Review Article

A Review on the Mechanical, Thermomechanical Properties and Crystallinity Aspects of 3D-Printed Nanocomposites Used for Fabricating Electronic/Structural Parts

Thiruchitrambalam M[1]

1. Cosmos Design Consultants, India

Thermoplastic nanocomposites are fabricated without using solvents, i.e., by the melt extrusion method, and for this reason, this category of materials has a distinct advantage over thermoset nanocomposite materials. By using thermoplastic nanocomposites for fabricating engineering products, sustainability can be improved significantly. In addition, by adopting the additive manufacturing method, the wastage of materials can be reduced. In this short review, we report and compare the mechanical/thermomechanical properties of various 3D-printed thermoplastic nanocomposite materials. Structural integrity under operating conditions must be considered when designing electrical, electronic, or load-bearing components/products. Understanding the mechanical/thermomechanical behavior of the nanocomposite material before the design stage of the component/product is an important phase. A material having the combination of suitable properties can be selected according to the operating conditions. These nanocomposites are multifunctional, and a variety of applications can be developed, such as biodegradable electrical conductors, wearables, energy harvesters, antistatic closures, and bio-implants.

Corresponding author: M. Thiruchitrambalam, thirucbe2014@gmail.com

I. Introduction

Additive manufacturing, or 3D printing, evolved from rapid prototyping [1]. Various materials can be used for 3D printing, i.e., thermoplastics, thermosets, metals, alloys, ceramics, and composite materials. Among the plastic materials, thermoplastics are used in preference to thermoset materials because they can be recycled, material and tooling costs are relatively low, and solvents are not used during fabrication. Nanocomposite materials can be tailored, and multifunctional products can also be developed using such materials. A detailed literature survey was carried out based on articles published during the last six years on topics related to the 3D printing of thermoplastic

nanocomposite materials and the mechanical/thermomechanical properties of such materials. Data extracted from the recent literature have been categorized, compared, and presented in this article. Researchers and engineers may find this article useful when planning further research or developmental work. The mechanical/thermomechanical properties of thermoplastic nanocomposites depend on the following factors: properties of the matrix and filler, distribution of the fillers, functionalization of the fillers, and processing method [2].

Sustainability Developmental Goals and Additive Manufacturing:

The United Nations has set 17 sustainability goals to be achieved by 2030. The three pillars of sustainability are environmental, economic, and social. By evaluating various aspects related to these pillars, businesses can reduce environmental pollution, implement fair business practices related to employees and society, and also create economic value [3]. The manufacturing industries can improve sustainability by using modern technologies such as Additive Manufacturing (AM), Artificial Intelligence (AI), the Internet of Things (IoT), Data Analytics, Machine Vision, and other related technologies [Mohd. Javid 2022]. Additive manufacturing or 3D printing technologies are useful in attaining the following sustainability goals: SDG 12 – promoting responsible production and consumption, SDG 9 – industry, innovation, and infrastructure, SDG 3 – good health and well-being, SDG 4 – quality education, and SDG 14 – life below water [4].

II. Thermomechanical Properties and Crystallinity

PLA (Polylactic acid) matrix nanocomposite 3D-printed specimens were used for determining the thermal behavior of PLA–CaCO3 nanocomposites [5][6]. In the case of PLA–0.5% CaCO3, when the printing speed increased from 20 to 60 mm/s, the crystallinity decreased from 3% to 0.25%. When the printing speed was fixed and the composition was changed from 0.5% to 1% CaCO3, the crystallinity increased.

DSC tests were performed to understand the effect of co-continuity on the degree of crystallinity, and it was observed that a hybrid composite containing [7] 90% of a (PLA 65/PCL 35) blend and 10% graphene exhibited the highest level of crystallinity in both phases, i.e., PLA and PCL. The presence of PCL acted as a nucleating agent. The crystallinity of the PCL in the co-continuous composite increased to 58.5% in comparison to the neat PCL's crystallinity of 49.5% due to the presence of a continuous graphene network.

For scaffolds made of PLA–nano carbonated hydroxyapatite (CHA) fabricated by a 3D printing method [8], when CHA was 5%, crystallinity increased marginally, but for 10%, it improved considerably. Due to the presence of CHA, the thermal degradation of scaffolds (during fabrication) was reduced significantly.

PLA–carbon nanopowder filaments [9] were fabricated and characterized, and the Differential Scanning Calorimetry results indicated that Tg increased from 50.35 ^{0}C for neat PLA to 62.17 ^{0}C for the nanocarbon composite.

Zahid Sarwar et al. fabricated filaments and membranes made of PEBA-graphene nanocomposite [10]. DSC tests indicated that due to the addition of graphene to the PEBA block copolymer, the crystallinity improved significantly; for example, in the case of a filament having a composition of 0.2% paraffin and 0.4% graphene, the crystallinity was 25.5%, whereas for neat PEBA, it was only 6.96%. In the case of membranes, for the composite having the same composition, it was 10.58%. TGA (Thermogravimetric Analysis) studies indicated that due to the addition of graphene, the decomposition temperature increased.

William K. Ledford and S. Michael Kilbey II [11] synthesized novel copolymer (UPyMA)-grafted silica nanoparticles (CPGNP) and used them to reinforce PMMA (Poly(methyl methacrylate)), which resulted in improved mechanical properties (Table 1) of the 3D-printed parts. CPGNPs were synthesized by two different methods, i.e., mechanical mixing (MM) and solution mixing (SM); the nanoparticles synthesized by the latter method could be well-dispersed easily in the PMMA matrix. DMA (Dynamic Mechanical Analysis) test specimens were fabricated by a 3D printing method. The Young's modulus of the composite containing CPGNP prepared by the solution method exhibited a higher Young's modulus in comparison to MM samples, as shown in Table 2D, and the storage modulus was the highest of all the reported values.

