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Mechanical behavior of additively manufactured nanoclay/HDPE

nanocomposites

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ARTICLEINFO

ABSTRACT

Keywords:

Nanoclay (NC) has blended with relatively inexpensive, widely consumed HDPE (high density polyethylene) for Nanoclay

the development of filament to be used in 3D printers. NC/HDPE blends are prepared by varying NC wt. % (0.5, HDPE

1, 2, and 5) and are subjected to melt flow index (MFI) measurements [Code a1]. MFI has noted to be decreasing with NC

Nanocomposite

loadings [Code a1]. NC/HDPE nanocomposite blends are further extruded using a single screw extruder. Developed na-Filament

nocomposites filaments are fed to the fused filament fabrication (FFF) based 3D printer for realizing NC/HDPE

3D printing

nanocomposite prints. [Code a2] The density of printed sample increases with filler content [Code a4]. Filament and printed samples thermal study is carried out using differential scanning calorimeter (DSC) [Code a3]. NC addition increases crystallinity and crystallization temperature without significant change in melting peak temperature. Freeze fractured prints reveal the uniform distribution of NC in HDPE [Code a4]. The tensile test is conducted on the filaments and prints. Further printed nanocomposites are subjected to flexural investigations. [Code a3] Tensile modulus and strength of filament increase with NC additions in HDPE matrix. Tensile and flexural properties (modulus and strength) of the nanocomposite prints increases with NC content [Code a4]. Finally, results obtained from the tensile and flexural tests of prints are compared with different HDPE composites available in the literature. [Code a5]

1. Introduction

polybutylene terephthalate [15], polyamide [16], polypropylene
[17,18] and HDPE [19,20]. Major issues associated with printing with Among the polymer based additive manufacturing (AM) techniques, thermoplastic material includes layer delamination and part shrinkage/
FFF is the most commonly used, widely exploited approach in devel—
warpage as a result of repetitive heating and cooling cycles [21,22]. 3D
oping custom made geometrically complex components. AM re—
printed composite parts printed by FFF have superior properties com—

searchers, academicians, and industrial practitioners use FFF based AM

pared to their neat counterparts [23]. The FFF method has been com-to rapidly develop tangible objects and functional parts. It allows user monly preferred in various sectors such as medical [24,25,87], auto-to manufacture highly complex parts very easily as compared to con—

motive [26], and aeronautics [27]. In such scenarios, need for widening ventional manufacturing processes [1–3]. In the FFF process, the ther-the scope of newer filaments developments is crucial and is the focus of moplastic based filament is passed to liquefier of 3D printer through the present work. Recently researchers are taking up intensive developelectromechanical drive. In the liquefier, plastic gets converted into

mental works to explore and enhance filaments material properties by semi-molten state. The extrusion head of the printer, layer it down as

combining a wide range of fillers with thermoplastics using comper part geometry defined by the STL file [4]. Limited options of pounding techniques. Fillers such as iron particles [28], carbon and commercial filaments limit the exploitation of the FFF process to

glass fiber [29], Al2O3 powder [30], glass microspheres [31], and fly manufacture the complex functional products. The newly developed

ash cenospheres [32,33] are being used in the literature to enhance filament must have certain mechanical properties and should be com-thermoplastic filaments mechanical behavior. Present work is focused

patible with existing machines without modifying its software/hard—

on increasing filament material choices for the FFF technique by de—

ware components [5–7]. Till date, commonly used filament materials veloping nanocomposite feedstock.

include but not limited to, polyetherimide, acrylonitrile butadiene

```
In recent years, the composite community widely explored organi—
styrene [8], polylactide [9], polymethylmethacrylate [10], poly-cally
modified nanoclay like montmorillonite (MMT) by reinforcing it
carbonate [11] and their blends [12,13], polycaprolactone [14],
in polymers [34–37]. The ability of tailoring the different properties by
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Nomenclature
ρ
Theoretical density (kg/m3)
th
ρ
Experimental density (kg/m3)
exp
```

```
ρ
Composite density (kg/m3)
T
C
Melt
Peak melting temperature (°C)
ρ
HDPE density (kg/m3)
Τ
Η
Cryst
Crystallization temperature (°C)
ρ
NC density (kg/m3)
α
NC
Cryst
Degree of crystallinity (%)
wH
HDPE (wt. %)
```

