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Mechanical behavior of additively manufactured nanoclay/HDPE nanocomposites Pavan Beesettya, Aditya kalea, Balu Patilb, Mrityunjay Doddamania^{*}*

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ABSTRACT

Nanoclay (NC) has blended with relatively inexpensive, widely consumed HDPE (high density polyethylene) for the development of filament to be used in 3D printers [Code a1]. NC/HDPE blends are prepared by varying NC wt. % (0.5, 1, 2, and 5) and are subjected to meltflow index (MFI) measurements [Code a3]. MFI has noted to be decreasing with NC loadings. [Code a4] NC/HDPE nanocomposite blends are further extruded using a single screw extruder. [Code a3] Developed nanocompositesfilaments are fed to the fusedfilament fabrication (FFF) based 3D printer for realizing NC/HDPE nanocomposite prints. [Code a3] The density of printed sample increases withfiller 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. [Code a4] Freeze fractured prints reveal the uniform distribution of NC in HDPE. [Code a4] The tensile test is conducted on thefilaments and prints. Further printed nanocomposites are subjected toflexural investigations [Code a3]. Tensile modulus and strength offilament increase with NC additions in HDPE matrix. [Code a4] Tensile andflexural properties (modulus and strength) of the nanocomposite prints increases with NC content. [Code a4] Finally, results obtained from the tensile andflexural tests of prints are compared with different HDPE composites available in the literature. [Code a5]

1. Introduction

Among the polymer based additive manufacturing (AM) techniques, FFF is the most commonly used, widely exploited approach in developing custom made geometrically complex components. AM researchers, academicians, and industrial practitioners use FFF based AM to rapidly develop tangible objects and functional parts. It allows user to manufacture highly complex parts very easily as compared to conventional manufacturing processes[1–3]. In the FFF process, the thermoplastic basedfilament is passed to

liquefier of 3D printer through the electromechanical drive. In the liquefier, plastic gets converted into semi-molten state. The extrusion head of the printer, layer it down as per part geometry defined by the STL file [4]. Limited options of commercial filaments limit the exploitation of the FFF process to manufacture the complex functional products. The newly developed filament must have certain mechanical properties and should be compatible with existing machines without modifying its software/hard—ware components [5–7]. Till date, commonly used filament materials include but not limited to, polyetherimide, acrylonitrile butadiene styrene [8], polylactide [9], polymethylmethacrylate [10], polycarbonate [11] and their blends [12,13], polycaprolactone [14],

polybutylene terephthalate [15], polyamide [16], polypropylene [17,18] and HDPE[19,20]. Major issues associated with printing with thermoplastic material includes layer delamination and part shrinkage/ warpage as a result of repetitive heating and cooling cycles[21,22]. 3D printed composite parts printed by FFF have superior properties compared to their neat counterparts[23]. The FFF method has been commonly preferred in various sectors such as medical [24,25,87], automotive[26], and aeronautics[27]. In such scenarios, need for widening the scope of newerfilaments developments is crucial and is the focus of present work. Recently researchers are taking up intensive developmental works to explore and enhancefilaments material properties by combining a wide range of fillers with thermoplastics using compounding techniques. Fillers such as iron particles [28], carbon and glass fiber [29], Al₂O₃ powder [30], glass microspheres [31], and fly ash cenospheres [32,33] are being used in the literature to enhance thermoplastic filaments mechanical behavior. Present work is focused on increasing filament material choices for the FFF technique by developing nanocomposite feedstock.

In recent years, the composite community widely explored organi-cally modified nanoclay like montmorillonite (MMT) by reinforcing it in polymers [34–37]. The ability of tailoring the different properties by

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Nomenclature

pth Theoretical density (kg/m³)

ρexp

Experimental density (kg/m³)

 ρC Composite density (kg/m³) ρ_H HDPE density (kg/m³) ρNC NC density (kg/m³) w_H HDPE (wt. %) w_{NC} NC (wt. %)

 T_{Melt} Peak melting temperature (°C) T_{Cryst} Crystallization temperature (°C) α_{Cryst} Degree of crystallinity (%) Flnt Filament

Prnt 3D Print

combining various matrixandfiller widens the application domain of nanocomposites. Strong molecular interaction between polymer resin and nanofiller improves the thermal, mechanical, and physical properties of nanocomposites[38]. Polymer nanocompositesfind their application in various sectors such as automotive (body interior, under—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 dentistry, cosmetics, beverage and food packaging, biomedical applications, military, and aerospace [39]. Clay based nanocomposites are specifically utilized infire retardancy applications [40]. NC has ideally used reinforcement among the available nanoparticles due to lower cost, easy availability, higher cation exchange capacity and aspect ratio. It can be surface treated as well with various surfactants for enhancing mechanical properties [41]. HDPE is widely used industrial thermoplastic polymer because of its more distinct physical and mechanical properties compared to other thermoplastics [42]. HDPE find its applications in milk jugs, household utilitarian products, packaging industries and in many structural applications [43,44]. Some of the commonly used fillers with HDPE are carbon nanotubes [45], fly ash cenospheres [46–48], glass microballoons [49–51], carbon [52], calcium carbonate[53], graphite nanofibers[54], etc. Compared to conventional macro/micro filler reinforced composites, NC, in small quantities (≤5 wt. %) exhibits significant improvement in mechanical properties [55].