	E MPa	**E′ or G′ MPa**
Neat PMMA	1225	1325
PMMA + 10% UPyMA-CPGNP	1800	1802

Table 1. Young's Modulus and Storage Modulus

doi.org/10.32388/Q8EF9H

Polymer nanocomposite	Tensile strength MPa	% increase	Tensile Modulus MPa	% increase	Flexural strength MPa	% increase	Flexural Modulus MPa	% increase	Impact Strength kJ/m^2	% increase	Ref
PLA – 0.5% Nano CaCO3	34.1	0.65	2662	10.7	Tensile properties correspond to a specimen with a filling ratio of 75%, printing speed of 40 mm/s, and a printing orientation of 0°						[5]
PLA – 4% TiN (filament)	51.7	29	900	24.7							[12]
PLA – 4% TiN (3D printed)	63.2	43.4	3478	21.4	107.8 ASTM D790	51.5	3600	34.8	4.1	58%	[12]
PLA – 2.5% Carbon black	51.3	5.9	316.5	6.8	92.4	38.3	2940	31.3	4.31	4.1	[13]
PLA – 8% Nano silica	55.78 ASTM D638	57.5			59.06	39.5			5.4	92.8	[14]
PLA – 2% GNP	67	43.6	2050	21	160	28.5					[15]
PLA – 1% CNT	49.7	2	2927	0.2	Elongation at break: neat PLA (7.35%), PLA – 1% CNT (4.73%)					(-35.6)	[16]
PLA – 1% CNT + 30% carbon fiber	59.98	----	12120	---						----	[16]
PLA – 0.75% CNT + 30% carbon fiber + OLA plasticizer	Specific Tensile strength 35.1 (Nm/kg), Tensile Modulus 10720 MPa - build/printing orientation - 0° Specific Tensile strength 23.5 (Nm/kg), Tensile Modulus – 6530 MPa - build/printing orientation - 90°									----	[16]
PLA – 10% nano pyrolytic carbon	52	-16.2									[17]
PLA – layered silicate nanocomposite	59.4	---	1397	---	---		Properties vary with respect to printing temperature and printing speed; only the highest values of tensile strength and tensile modulus are reported here				[18]

doi.org/10.32388/Q8EF9H

Table 2A. Tensile, Flexural, and Impact properties (Filament/3D printed specimens – % increase is reported with respect to neat/virgin thermoplastic material)

Polymer nanocomposite	Tensile strength MPa	% increase	Tensile Modulus MPa	% increase	Flexural strength MPa	% increase	Flexural Modulus MPa	% increase	Impact Strength kJ/m^2	% increase	Ref
ABS – 4% WC	42.6	29.4	288	32	63.9	20.4	2120	20.4	11	-46	[19]
ABS – 0.2% rGO (Solvent Mixing method) - filament	39	neat ABS 35 MPa									[20]
ABS – 10% MWCNT (filament)	45	45	610	90.6	--	--	---	----			[21]
ABS – 10% MWCNT	42	35.7	950	44	70	62.8	2950	84			[21]
ABS – 6% TiN (filament)	34	14	700	16.7	The tensile test was conducted according to ASTM D3822.						[22]
ABS – 6% TiN	40.1	18	27.2	22.2	66.1	36.9	2400	41.2	19.5	-14.1	[22]
ABS – 20 PBT – 0.5% CNT	36	23.3	-	----	59	40.8	2400	47.2	6.4	30.6	[23]
ABS – CNT/CNC Printing orientation 45°	34	81	2100	50	46	4.5	Interlaminar shear strength – for neat ABS is 6.5 MPa and for ABS-0.5% CNT is 12 MPa – ASTM D2344				[24]
ABS – 5% nano CaCO3 (Triangular fill)	28	133	2150	126							[25]
ABS – 6% MWCNT (filament)	47.1	10.1	2625	1.8							[26]
ABS-6% MWCNT printing orientation 0°	44.9	8.5	2735	22.4							[26]
ABS – 5% ZnO	27.8		600		48		1520				[27]

Table 2B. Tensile, flexural, and impact properties (Filament/3D printed specimens) – (% increase is reported with respect to neat/virgin thermoplastic material)

doi.org/10.32388/Q8EF9H

Polymer nanocomposite	Tensile strength MPa	% increase	Tensile Modulus MPa	% increase	Flexural strength MPa	% increase	Flexural Modulus MPa	% increase	Impact Strength kJ/m^2	% increase	Ref
PA 12- 2.5% PEG – 5% AgNO3 (filament)	43.5	238	260	35							[28]
PA 12- 2.5% PEG – 5% AgNO3 – 3D printed	41.8 (ASTM – 638 – 02a)	26	160	43.2	57.2 – ASTM D790-02	26	1310	44	9.9	-12%	[28]
PA6 – 1% GNP (NH_2 functionalized)	23	130	950	260	47	327	1400	460	-----	------	[29]
PA6 – 1% GNP (NH_2 functionalized) – 11% (continuous) Kevlar fiber	87	770	4400	1660	95		3100	1140	------	-----	[29]
PA – 6% GNP	40.8	9.7	2540	61.8	46.3	36.5	1190	54.5	7.93	-22	[30]
PA12- 5% MWCNT	49	40	187	32	56	55	1120	55.6			[19]/110
PC – 2% AlN – filament	61.7	27.6	1014	24.4							[31]
PC – 2% AlN – 3D printed	70.4	32.8	347	24.1	84	-1.2	1700	-0.1	13.5 – 3.8 ASTM-6110-04		[31]
PC – 0.5% cellulose nanofiber	69.2	10	281.7	2.7	94.2	3.3	1800	1	18.2	12.5	[32]
PC – 2% SiC	63.4	19.6	301.6	7.9	102	9.6	1900	11.7	16.4	35.9	[33]
PC/ABS (70/30) – 0.8% Graphene	32.2	57	Fracture strain for PC/30% ABS is 1.2% and for PC/30% ABS-0.8% is 0.57%								[34]