Flnt

Filament

wNC

NC (wt. %)

Prnt

3D Print

combining various matrix and filler widens the application domain of estimations (ASTM D1238-13) of NC/HDPE nanocomposite blends. MFI nanocomposites. Strong molecular interaction between polymer resin

provides basic knowledge of material flow with respect to the unit time and nanofiller improves the thermal, mechanical, and physical prop-and viscosity change due to nanoparticle addition, which in turn helps

erties of nanocomposites [38]. Polymer nanocomposites find their ap-to set optimum printing parameters in the commercially available 3D

plication in various sectors such as automotive (body interior, under—printers.

the-hood, and exterior), electrical and electronics industries (electric components and printed circuits), construction (shaped extrusions,

panels, etc.), food packaging (films, containers), filling materials in 2.2. Filament development and 3D printing

dentistry, cosmetics, beverage and food packaging, biomedical applications, military, and aerospace [39]. Clay based nanocomposites are NC/HDPE pellets obtained from Brabender (Fig. 1a) are fed into the specifically utilized in fire retardancy applications [40]. NC has ideally single screw

extruder to extrude nanocomposite filament (Fig. 1b). The used reinforcement among the available nanoparticles due to lower

single screw extruder and 3D printer being used in this study are re—

cost, easy availability, higher cation exchange capacity and aspect ratio.

spectively from Asabi Machinery Pvt. Ltd., Mumbai (L/D ratio -25:1,

It can be surface treated as well with various surfactants for enhancing 25SS/MF/26) and Star, AHA 3D Innovations, Jaipur. The extruder has

mechanical properties [41]. HDPE is widely used industrial thermo-three heating zones with a temperature setting of 160, 165, and 150 °C, plastic polymer because of its more distinct physical and mechanical

respectively. Feed section temperature is maintained constant at 155 °C.

properties compared to other thermoplastics [42]. HDPE find its ap-These parameters are optimized based on the uniform and consistent

plications in milk jugs, household utilitarian products, packaging in—

flow through the die [6]. Take-up unit and screw rotation are set as dustries and in many structural applications [43,44]. Some of the 12.5 and 25 rpm respectively to extrude the H–H5 filaments with a

commonly used fillers with HDPE are carbon nanotubes [45], fly ash consistent diameter of 2.85 ± 0.05 mm (Fig. 1b). Fig. 1b shows an cenospheres [46–48], glass microballoons [49–51], carbon [52], cal-image of a representative H5 filament having consistent diameter

cium carbonate [53], graphite nanofibers [54], etc. Compared to conwithout any surface irregularities/defects. A similar setting is main—

ventional macro/micro filler reinforced composites, NC, in small tained for extruding other compositions as well. Extruded NC/HDPE

quantities (≤5 wt. %) exhibits significant improvement in mechanical

filaments are fed to a commercially available 3D printer. Table 2 proproperties [55].

vides details of optimized printing parameters based on uniform flow

Commonly used polymers with nanoclay are polyethelene [56],

through the nozzles, defect-free deposition (inter and intra-layer), and polypropelene [57–59], polyethylene terephthalate [60], polystyrene warpage-free samples [6]. Printing speed is maintained at 100 mm/s,

[61,62] and polyamide [63]. HDPE is yet to be explored with NC for which is 3.7 times higher compared to our earlier works reported in

realizing complex geometrical components through 3D printing. Ex—

Ref. [6]. Higher print speed is chosen by keeping industrial require-cellent biocompatibility and mechanical properties of HDPE can be

ments in focus amid compromising mechanical properties of neat HDPE

exploited further by reinforcing it with NC. Such an NC inclusion might in particular as compared to reported investigations [6]. Infill is kept at effectively reduce the warpage/shrinkage related issues in 3D printing

100% for comparative analysis with other dense HDPE composites.

