses, stress yield and Young’s modulus) was determined for each sample. Table 2 displays the mechanical characteristics for every concentration of the recycled polymer ABS that was provided.

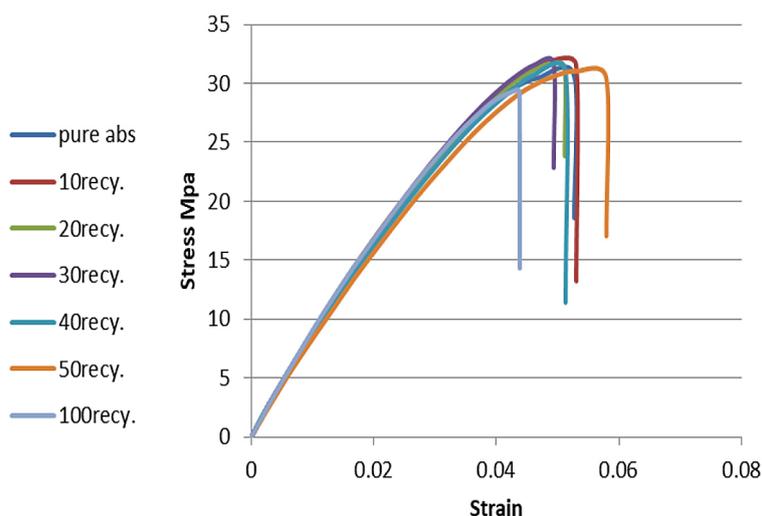


Figure 5. Stress-strain curves for different concentration of recycle of ABS

Table 2. Tension test for different concentrations of recycle polymers

Test No.	Additive ratio (% wt)	Stresses ultimate) (MPa)	Young's modulus (GPa)	Stress yield (MPa)
1	0 rABS@100 vABS	30.675	0.835	17.678
2	10 rABS@90 vABS	31.12	0.829	10.37
3	20 rABS@80 vABS	31.829	0.824	9.709
4	30 rABS@70 vABS	32.034	0.82	15.825
5	40 rABS@60 vABS	31.68	0.782	18.322
6	50 rABS@50 vABS	31.046	0.763	13.683
7	100 rABS@0 vABS	29.517	0.86	7.505

### Tensile test result for recycle ABS with ZnO nano particle

Table 3 shows the results obtained using the testometric instrument according to the ASTM D638 standards with adding nano filler (ZnO) for recycled ABS polymer, and after plotting the stress strain curve in (Fig. 6) with different concentrations of nano particle from 0% nano (0 N) to 5% nano (5 N), whereas (Fig. 7) explains the effect of concentration of filler nano particle ZnO with the recycled ABS polymer on the ultimate stress.

### Flexural test results

A testometric device was used in 3-point bending test, according to the ASTM D790 standard. The FDM printed samples were tested at different concentration of ZnO nano particle (1,2,3,4 and 5 wt.%) with the recycle of polymers ABS in testing instrument and shown in Table 4. Load deflection curve were explained in (Fig. 8), were explained the effective of concentration of filler ZnO nano particle on load.

Table 3. Tension test for different concentrations of Zno nano particle with recycle polymers ABS

Test No.	Additive ratio (% wt. nano)	Stresses ultimate (MPa)	Youngs Modulus (GPa)	Stress yield (MPa)
1	0 N	29.517	0.86	7.505
2	1 N	30.796	0.809	25.786
3	2 N	33.267	0.891	8.829
4	3 N	34.776	0.916	31.928
5	4 N	32.481	0.856	11.75
6	5 N	30.736	0.883	24.952