Polymer nanocomposite	Tensile strength MPa	% increase	Tensile Modulus MPa	% increase	Flexural strength MPa	% increase	Flexural Modulus MPa	% increase	Impact Strength kJ/m^2	% increase	Ref
HDPE – 1% MWCNT (functionalized) – filament – 3 times recycled	17.4	9.4	831	23	Fracture strain for the as-prepared filament is 89.2% and for the filament (3 times recycled) is 108.4%						[35]
3D printed-HDPE – 1% MWCNT – 3 times recycled	25.5	67.8	1630	97.8	Fracture strain for the as-prepared filament is 7.64% and for the filament (3 times recycled) is 4.7%						[35]

Table 2C. Tensile, Flexural, and Impact properties (Filament/3D printed specimens) – (% increase is reported with respect to neat/virgin thermoplastic material)

doi.org/10.32388/Q8EF9H

Polymer nanocomposite	Tensile strength MPa	% increase	Tensile Modulus MPa	% increase	Flexural strength MPa	% increase	Flexural Modulus MPa	% increase	Impact Strength kJ/m^2	% increase	Ref
TPU – 3% MWCNT (filament)	Tensile stress is 47.7 MPa when the strain is 300%										[36]
TPU – 10 wt% biochar (film)	38	111	Dart Impact Strength – 48.4 g (ASTM – D1709)								[37]
PEBA – 0.4 Graphene – 0.2 Paraffin liquid (filament)	21.06	-0.33	77	7.5		Fracture strain – 526%					[38]
Poly EMMA – 0.1% MWCNT	35 Notched	6.1	341	13.7							[39]
PEEK – 1% Graphene	139	25	2676	25							[40]
PEI – 5% MWCNT (filament)	97	-6.45	3310	55	Fracture strain for the neat PEI is 57% and for PEI-5% CNT is 2%						[41]
PMMA – 3% Nanosilica (Solution Mixing Method)	52	147%	198	-1%	98	2.3					[42]

Table 2D. Tensile, Flexural, and Impact properties (the values reported for the "% increase" are with respect to the respective neat or virgin polymer/plastic)

TPU – Thermoplastic Polyurethane, PEBA- Polyether block amide is a thermoplastic elastomer, PEEK – Polyether Ether Ketone, PEI – Polyetherimide

Polymer nanocomposite	Tensile strength-neat polymer MPa	Tensile Strength Composite MPa	Fracture strain-neat polymer	Fracture strain-Composite	Compressive strength neat polymer MPa	Compressive strength Composite MPa	Vicker's Micro Hardness neat polymer-	Vicker's Micro Hardness composite	Ref
PLA – 4 % TiN (3D printed)	40.2	63.2	20 %	18 %					[12]
PLA – 2.5 % Carbon black	44.1	51.3	20 %	20 %					[13]
PLA – 8 % Nano silica	35.4 ASTM D638	52			7	12			[14]
PLA – 2 % Graphene	47	67	8.2	14.3					[15]
ABS – 4 % WC	35	42.6	20 %	25 %	48.4	60.9	12.5	16.1	[19]
ABS – 5 % ZnO	26.4	27.8	4	7			0.38	0.27	[27]
PA 12 – 2.5 PEG -5%AgNO3	35.1	43.5	4.5 %	1.1 %	37.1	46.1	10.7	13.5	[1]

Table 2E. Compressive Strength – Hardness

for the composite reinforced with CPGNP-SM. The storage modulus increased with increasing CNGNP content.

PP (Polypropylene)-Al2O3 nanocomposite filament reinforced with [43] nano alumina (0.5, 1, 2, and 4 wt %) and later specimens for DMA were fabricated using a 3D printer. A composite with 2 wt % exhibited the highest damping capacity, i.e., Tan δ. Up to a temperature range of 90-1000°C, the Tan δ values increased; when T > 1000°C, it decreased, indicating the softening of the composite.

PP-SiO2 nanocomposites were fabricated [44], and it was observed that the PP-2% SiO2 composite exhibited the highest storage modulus. For a composite with 4% SiO2, the storage modulus decreased in the low-temperature range, i.e., 30°C to 60°C. An increase in storage modulus indicates that the interfacial adhesion improved. PP-TiO2 nanocomposites[45] also exhibited similar behavior to PP-SiO2 nanocomposites during dynamic mechanical analysis.

While recycling HDPE (High-Density Polyethylene)-MWCNT filament [35], after each attempt, the crystallinity increased, i.e., it increased after the first attempt, further increased after the second recycling, and further increased after the third recycling attempt. The degree of crystallinity of the printed specimens is higher than that of the filament because of the slow cooling and, in consequence, additional crystallization during 3D printing.

In the case of polycarbonate nanocomposites reinforced with 1, 2, and 3 wt % nano TiC, there was not any significant change in the storage modulus, loss modulus, Tg, and Tan δ in comparison to the neat PC, i.e., according to the DMA test conducted according to the ASTM (American Society for Testing and Materials) D4065-12.

In the case of Polycarbonate–cellulose nanofiber composites, after a DMA test, it was observed [32] that the storage modulus increased by 100% and the tensile strength increased by 10% for a composite containing 0.5 wt % cellulose. Due to the strong adhesion of CNS to PC, the relative movement of polymer chains is restricted, and due to this, the tensile strength and storage modulus increased.