[19,64]. Present work focusses on the development of NC/HDPE

blends, filaments and prints. Blends are investigated for MFI first. The compounded blend of nanocomposite is used to extrude feedstock fi-2.3. Density measurement

lament. Prior to printing, filaments are investigated for α Cryst and tensile behavior. Subsequently these nanocomposite filaments are used as

Printed nanocomposites density is experimentally measured as per

feedstock inputs in FFF based 3D printer. Further, 3D printed nano—the ASTM D792-13 standard, and the average values are reported in composites are investigated for crystallinity, tensile and flexural re-

Table 3. Theoretical densities of all the compositions are computed sponses. Finally present work is compared with other HDPE composites

based on individual constituent materials density using, in the property map.

1

 $\rho =$

C

wH + wNC

D

ρ

Η

NC

(1)

2. Experimental

Densities of HDPE and NC are taken as 950 and 1980 kg/m3 re—

2.1. Materials, blend preparation and MFI measurements spectively.

HDPE (HD50MA180) granules used in the present study are sup—

Table 1

plied by Reliance Polymers, Mumbai. Table 1 provides property details Typical characteristics of HDPE granules [6].

of HDPE resin [6]. Montmorillonite K 10 powder (NC) is procured from Property

Typical value

SIGMA-ALDRICH, India. It is off white in appearance, having a density

of 1980 kg/m3. Compounding of HDPE and NC (0.5, 1, 2, and 5 wt. %)

MFI (190 °C/2.16 kg)

20 gm/10 min.

in as received conditions (without any surface treatment) is materi—

Density (23 °C)

950 kg/m3

alized using 16CME SPL Brabender at 210 $^{\circ}\text{C}$ [65] to get the nano-Tensile strength at yield

22 MPa

Elongation at yield

12 %

composite pellets (Fig. 1a). Blends with 0.5, 1, 2, and 5 wt. % NC in neat Flexural modulus

750 MPa

HDPE (H) are designated as H0.5, H1, H2, and H5, respectively. Dy—

Vicat softening point

124 °C

nisco LMI5000 laboratory melt flow indexer is utilized for MFI

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Fig. 1. Representative (a) NC/HDPE blend and (b) H5 nanocomposite filament.

Table 2

2.5. Tensile and flexural characterization

Printer setting and parameters selected in the present work [6].

Tensile property characterization of the filament and 3D prints is

Printing parameters

Typical value

carried out through Zwick Roell (Z020, load cell: 20 kN) UTM at 5 mm/

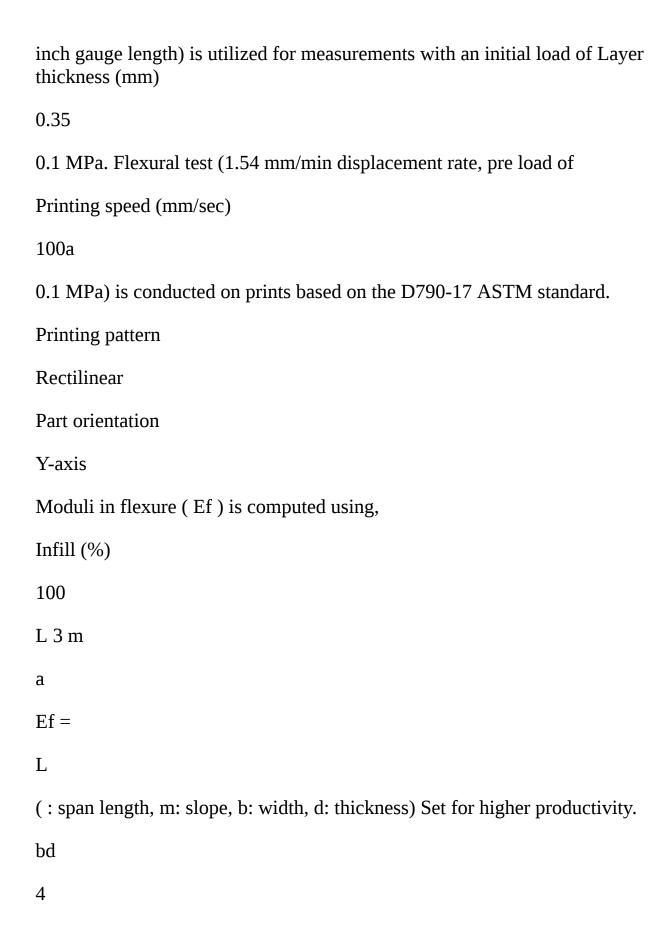
Nozzle temperature (°C)