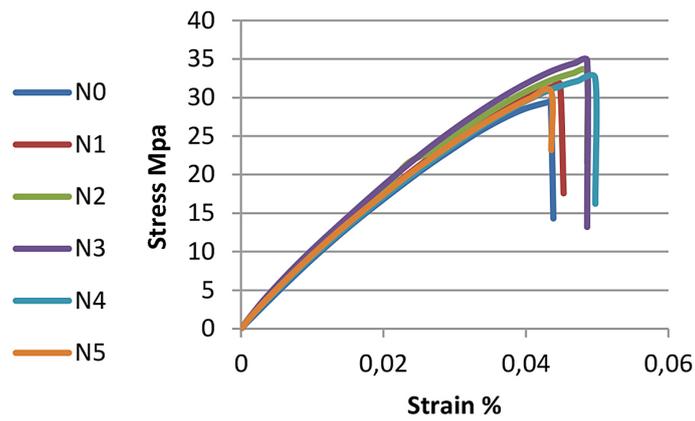


Figure 6. Stress-strain curves for recycle ABS with ZnO nano particle

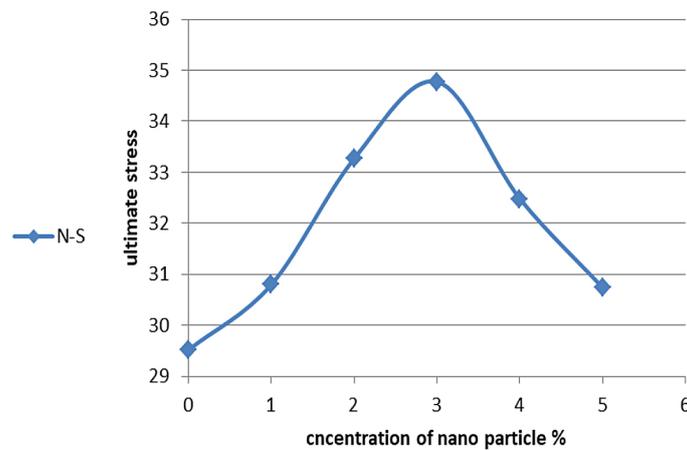


Figure 7. Ultimate stress with different concentration of ZnO nano particle

Table 4. Bending test for different concentrations of ZnO nano particle with recycle polymers ABS

Test.no	Additive ratio (% wt. nano)	Load (N)	Deflection (mm)	Bending stress (MPa)
1	0 N	61	12.5	52.75
2	1 N	62.5	12	54
3	2 N	64	11.3	55.35
4	3 N	64.5	12.7	55.8
5	4 N	50	12	43.25
6	5 N	43	12.7	31.2

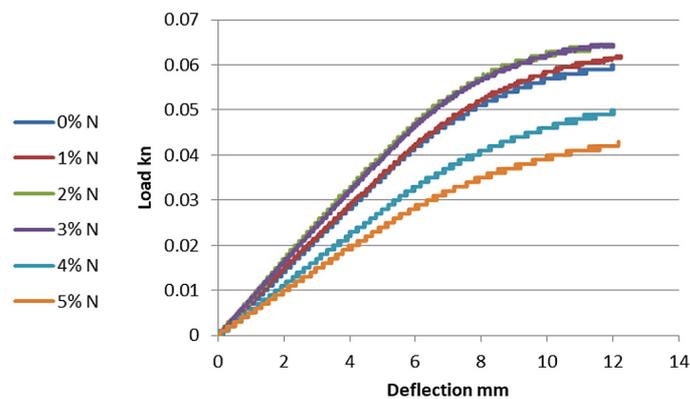


Figure 8. Load-deflection curve for different concentration of ZnO nano particle with recycle ABS



Figure 9. Alternative bending fatigue machine

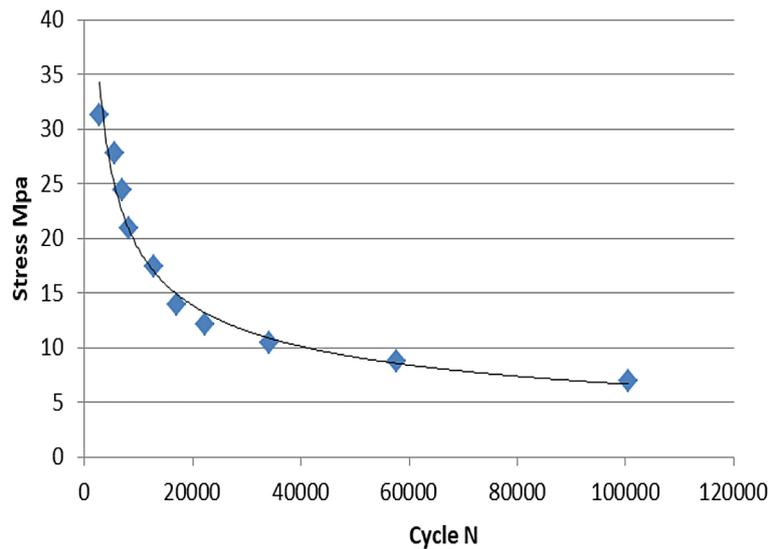


Figure 10. S-N curves for recycle polymer ABS with ZnO nano particle

### Results of fatigue tests

Alternating bending fatigue (HI-TECH) machines with constant amplitude are the kind used for fatigue testing. The fatigue test device is depicted in Figure 9. One side of the specimens was fixed to create the bending stresses, while the other side was exposed to deflection perpendicular to the specimen axis. The geometry of the fatigue specimens was as stated. The maximum alternate bending stress was calculated using the deflection measured by a dial gauge. Figure 10, S-N curve for recycling polymer ABS mixed with ZnO nano particle at 3% wt.