In the case of PA 12 (Nylon)–MWCNT composites, a DMA test was conducted according to ASTM D4065-12, and the results indicated that with increasing MWCNT content, the storage modulus increased up to 5% MWCNT and then decreased. Flame-retardant PA 11-nano alumina was developed by William P. Fahy et al. [46]. Microscale combustion calorimetry was conducted according to ASTM D 7309–2007. The addition of functionalized alumina resulted in a higher (onset of) level of heat release temperature and thermal stability.

The presence of graphene in the PA6 (Nylon) matrix [30] considerably reduced the peak crystallization temperature; for example, for the neat PA6, it was 171.62°C, and it decreased to 159.23°C. Upon the addition of 6% graphene, the crystallinity increased by 115%. Crystallization plays an important role in improving the mechanical properties, i.e., tensile strength, tensile modulus, flexural strength, and flexural modulus, as shown in Table 2C. The role of crystallinity in the electrical properties is not clearly understood. This composite can possibly be used for developing electrostatic discharge applications.

In the case of ABS-based composites, DMA tests indicated that at ~130°C, samples CNT-HC and CNT6-H45 exhibited a storage modulus 5 times higher than ABS-HC and ABS-H45. It was observed that the storage modulus of 3D-printed specimens is lower than that of the composite filament, as expected, due to the presence of voids in the 3D-printed specimens [26].

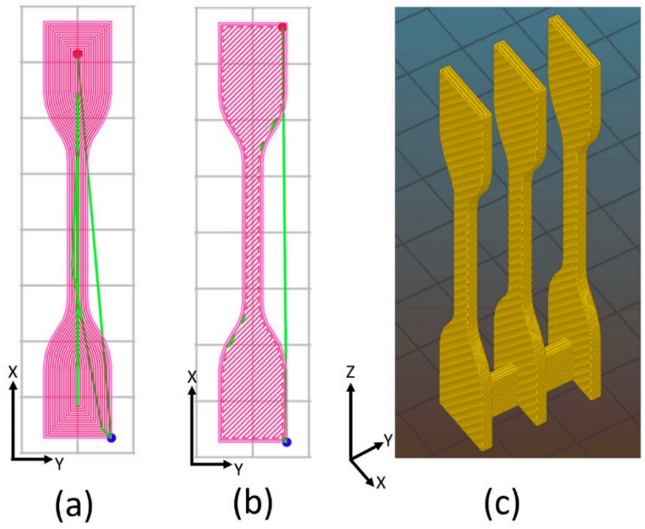

Figure 1. a) Horizontal concentric (HC). b) Horizontal 45° (H 45). c) Vertical – 3D printing orientations.

III. Tribological Properties

PLA matrix nanocomposite pellets containing Graphene and MWCNT (Multiwalled Nanocarbon Tube) were used for fabricating filaments and then 3D-printed parts [18]. Scratch and wear tests were conducted, and the Coefficient of Friction

(COF) was determined. Reciprocating wear tests were conducted using a steel ball. When comparing the COF of various composites, it was realized that the monofiller composite had the lowest COF values, as reported in Table 3. For the bifiller composites, the COF was always greater than that of the monofiller composites.

	Coefficient of friction (COF) / % decrease in COF with respect to neat PLA
PLA – 2.5 % Graphene	0.06 /167
PLA – 3 % MWCNT	0.075 /158
PLA – 9 % MWCNT	0.062 /118

Table 3. COF of PLA nanocomposites

doi.org/10.32388/Q8EF9H

IV. Mechanical Properties

PLA is a widely used, semi-crystalline thermoplastic material for 3D printing because of its low melting point, biodegradability, relatively low cost, and high dimensional accuracy after printing. Various nanofillers have been used to fabricate PLA composites, including $CaCO_3$[5], carbon black [13], AlN [31], SiO_2 [14], graphene [15], carbon nanotubes[16], pyrolytic carbon[47], layered silicate [48], and short carbon fiber [13]. Of all the 3D-printed composites, PLA – 8 % SiO_2 exhibited the highest tensile strength [49]. When short carbon fiber is added, the tensile (Young's) modulus increases significantly. The highest tensile modulus was exhibited by a PLA-based composite containing 1% CNT and 30% short carbon fiber, i.e., 12.12 GPa; in comparison, a composite containing 1% CNT exhibited a tensile modulus of 2.927 GPa, as shown in Table 2A. It can be observed that the impact strength of ABS-WC [23] and ABS-TiN [22] composites is considerably lower than that of the corresponding neat or virgin plastic materials, as shown in Table 2B, possibly due to the poor interfacial bond strength, and in all cases, notched specimens were used. On the other hand, the following composites, PLA-4 % TiN [12], PLA- 8 % nano SiO_2 [14], and PC–nanocellulose composite [47], exhibited higher impact strength than the neat plastic due to the high interfacial bond strength [50]. PLA-4 % TiN [12] exhibited the highest flexural modulus of 3,600 MPa, whereas PLA-2% graphene exhibited the highest flexural strength of 160 MPa [15].

Mirsadegh et al. have carried out [5][25] an extensive investigation on PLA–$CaCO_3$ and ABS–$CaCO_3$ regarding the tensile and fracture behavior of the 3D-printed specimens. A Taguchi L27 orthogonal array was designed by choosing printing parameters such as printing speed, printing pattern, layer thickness, and infill ratio. Tensile specimens having a 100% infill ratio and various infill patterns, such as linear, triangular, and hexagonal, were used while printing the test specimens, as shown in Figure 2. PLA–$CaCO_3$ nanocomposite can be used as a bioimplant material, and these data may be useful when designing and fabricating bioimplants.