250

min as per the procedure outlined in ASTM D638-14. Extensometer (2—

Printing bed temperature (°C)

70



3
(3)
2.4. Differential scanning calorimetry of feedstock filament and their prints Flexural stress (ρ) is estimated using,
fm
PL
3
DSC analysis of the filaments and prints is carried out using Perkin
ρ
=
(P – load)
fm
bd
2
3
(4)
Elmer DSC-6000, USA with the cycles a) 0–200 °C heating and 3 min
hold at 200 °C b) $200-0$ °C cooling and holding at 0 °C for 3 min., and c) second heating cycle from 0 to 200 °C. Approximately 10 mg of
3. Results and discussion

sample mass in 30 μ l Al crucible is used. 10 °C/min heating and cooling rate is maintained constant throughout the test. Thermal stresses em-3.1. MFI

bedded in the previous processing step are removed using the first

heating cycle. TCryst and TMelt are estimated from cooling and heating MFI of NC/HDPE nanocomposites representing the flowability

cycles. DSC curves typically comprise exothermic and endothermic

characteristic is presented in Fig. 2a. It is well-known fact that, the peaks and cold crystallization melting enthalpy peak. α Cryst is computed variation in MFI is inversely proportional to the change in melt visc-from melting enthalpy values using,

osity. NC particles resist the polymer chain mobility and reflect into the H

Δ

lower MFI values in nanocomposites [67]. With increasing NC content α

m

Cryst =

× 100

*

Η

Λ

in the HDPE matrix, MFI decreases, which accounts for 18.04, 17.14,

m

(2)

15.29, and 13.97 gm/10 min, respectively, for H0.5–H5. Pristine HDPE where, Η Λ registered MFI of 23.06 gm/10 min [6]. MFI decreases in the range of m is heat of fusion (J/g) and * Η Δ m is the fusion heat for crystalline HDPE/gram (293 J/g [66]). 21.77–39.42 % for H0.5–H5 nanocomposites, respectively, as compared H. A similar trend is observed in Ref. [67,68]. As MFI reductions in the developed nanocomposite blends are less than 60%, a multiplier is set at '1' in the commercially available printer for all the compositions. Table 3 ρ,ρ,Τ th exp Cryst , αCryst and TMelt estimations of samples. Material Prnt.

TCryst $\alpha Cryst \\$ TMelt ρth ρexp Flnt Prnt Flnt Prnt Flnt Prnt Н 950.00 948.93 ± 13 108.02 109.05 55.5

131.07 131.02

57.1

H0.5

952.48

 998.30 ± 16

111.44

111.77

56.7

72.9

131.66

130.90

H1

954.97

 998.60 ± 26

112.32

112.67

57.1

73.8

131.03

131.67

H2

959.99

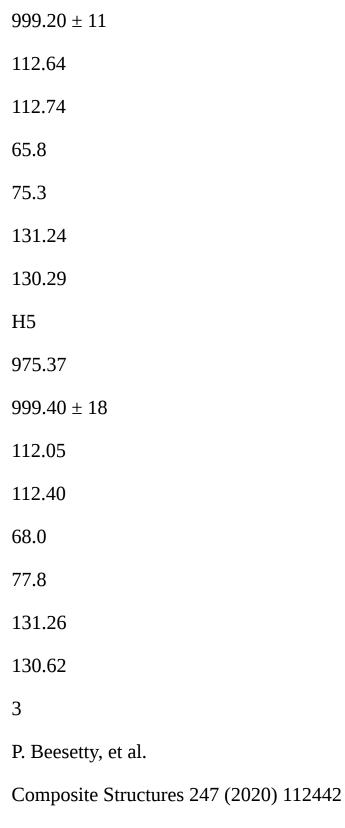


Fig. 2. (a) MFI of NC/HDPE nanocomposites and (b) Micrograph of a representative freeze fractured H2 print.