### CONCLUSIONS

This work produced filaments for fused filament fabrication (FFF) using varying ratios of recycled ABS polymer and zinc oxide nanoparticles. It was shown that the fabrication approach described here can be used to integrate a practical, solvent-free, commercially applicable process with the creation of homogenous, mechanically and physically improved nano composite materials for immediate commercial or industrial usage. Through a thorough examination of the results, the following conclusions were drawn:

In terms of tensile qualities, it was observed that when nanoparticle ZnO was combined with recycled polymer ABS at a concentration of 3%, the ultimate stress increased by 17%, and the stress yield increased by 74% at the same concentration of nanofiller. The addition of nanomaterial to the recycled polymer at a rate of 3% strengthened the connection between the molecules of the polymer, increasing the mechanical characteristics of the polymer. The recycled polymers will be far stronger than the conventional ones now on the market owing to the improvement in their mechanical qualities. Compared to recycled polymers alone, the recycled polymer with nano filler ZnO will withstand heavy loads and harsh mechanical conditions.

For the flexural test, there was a 5% increase in bending stress at a concentration of 3% nanoparticle ZnO. The disparity in the mechanical characteristics of nanoparticles significantly reduces the likelihood of recycled polymers failing under strong bending loads, in contrast to scenarios when just recycled polymers are utilised..

The applied load and material type have an impact on the lifespan of any polymers in fatigue testing. Recycling polymers with ZnO nanoparticles has a far longer lifespan than recycling polymers alone. Customers who have used the recycled polymers for a long time without the need for routine maintenance or the occasional new purchase will save money owing to this increase in lifespan.

## REFERENCES

1. Bieliński M., Sykutera D., Czyżewski P., Falkiewicz M., and Siutkowski S. Verification of additive manufacturing producibility of geometric objects with the help of FDM (Fused Deposition Modeling) technology. In: *Materials of Conference*, 2013.
2. Spoerk M., Savandaiah C., Arbeiter F., Sapkota J., and Holzer C. Optimization of mechanical properties of glass-spheres-filled polypropylene composites for extrusion-based additive manufacturing. *Polym. Compos.*, 2019; 40(2), 638–651, <https://doi.org/10.1002/pc.24701>
3. Czyżewski P. et al. Secondary use of ABS co-polymer recyclates for the manufacture of structural elements using the FFF technology, *Rapid Prototyp. J.*, 2018; 24(9), 1447–1454. <https://doi.org/10.1108/RPJ-03-2017-0042>
4. Ngo T. D., Kashani A., Imbalzano G., Nguyen K. T. Q., and Hui D. Additive manufacturing (3D printing): A review of materials, methods, applications and challenges, *Compos. Part B Eng.*, 2018; 143, 172–196, <https://doi.org/10.1016/j.compositesb.2018.02.012>
5. Wickramasinghe S., Do T., and Tran P. FDM-based 3D printing of polymer and associated composite: A review on mechanical properties, defects and treatments, *Polymers (Basel)*, 2020; 12(7), 1529, <https://doi.org/10.3390/polym12071529>
6. Bryll K., Piesowicz E., Szymański P., Ślącza W., and Pijanowski M. Polymer composite manufacturing by FDM 3D printing technology, in *MATEC Web of Conferences*, EDP Sciences, 2018; 2006. <https://doi.org/10.1051/mateconf/201823702006>
7. Anderson I. Mechanical properties of specimens 3D printed with virgin and recycled polylactic acid, *3D Print. Addit. Manuf.*, 2017; 4(2), 110–115. <https://doi.org/10.1089/3dp.2016.0054>
8. Abbas M. F., Mohammed A. A., Mohammed A. A., Channapattana S., and Parlak Z., *Geothermal Energy Development in Türkiye: A Review*, *Al-Nahrain J. Eng. Sci.*, 2024; 27(2), 207–225. <https://doi.org/10.29194/NJES.27020207>
9. Zhang L. and Xu Z. Towards minimization of secondary wastes: Element recycling to achieve future complete resource recycling of electronic wastes, *Waste Manag.*, 2019; 96, 175–180, <https://doi.org/10.1016/j.wasman.2019.07.026>
10. Mikula K. et al. 3D printing filament as a second life of waste plastics—a review, *Environ. Sci. Pollut. Res.*, 2021; 28, 12321–12333. <https://doi.org/10.1007/s11356-020-10657-8>
11. Mwanza B. G. and Mbohwa C. Drivers to sustainable plastic solid waste recycling: a review, *Procedia Manuf.*, 2017; 8, 649–656. <https://doi.org/10.1016/j.promfg.2017.02.083>
12. Czyżewski P., Marciniak D., and Sykutera D. Mechanical properties of ABS samples manufactured under different process conditions, *Bull. Polish Acad. Sci. Tech. Sci.*, 2024; 72(1), <https://doi.org/10.24425/bpasts.2023.147065>
13. Marciniak D., Czyżewski P., Sykutera D., and Bieliński M. Recycling of ABS operating elements obtained from industry 3D printing machines, *Polimery*, 2019; 64(11–12), 803–810. <https://doi.org/10.14314/polimery.2019.11.9>
14. Vidakis N., Petousis M., Savvakis K., Maniadi A., and Koudoumas E. A comprehensive investigation of the mechanical behavior and the dielectrics of pure polylactic acid (PLA) and PLA with graphene (GnP) in fused deposition modeling (FDM), *Int. J. Plast. Technol.*, 2019; 23(2), 195–206. <https://doi.org/10.1007/s12588-019-09248-1>
15. Collares F. M. et al. Exploring needle-like zinc oxide nanostructures for improving dental resin sealers: Design and evaluation of antibacterial, physical