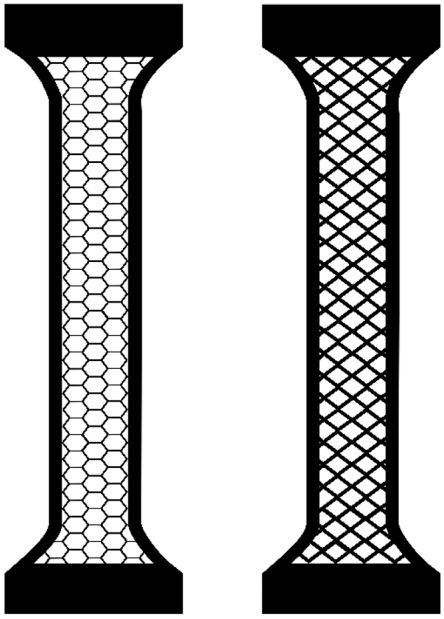

Figure 2. Internal Architecture[25]

Mia Corrola et al. [24] developed a process for improving the dispersion of CNTs in ABS, as shown in Figure 3. Crystalline nanocellulose was dispersed in a flask containing deionized water, and then CNT was added. Later, ABS pellets were added, soaked in the suspension, and then dried and extruded.

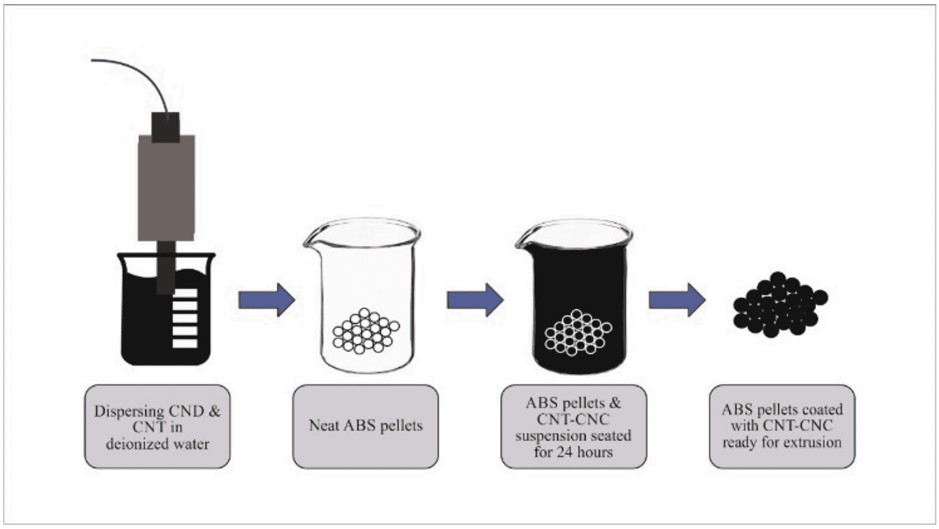

Figure 3. Dispersion of CNC & CNT

doi.org/10.32388/Q8EF9H

Effective dispersion was achieved, as indicated by the significant improvement in tensile strength, Young's modulus, and interlaminar shear strength, as shown in Table 2B. It was observed that the printing orientation affects the properties; significant improvements in the mechanical properties were achieved for the specimens printed at an angle of 0 deg.

The presence of nanoparticles in the thermoplastic matrix can lead to a significant increase in tensile strength, tensile modulus, flexural strength, and flexural modulus (Tables 2A, B, C & D) for the following reasons: nanoparticles restrict the motion of polymer chains, and load is transferred from the matrix to the nanoparticle. The impact strength of the PLA (Table 2A) and PC (Table 2C) matrix nanocomposites increased in comparison to the neat polymer, whereas for the ABS (Table 2B) and PA (Table 2C) matrix composites, it decreased. In the case of the 3D-printed ABS/PBT blend, the impact strength declined by 38% in comparison to ABS for the following reasons: the PBT blend is immiscible in ABS, PBT has a high sensitivity to notched defects and pores, and the presence of PBT disrupts continuity. The addition of 0.5% CNT to the ABS/PBT increases the impact strength by 30% in comparison to the ABS/PBT blend [23].

Although the infill % was 100%, the presence of large voids between the layers can be seen. Functionalization of the fillers improved adhesion to the matrix, and agglomeration could also be prevented; for these reasons, the mechanical properties of the filaments and 3D-printed specimens increased. Functionalization of the fillers can increase crystallinity, and for this reason, the mechanical properties increase[35][29]. Filaments exhibit a higher level of tensile strength because of the orientation of polymer chains along the length of the filament [D M Higg, 1988, 39] and due to the presence of fewer defects in comparison to the 3D-printed specimens[28].

In the case of semi-crystalline polymers, such as PLA, PA6, and PA 12, an increase in crystallinity results in improved mechanical properties [D.M Higg]. It is to be noted that the presence of nanofillers can promote crystallization in the 3D-printed nanocomposites [30].

V. Effect of Functionalization

PLA-2% Graphene composites were fabricated by a solution method, and then the filament was extruded. To disperse graphene, it was functionalized using L-Arginine, an amino acid [15]. Functionalization of graphene significantly improves the mechanical properties of PA6-1% GNP [37] and PLA-2% GNP, as shown in Table 2A, due to the highly effective distribution of graphene in the matrix, i.e., PA and PLA. The tensile fracture strain of most of the printed nanocomposites listed in Table 2E was lower than that of the respective neat polymer, but a nanocomposite containing PLA–2% Graphene exhibited a fracture strain of 14.3%, which is about 74% more than that of the neat PLA; in this case, graphene was functionalized using L-Arginine, an amino acid. In the case of the PA6-1% GNP composite, commercially available amino (NH2) functionalized graphene nanoparticles having a few layers were used [29].

The tensile and flexural properties improved significantly, as shown in Table 2C.