Fig. 3. DSC curves for filaments (a), (b) and prints (c), (d).

3.2. Density and DSC investigations

stiff NC particles into HDPE is clearly observed through SEM of representative 3D printed sample (Fig. 2b). Interfacial bonding between The densities of prepared filaments and prints are presented in

NC and HDPE is observed to be poor as constituents materials utilized

Table 3. The addition of hard and stiff NC into HDPE increases the in the present work are not surface treated. DSC results of filaments and composite density. Among all the compositions, H5 has shown the

prints are presented in Table 3. Fig. 3 presents the DSC curves of the highest density as expected. Higher experimental densities, as com-filament and printed HDPE and their nanocomposites. Compared to

pared to the respective theoretical ones except H, clearly indicate dense HDPE all the filament and 3D printed samples have shown higher TCryst prints and absence of matrix porosity. Uniform distribution of hard and temperature indicating strong interaction between HDPE resin and

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Table 4

Tensile test result of filament and 3D prints.

Material

Modulus (MPa)

UTS (MPa)

Elongation at UTS (%)
Fracture strength (MPa)
Fracture strain (%)
Flnt
Prnt
Н
525 ± 11
874 ± 12
11.1 ± 0.1
13.8 ± 0.2
11.4 ± 0.2
13.0 ± 0.2

_

$$6.0 \pm 0.19$$

_

$$160.1 \pm 3.3$$

H0.5

$$677\pm15$$

 904 ± 13

$$13.8 \pm 0.3$$

 15.0 ± 0.3

$$12.6 \pm 0.4$$

 12.1 ± 0.2

$$9.8 \pm 0.12$$

 14.1 ± 0.22

 26.1 ± 0.6

 19.0 ± 0.6

H1

$$683 \pm 16$$

 914 ± 17

$$13.9 \pm 0.3$$

 15.1 ± 0.4

 11.8 ± 0.2

 11.0 ± 0.4

 2.30 ± 0.08

 13.9 ± 0.54

 51.9 ± 1.1

 19.6 ± 0.3

H2

 710 ± 20

 946 ± 22

 14.3 ± 0.5

 15.6 ± 0.3

 11.4 ± 0.4

 8.8 ± 0.3

 1.57 ± 0.05

 12.0 ± 0.47

 63.5 ± 2.1

 19.6 ± 0.6

H5

 741 ± 21

 949 ± 20

```
14.9 \pm 0.2
```

 16.9 ± 0.1

 11.4 ± 0.3

 8.1 ± 0.1

 1.49 ± 0.05

 9.0 ± 0.29

 69.2 ± 1.2

 9.0 ± 0.33

Fig. 4. Representative (a) tensile stress—strain plots of neat H–H5 (b) micrograph of H5 and (c) H2 filaments.

nanoclay particles. During cooling cycle of H, at significantly higher samples as against respective nanocomposite filaments is attributed to temperature, the melt nucleates on the NC surface leading to the for—the different cooling modes in the respective processing routes [72]. mation of larger thickness crystal lamellas resulting in higher TCryst [69,70]. 3D prints and filament shows similar TCryst trend which in-3.3. Tensile testing of filaments and prints

dicates that the second material extrusion through printers nozzle has no remarakable impact. No significant difference is observed in TMelt of The filament should have sufficient strength and stiffness to be used the filament and prints (Table 3). Polymer chains have a tendency to as feedstock in commercially available 3D printers. It should not rup-

crystallize by their own (self-nucleation effect) or due to external nu-ture or buckle while passing through a filament drive mechanism [73].

cleating agents. In the present nanocomposite filaments and prints, NC

Filament buckling can be avoided by making it stiff enough such that it has played the role of external nucleating agent enhancing crystal-will pass through the drive mechanism successfully. Inclusion of NC

lization. The higher percentage of crystallization in 3D prints as against improves the stiffness of nanocomposite filament. Modulus of nanorespective filaments is attributed to more aligned martial extrusion and composites filament has increased with NC addition. Among the na-natural cooling of the prints in the printer chamber [71]. Prints cool nocomposites filament, H5 has registered the highest modulus 741 MPa

down by natural convective mode, whereas hot extruded filament is

(Table 4) and is 41.14% higher compared to H. Filament stiffness is being quenched in a water bath during filament extrusion. Thus the

improved by stiff and hard NC additions in compliant HDPE resin.