- and chemical properties, *Polymers (Basel)*, 2020; 12(4), 789. <https://doi.org/10.3390/polym12040789>
16. Torrado Perez A. R., Roberson D. A., and Wicker R. B. Fracture surface analysis of 3D-printed tensile specimens of novel ABS-based materials, *J. Fail. Anal. Prev.*, 2014; 14, 343–353. <https://doi.org/10.1007/s11668-014-9803-9>
  17. Cheng Y., Yu G., Zhang X., and Yu B., The research of crystalline morphology and breakdown characteristics of polymer/micro-nano-composites. *Materials (Basel)*, 2020; 13(6), 1432, <https://doi.org/10.3390/ma13061432>
  18. Žur P., Kołodziej A., Baier A., and Kokot G. Optimization of Abs 3D-printing method and parameters, *Eur. J. Eng. Sci. Technol.*, 2020; 3(1), 44–51.
  19. Nam Y., Lee S., Jee S. M., Bang J., Kim J. H., and Park J. H. High efficiency upcycling of post-consumer acrylonitrile-butadiene-styrene via plasma-assisted mechanochemistry, *Chem. Eng. J.*, 2024; 480, 147960. <https://doi.org/10.1016/j.cej.2023.147960>
  20. Zaid H. M. A., Abed A. R. N., and Hasan H. S. Effect of Alumina ( $Al_2O_3$ ) Particles on the mechanical properties of magnesium (Mg), *Al-Nahrain J. Eng. Sci.*, 2019; 22(2), 124–130, <https://doi.org/10.29194/NJES.22020124>
  21. Geng F., Gang L., Wang Y., Li Y., and Yuan Z. Numerical investigation on particle mixing in a ball mill, *Powder Technol.*, 2016; 292, 64–73. <https://doi.org/10.1016/j.powtec.2015.11.038>
  22. Çevik Ü. and Kam M. A review study on mechanical properties of obtained products by FDM method and metal/polymer composite filament production, *J. Nanomater.*, 2020; 2020(1), 6187149. <https://doi.org/10.1155/2020/6187149>
  23. Mohammed A. and Abdullah A. Scanning electron microscopy (SEM): A review, in *Proceedings of the 2018 international conference on hydraulics and pneumatics—HERVEX, Băile Govora, Romania, 2018; 7–9*. <https://doi.org/10.1155/2020/6187149>
  24. Standard A. D638: Standard test method for tensile properties of plastics, *West Conshohocken ASTM Int.*, 2010. <https://doi.org/10.1155/2020/6187149>
  25. Radulović J. Characterization of filamentwound polymeric composite materials, *Sci. Tech. Rev.* 2008; 206, 1820.
  26. Hussain H. S. and Takhakh A. M. Mechanical properties of hybrid and polymer matrix composites that used to manufacture partial foot prosthetic, *Al-Nahrain J. Eng. Sci.*, 2017; 20(4), 887–893.