VI. Conclusions and Recommendations

1. An appropriate method/compound for functionalizing can be chosen, and the effect on the mechanical/electrical properties can be investigated.
2. The effect of post-processing heat treatment on the mechanical/electrical properties can be investigated.
3. With regard to the filaments, there is no standard test for determining the tensile properties; further research regarding this can be carried out.
4. Further investigations can be carried out with regard to the PEI nanocomposites by using 3D printers that can operate at a relatively high temperature (~370 ^{0}C) and a temperature-controlled build chamber.

References

1. ^a ^b *Rayna T, Striukova L (2016). "From Rapid Prototyping to Home Fabrication: How 3D Printing Is Changing Business M odel Innovation." Technological Forecasting and Social Change.* ***102****:214–224. doi:10.1016/j.techfore.2015.07.023.*
2. ^ *Tjong SC (2006). "Structural and Mechanical Properties of Polymer Nanocomposites." Mater Sci Eng R.* ***53****:73–197.*
3. ^ *Piccarozzi M, Silvestri C, Aquilani B, Silvestri L (2022). "Is This a New Story of the 'Two Giants'? A Systematic Literature Review of the Relationship Between Industry 4.0, Sustainability and Its Pillars." Technol Forecast Soc Change.* ***177****:121511. doi:10.1016/j.techfore.2022.121511.*
4. ^ *Muth J, Klunker A, Völlmecke C (2023). "Putting 3D Printing to Good Use—Additive Manufacturing and the Sustainable Development Goals." Front Sustain.* ***4****. doi:10.3389/frsus.2023.1196228.*
5. ^a ^b ^c ^d *Seyedzavvar M, Boğa C, Zehir B (2023). "Experimental Study and Hybrid Optimization of Material Extrusion Pro cess Parameters for Enhancement of Fracture Resistance of Biodegradable Nanocomposites." Eng Fail Anal.* ***150****:107294. doi:10.1016/j.engfailanal.2023.107294.*
6. ^ *Seyedzavvar M (2023). "A Hybrid ANN/PSO Optimization of Material Composition and Process Parameters for Enhanc ement of Mechanical Characteristics of 3D-Printed Sample." Rapid Prototyp J.* ***29****(6):1270–1288. doi:10.1108/RPJ-10-2022-0338.*
7. ^ *Masarra N-A (2022). "Influence of Polymer Processing on the Double Electrical Percolation Threshold in PLA/PCL/GNP Nanocomposites." Sensors.* ***22****(23):9231. doi:10.3390/s2223923.*
8. ^ *Oladapo BI, Ismail SO, Zahedi M, Khan A, Usman H (2020). "3D Printing and Morphological Characterisation of Polym eric Composite Scaffolds." Eng Struct.* ***216****:110752. doi:10.1016/j.engstruct.2020.110752.*
9. ^ *Jain SK, Tadesse Y (2019). "Fabrication of Polylactide/Carbon Nanopowder Filament Using Melt Extrusion and Filamen t Characterization for 3D Printing." Int J Nanosci.* ***18****(5):1850026. doi:10.1142/S0219581X18500266.*

10. ^*Sarwar Z, Yousef S, Tatariants M, Krugly E, Čiužas D, Danilovas PP, Baltusnikas A, Martuzevicius D (2019). "Fibrous PEBA-Graphene Nanocomposite Filaments and Membranes Fabricated by Extrusion and Additive Manufacturing." Eur Polym J. **121**:109317. doi:10.1016/j.eurpolymj.2019.109317.*
11. ^*Ledford WK, Kilbey SM II (2023). "Impact of Hydrogen Bonding Pendant Groups in Polymer Grafted Nanoparticles on Interlayer Adhesion and Mechanical Properties in Material Extrusion Printing." Addit Manuf. **63**:103419. doi:10.1016/j.addma.2023.103419.*
12. a, b, c, d, e*Petousis M (2023). "On the Substantial Mechanical Reinforcement of Polylactic Acid With Titanium Nitride Ceramic Nano Fillers in Material Extrusion 3D Printing." Ceram Int. **49**(10):16397–16411. doi:10.1016/j.ceramint.2023.02.00.*
13. a, b, c, d*Kechagias JD (2023). "Hybrid 3D Printing of Multifunctional Polylactic Acid / Carbon Black Nanocomposites Made With Material Extrusion and Post-Processed With CO2 Laser Cutting." Int J Adv Manuf Technol. **124**(5-6):1843–1861. doi:10.1007/s00170-022-10604-6.*
14. a, b, c, d*Ramachandran MG, Rajeswari N (2021). "Influence of Nano Silica on Mechanical and Tribological Properties of Additive Manufactured PLA Bio Nanocomposite." Silicon. **14**(2):703–709. doi:10.1007/s12633-020-00878-4.*
15. a, b, c, d, e*Wang Y, Lei M, Wei Q, Wang Y, Zhang J, Guo Y, Saroia J (2020). "3D Printing Biocompatible L-Arg/GNPs/PLA Nanocomposites With Enhanced Mechanical Property and Thermal Stability." J Mater Sci. **55**(12):5064–5078. doi:10.1007/s10853-020-04353-8.*
16. a, b, c, d*Petrény R, Tóth C, Horváth A, Mészáros L (2022). "Development of Electrically Conductive Hybrid Composites With a Poly(Lactic Acid) Matrix, With Enhanced Toughness for Injection Molding, and Material Extrusion-Based Additive Manufacturing." Heliyon. **8**(8):e10287. doi:10.1016/j.heliyon.2022.e10287.*
17. ^*Zhang Y, Zhao P, Lu Q, Zhang Y, Lei H, Yu C, Huang Y, Yu J (2023). "Functional Additive Manufacturing of Large-Size Metastructure With Efficient Electromagnetic Absorption and Mechanical Adaptation." Compos Part A Appl Sci Manuf. **173**:107652. doi:10.1016/j.compositesa.2023.107652.*
18. a, b*Ginoux G, Vroman I, Alix S (2020). "Influence of Fused Filament Fabrication Parameters on Tensile Properties of Polylactide/Layered Silicate Nanocomposite Using Response Surface Methodology." J Appl Polym Sci. **138**(14):50174. doi:10.1002/app.50174.*
19. a, b, c*Vidakis N, Moutsopoulou A, Petousis M, Michailidis N, Charou C, Papadakis V, Mountakis N, Dimitriou E, Argyros A (2023). "Rheology and Thermomechanical Evaluation of Additively Manufactured Acrylonitrile Butadiene Styrene (ABS) With Optimized Tungsten Carbide (WC) Nano-Ceramic Content." Ceram Int. **49**(22):34742–34756. doi:10.1016/j.ceramint.2023.08.144.*
20. ^*Santo J, Moola AR, Penumakala PK (2022). "Interface Stress Transfer in an Extruded ABS-rGO Composite Filament." Adv Compos Mater. **32**(2):211–224. doi:10.1080/09243046.2022.2080991.*
21. a, b*Vidakis N, Maniadi A, Petousis M, Vamvakaki M, Kenanakis G, Koudoumas E (2020). "Mechanical and Electrical Properties Investigation of 3D-Printed Acrylonitrile–Butadiene–Styrene Graphene and Carbon Nanocomposites." J Mater Eng Perform. **29**(3):1909–1918. doi:10.1007/s11665-020-04689-x.*