polymer melt has less time to crystallize, enabling the chains to align in Stress—strain plots for HDPE and the composite filament is plotted in

random order. Degree of crystallinity increases as nanoclay con-

Fig. 4a until 15% strain as neat HDPE filament exhibits more than 150%

centration increases in filaments and prints. αCryst increased from 57.1%

strain level. The test is stopped due to stroke distance and time con—

to 77.8% for H–H5, respectively, in prints. Higher αCryst in 3D printed straints. Such a higher strain value signifies the ductile behavior of neat 5

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Fig. 5. Representative (a) stress—strain curve for 3D prints and freeze fractured micrographs of (a) H and (b) H5 prints post tensile test.

Table 5

Material

HDPE. On the contrary, nanocomposite filament elongation decreased Specific tensile properties of printed H–H5.

severely. The tensile strength of H5 (14.90 MPa) is highest among all the composition, which is \sim 35% higher compared to neat HDPE fila—

Sp. Modulus (MPa/kg/m3)

Sp. Strength (MPa/kg/m3) \times 10–3

ment. Uniform distribution of NC in H for H5 (Fig. 4b) compared H2

Η

0.921

14.58

(Fig. 4c) might be the reason for such an observation. Further, there H0.5

0.906

15.03

may be better molecular level interface inconsonance occurring be—

H1

0.916

tween the polymer chain and nanoclay at H5. Elongation at UTS is

H2

0.947

15.61

highest for H0.5 in

H5

0.950

16.91

filaments. The fracture strength and strain of nanocomposite filaments are significantly lower compared H, which

might be due to a reduction in HDPE deformation post-NC additions.

The tensile behavior of printed H–H5 is presented in Fig. 5, and the values are presented in Table 4. Printed samples failed typically in Fig. 6. Representative (a) flexural stress–strain plot for 3D prints and (b) SEM of H5 post flexural test.

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Table 6

Flexural properties of prints.

Material

Modulus (MPa) Strength (MPa) Specific modulus (MPa/kg/m3) Specific strength (MPa/kg/m3) \times 10–3 Η 656 ± 13 19.90 ± 0.06 0.69 20.97 H0.5 662 ± 12 20.20 ± 0.04 0.66 20.23 H1 672 ± 13 20.80 ± 0.02

20.83

0.67

H2

 697 ± 16

 21.50 ± 0.03

0.70

21.52

H5

 735 ± 13

 22.24 ± 0.03

0.74

22.25

Fig. 7. (a) Tensile modulus and (b) strength of HDPE composites.

Fig. 8. (a) Flexural modulus and (b) strength of HDPE composites.

brittle mode except for neat HDPE. Printed H exhibited ~160% fracture

neat HDPE. Specific mechanical properties are crucial from a structural strain though plots in Fig. 5a are graphed until 18% strain. Fig. 5b application perspective. Specific strength of H5 outperformed H by 16%

shows a micrograph of H, which clearly indicates substantial plastic (Table 5).

deformation of the HDPE matrix. Nanocomposites modulus increases as

filler loading rises (Table 4). H5 composition has shown maximum modulus across all the NC variations and is 8.58% higher relative to H.