22. a, b, c *Vidakis N, Mangelis P, Petousis M, Mountakis N, Papadakis V, Moutsopoulou A, Tsikritzis D (2023). "Mechanical Reinforcement of ABS With Optimized Nano Titanium Nitride Content for Material Extrusion 3D Printing." Nanomaterials.* ***13****(4):669. doi:10.3390/nano13040669.*

23. a, b, c *Farajian J, Alipanahi A, Mahboubkhah M (2023). "Analyses of Mechanical Properties and Morphological Behavior of Additively Manufactured ABS* ***Polymer****, ABS/PBT Blend, and ABS/PBT /CNT Nanocomposite Parts." J Thermoplast Compos Mater.* ***36****(6):2390–2411. doi:10.1177/08927057221092952.*

24. a, b *Carrola M, Motta de Castro E, Tabei A, Asadi A (2023). "Cellulose Nanocrystal-Assisted Processing of Nanocomposite Filaments for Fused Filament Fabrication." Polymer.* ***278****:125980. doi:10.1016/j.polymer.2023.125980.*

25. a, b, c *Seyedzavvar M, Boğa C (2022). "A Study on the Effects of Internal Architecture on the Mechanical Properties and Mixed-Mode Fracture Behavior of 3D Printed* $CaCO_3$*/ABS Nanocomposite Samples." Rapid Prototyp J.* ***29****(1):185–206. doi:10.1108/RPJ-09-2021-0244.*

26. a, b, c *Dul S, Fambri L, Pegoretti A (2018). "Filaments Production and Fused Deposition Modelling of ABS/Carbon Nanotubes Composites." Nanomaterials.* ***8****(1):49. doi:10.3390/nano8010049.*

27. a, b *Vidakis N, Petousis M, Maniadi A, Koudoumas E, Kenanakis G, Romanitan C, Tutunaru O, Suchea M, Kechagias J (2020). "The Mechanical and Physical Properties of 3D-Printed Materials Composed of ABS-ZnO Nanocomposites and ABS-ZnO Microcomposites." Micromachines.* ***11****(6):615. doi:10.3390/mi11060615.*

28. a, b, c *Vidakis N, Petousis M, Michailidis N, Mountakis N, Papadakis V, Argyros A, Charou C (2023). "Polyethylene Glycol and Polyvinylpyrrolidone Reduction Agents for Medical Grade Polyamide 12/Silver Nanocomposites Development for Material Extrusion 3D Printing: Rheological, Thermomechanical, and Biocidal Performance." React Funct Polym.* ***190****:105623. doi:10.1016/j.reactfunctpolym.2023.105623.*

29. a, b, c, d *Wang Y, Shi J, Liu Z (2020). "Bending Performance Enhancement by Nanoparticles for FFF 3D Printed Nylon and Nylon/Kevlar Composites." J Compos Mater.* ***55****(8):1017–1026. doi:10.1177/0021998320963524.*

30. a, b, c *Arigbabowo OK, Omer L, Tate J (2023). "Fused Filament Fabrication of Polyamide 6 Nanographene Composite for Electrostatic Discharge Applications." Mater Sci Eng B.* ***287****:116086. doi:10.1016/j.mseb.2022.116086.*

31. a, b, c *Vidakis N, Petousis M, Mangelis P, Maravelakis E, Mountakis N, Papadakis V, Neonaki M, Thomadaki G (2022). "Thermomechanical Response of Polycarbonate/Aluminum Nitride Nanocomposites in Material Extrusion Additive Manufacturing." Materials.* ***15****(24):8806. doi:10.3390/ma15248806.*

32. a, b *Vidakis N, Petousis M, Velidakis E, Spiridaki M, Kechagias JD (2021). "Mechanical Performance of Fused Filament Fabricated and 3D-Printed Polycarbonate Polymer and Polycarbonate/Cellulose Nanofiber Nanocomposites." Fibers.* ***9****(11):74. doi:10.3390/fib9110074.*

33. ^ *Petousis M, Vidakis N, Mountakis N, Grammatikos S, Papadakis V, David CN, Moutsopoulou A, Das SC (2022). "Silicon Carbide Nanoparticles as a Mechanical Boosting Agent in Material Extrusion 3D-Printed Polycarbonate." Polymers.* ***14****(17):3492. doi:10.3390/polym14173492.*

34. ^Tambrallimath V (2021). "Mechanical Properties of PC-ABS-Based Graphene-Reinforced Polymer Nanocomposites Fabricated by FDM Process." Polymers. **13**(17):2951. doi:10.3390/polym13172951.
35. a, b, c, dKumar S, Ramesh MR, Doddamani M (2023). "Recycling Potential of MWCNTs/HDPE Nanocomposite Filament: 3D Printing and Mechanical Characterization." J Mater Cycles Waste Manag. **25**(2):1168–1178. doi:10.1007/s10163-023-01607-w.
36. ^Stan F, Stanciu NV, Constantinescu AM, Fetecau C (2020). "3D Printing of Flexible and Stretchable Parts Using Multiwall Carbon Nanotube/Polyester-Based Thermoplastic Polyurethane." J Manuf Sci Eng. **143**(5):051002. doi:10.1115/1.4048442.
37. a, bMayakrishnan V, Mohamed JK, Selvaraj N, SenthilKumar D, Annadurai S (2022). "Effect of Nano-Biochar on Mechanical, Barrier and Mulching Properties of 3D Printed Thermoplastic Polyurethane Film." Polym Bull. **80**(6):6725–6747. doi:10.1007/s00289-022-04380-2.
38. ^Sarwar Z, Yousef S, Tatariants M, Krugly E, Čiužas D, Danilovas PP, Baltusnikas A, Martuzevicius D (2019). "Fibrous PEBA-Graphene Nanocomposite Filaments and Membranes Fabricated by Extrusion and Additive Manufacturing." Eur Polym J. **121**:109317. doi:10.1016/j.eurpolymj.2019.109317.
39. ^Calderón-Villajos R, López AJ, Peponi L, Manzano-Santamarí J, Ureña A (2019). "3D-Printed Self-Healing Composite Polymer Reinforced With Carbon Nanotubes." Mater Lett. **249**:91–94. doi:10.1016/j.matlet.2019.04.069.
40. ^Yaragalla S, Zahid M, Panda JK, Tsagarakis N, Cingolani R, Athanassiou A (2021). "Comprehensive Enhancement in Thermomechanical Performance of Melt-Extruded PEEK Filaments by Graphene Incorporation." Polymers. **13**(9):1425. doi:10.3390/polym13091425.
41. ^Richardson MJ (2017). "Flame Retardant Nylon 6 Nanocomposites for Fused Deposition Modeling (FDM) Applications." International SAMPE Technical Conference. pp. 230–244.
42. ^Ledford WK, Kilbey S (2023). "Impact of Hydrogen Bonding Pendant Groups in Polymer Grafted Nanoparticles on Interlayer Adhesion and Mechanical Properties in Material Extrusion Printing." Addit Manuf. **63**:103419. doi:10.1016/j.addma.2023.103419.
43. ^Vidakis N, Petousis M, Velidakis E, Mountakis N, Fischer-Griffiths PE, Grammatikos SA, Tzounis L (2022). "Fused Filament Fabrication 3D Printed Polypropylene/Alumina Nanocomposites: Effect of Filler Loading on the Mechanical Reinforcement." Polym Test. **109**:107545. doi:10.1016/j.polymertesting.2022.107545.
44. ^Vidakis N, Petousis M, Velidakis E, Tzounis L, Mountakis N, Korlos A, Fischer-Griffiths PE, Grammatikos S (2021). "On the Mechanical Response of Silicon Dioxide Nanofiller Concentration on Fused Filament Fabrication 3D Printed Isotactic Polypropylene Nanocomposites." Polymers. **13**(12):2029. doi:10.3390/polym13122029.
45. ^Vidakis N, Petousis M, Velidakis E, Tzounis L, Mountakis N, Kechagias J, Grammatikos S (2021). "Optimization of the Filler Concentration on Fused Filament Fabrication 3D Printed Polypropylene With Titanium Dioxide Nanocomposites." Materials. **14**(11):3076. doi:10.3390/ma14113076.

46. ^Fahy WP (2018). "Flame Retardant Polyamide 11 and Alumina Nano Composites for Additive Manufacturing." International SAMPE Technical Conference.

47. a, bVidakis N, Petousis M, Velidakis E, Spiridaki M, Kechagias JD (2021). "Mechanical Performance of Fused Filament Fabricated and 3D-Printed Polycarbonate Polymer and Polycarbonate/Cellulose Nanofiber Nanocomposites." Fibers. **9**(11):74. doi:10.3390/fib9110074.

48. ^Ginoux G, Vroman I, Alix S (2021). "Influence of Fused Filament Fabrication Parameters on Tensile Properties of Polylactide / Layered Silicate Nanocomposite Using Response Surface Methodology." J Appl Polym Sci. **138**(14):50174. doi:10.1002/app.50174.

49. ^Ginoux G, Vroman I, Alix S (2021). "Influence of Fused Filament Fabrication Parameters on Tensile Properties of Polylactide / Layered Silicate Nanocomposite Using Response Surface Methodology." J Appl Polym Sci. **138**(14):50174. doi:10.1002/app.50174.

50. ^Iyer SB, Dube A, Dube NM, Roy P, Sailaja RRN (2018). "Sliding Wear and Friction Characteristics of Polymer Nanocomposite PAEK-PDMS With Nano-Hydroxyapatite and Nano-Carbon Fibres as Fillers." J Mech Behav Biomed Mater. **86**:23–32. doi:10.1016/j.jmbbm.2018.06.006.

Declarations

Funding: No specific funding was received for this work.

Potential competing interests: No potential competing interests to declare.