3.4. Flexural response of prints

3D printed H–H5 modulus is 1.66, 1.34, 1.34, 1.33, and 1.28 times higher than their respective filament which is attributed to the polymer Neat HDPE and their nanocomposite prints did not fail until 10% chains realignment and augmented crosslinking in printing. H5 ex strain (Fig. 6a). Flexural moduli and strength of nanocomposite in-hibited the highest UTS of 16.9 MPa, which is 22.46% higher as com crease with NC loading (Table 6). The restrictions posed by NC particles pared to H. Higher surface area rendered by NC might be the reason for effectively hinders the matrix flow. The higher surface area of na effective load transfer between the constituents leading to such an noscale reinforcements might bind the polymer chains together, re observation. UTS of prints registered better responses compared to their sulting in the mechanical properties enhancements. Fig. 6b shows H5 respective filaments. Elongation at UTS decreases with increasing NC micrograph post flexural tests. NC is firmly embedded in the matrix content due to the reduction of compliant HDPE content with higher without any signs of locational shifts. This might be due to the en filler loadings. Fracture strength of H5 print is higher by 50% compared hanced mechanical interlocking between nanoscale NC and polymer to H, while the fracture strain of H5 is substantially lower compared to chains owing to higher surface area offered by nanoscale reinforcements. Highest flexural modulus and strength are exhibited by H5,

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which is 1.12 times respective values of H. H5 registered 1.07 and 1.06

CRediT authorship contribution statement

times higher specific modulus and strength respectively compared to

their neat counterparts.

Pavan Beesetty: Methodology, Investigation, Writing - original

Developed NC/HDPE nanocomposite prints reveal superior tensile

draft. Aditya kale: Methodology, Investigation, Writing - original draft.

and flexural properties compared to neat HDPE counterparts. These

Balu Patil: Methodology, Writing - review & editing. Mrityunjay

nanocomposite prints, especially H5, can be a potential candidate ma—

Doddamani:

Conceptualization,

Writing

-

review

&

editing,

terial in replacing a few geometrically complex injection and com—

Visualization, Supervision.

pression molded components. Further, NC addition reduces HDPE consumption to some extent. Nanocomposite filament development and Declaration of Competing Interest

its feasibility in 3D printing, as presented in this work, also widens feedstock filament choices availability for polymer-based additive. The authors declare that they have no known competing financial manufacturing community.

interests or personal relationships that could have appeared to influence the work reported in this paper.

4. Property chart

Acknowledgment

Tensile and flexural properties are plotted against the density of Authors thank the Department of Mechanical Engineering at NITK HDPE composites for different types of filler in Fig. 7 [6,46,74–81] and for providing

support

and

the

research

facilities.

Mrityunjay

Fig. 8 [74–76,79,82–86] respectively based on the data extraction from Doddamani acknowledges the grant (VGST/GRD-606/133) by Vision

published literature for comparative analysis. It is clearly depicted by Group on Science and Technology, Dept. of Information Technology,

these plots, that the solid particle reinforced composites have higher

Biotechnology and Science and Technology, Govt. of Karnataka.

density and modulus as expected. However, printed NC/HDPE nanocomposite exhibits higher density, lower modulus, and higher strength

Data availability

compared to 3D printed fly ash based composites (Fig. 7). Tensile modulus of nanocomposite print is better as compared to lignocellulose, The raw/processed data required to reproduce these findings cannot

carbon black, wood, cenospheres, CaCO3, and glass microsphere-based

be shared at this time as the data also forms part of an ongoing study.

HDPE composites (Fig. 7a). Tensile strength is higher compared to 3D

printed, injection and compression molded HDPE base system (Fig. 7b).

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The flexural moduli of the nanocomposites are lower as compared to 3D printed, injection and compression molded foam system (Fig. 8a).

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Printed nanocomposites strength in flexure is higher against wood

composite. Compos Commun 2020;19:177-81.

powder-filled and natural fiber composites, and less compared to

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Publishing; 2020. p. 407–38. https://doi.org/10.1007/978-3-030-31065-3 14.

printed and injection molded fly ash based foams. This property chart

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reveals the potential usage of NC in the HDPE matrix that can be

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exploited over a wide range of mechanical properties for different

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functional components.

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5. Conclusions

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NC/HDPE nanocomposite feedstock filaments feasibility is success-

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filaments and 3D prints are studied for their thermal and mechanical

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properties. Observations are listed below as:

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Document Outline

- Mechanical behavior of additively manufactured nanoclay/HDPE nanocomposites
 - Introduction
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 - Materials, blend preparation and MFI measurements
 - Filament development and 3D printing
 - Density measurement
 - Differential scanning calorimetry of feedstock filament and their prints

- Tensile and flexural characterization
- Results and discussion
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