Commonly used polymers with nanoclay are polyethelene[56], polypropelene[57–59], polyethylene terephthalate[60], polystyrene [61,62] and polyamide[63]. HDPE is yet to be explored with NC for realizing complex geometrical components through 3D printing. Ex- cellent biocompatibility and mechanical properties of HDPE can be exploited further by reinforcing it with NC. Such an NC inclusion might effectively reduce the warpage/shrinkage related issues in 3D printing [19,64]. Present work focusses on the development of NC/HDPE blends, filaments and prints. Blends are investigated for MFIfirst. The compounded blend of nanocomposite is used to extrude feedstock fi- lament. Prior to printing, filaments are investigated for α_{Cryst} and tensile behavior. Subsequently these nanocomposite filaments are used as feedstock inputs in FFF based 3D printer. Further, 3D printed nanocomposites are investigated for crystallinity, tensile and flexural responses. Finally present work is compared with other HDPE composites in the property map.

1. Experimental

2.1. Materials, blend preparation and MFI measurements

HDPE (HD50MA180) granules used in the present study are sup— plied by Reliance Polymers, Mumbai. Table 1 provides property details of HDPE resin [6]. Montmorillonite K 10 powder (NC) is procured from SIGMA-ALDRICH, India. It is offwhite in appearance, having a density of 1980 kg/m³. Compounding of HDPE and NC (0.5, 1, 2, and 5 wt. %) in as received conditions (without any surface treatment) is materialized using 16CME SPL Brabender at 210 °C[65] to get the nanocomposite pellets (Fig. 1a). Blends with 0.5, 1, 2, and 5 wt. % NC in neat HDPE (H) are designated as H0.5, H1, H2, and H5, respectively. Dy-

estimations (ASTM D1238-13) of NC/HDPE nanocomposite blends. MFI provides basic knowledge of materialflow with respect to the unit time and viscosity change due to nanoparticle addition, which in turn helps to set optimum printing parameters in the commercially available 3D printers.

2.2. Filament development and 3D printing

NC/HDPE pellets obtained from Brabender (Fig. 1a) are fed into the single screw extruder to extrude nanocompositefilament (Fig. 1b). The single screw extruder and 3D printer being used in this study are respectively from Asabi Machinery Pvt. Ltd., Mumbai (L/D ratio -25:1, 25SS/MF/26) and Star, AHA 3D Innovations, Jaipur. The extruder has three heating zones with a temperature setting of 160, 165, and 150 °C, respectively. Feed section temperature is maintained constant at 155 °C. These parameters are optimized based on the uniform and consistent flow through the die [6]. Take-up unit and screw rotation are set as 12.5 and 25 rpm respectively to extrude the H–H5 filaments with a consistent diameter of 2.85 ± 0.05 mm

(Fig. 1b). Fig. 1b shows an image of a representative H5 filament having consistent diameter without any surface irregularities/defects. A similar setting is maintained for extruding other compositions as well. Extruded NC/HDPE filaments are fed to a commercially available 3D printer. Table 2 provides details of optimized printing parameters based on uniformflow through the nozzles, defect-free deposition (inter and intra-layer), and warpage-free samples[6]. Printing speed is maintained at 100 mm/s, which is 3.7 times higher compared to our earlier works reported in Ref. [6]. Higher print speed is chosen by keeping industrial require—ments in focus amid compromising mechanical properties of neat HDPE in particular as compared to reported investigations[6]. Infill is kept at 100% for comparative analysis with other dense HDPE composites.

2.3. Density measurement

Printed nanocomposites density is experimentally measured as per the ASTM D792-13 standard, and the average values are reported in Table 3. Theoretical densities of all the compositions are computed based on individual constituent materials density using, 1

```
\rho =
c wH wNC
```

+

 $\rho H \ \rho NC$ (1) Densities of HDPE and NC are taken as 950 and 1980 kg/m³respectively.

Table 1

Typical characteristics of HDPE granules [6].

Property Typical value

MFI (190 °C/2.16 kg) 20 gm/10 min.

Density (23 °C) 950 kg/m³

Tensile strength at yield 22 MPa

Elongation at yield 12 %

Flexural modulus 750 MPa

Vicat softening point 124 °C

nisco LMI5000 laboratory melt flow indexer is utilized for MFI



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

Table 2

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

Printing parameters Typical value Nozzle temperature (°C) 250

Printing bed temperature (°C) 70

Layer thickness (mm) 0.35

Printing speed (mm/sec) 100a

Printing pattern Rectilinear

Part orientation Y-axis

Infill (%) 100

^a Set for higher productivity.

2.4. Differential scanning calorimetry of feedstock filament and their prints

DSC analysis of thefilaments and prints is carried out using Perkin 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 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 embedded in the previous processing step are removed using the first heating cycle. T_{Cryst} and T_{Melt} are estimated from cooling and heating cycles. DSC curves typically comprise exothermic and endothermic peaks and cold crystallization melting enthalpy peak. α_{Cryst} is computed from melting enthalpy values using,

2.5. Tensile and flexural characterization

Tensile property characterization of the filament and 3D prints is carried out through Zwick Roell (Z020, load cell: 20 kN) UTM at 5 mm/ min as per the procedure outlined in ASTM D638-14. Extensometer (2— inch gauge length) is utilized for measurements with an initial load of 0.1 MPa. Flexural test (1.54 mm/min displacement rate, pre load of 0.1 MPa) is conducted on prints based on the D790-17 ASTM standard. Moduli in

flexure (E_f) is computed using, $E = L3m(L: span length,m: slope,b: width,d: thickness) 4bd <math>^f$ 3 (3) Flexural stress (ρ fm) is estimated using, ρ fm = 3PL (P - load) 2 3 (4)bd

1. Results and discussion

3.1. MFI

MFI of NC/HDPE nanocomposites representing the flowability characteristic is presented in Fig. 2a. It is well-known fact that, the variation in MFI is inversely proportional to the change in melt viscosity. NC particles resist the polymer chain mobility and reflect into the

$$\alpha$$
Cryst = Δ Hm × 100

 $\Delta H *$

m

(2)

lower MFI values in nanocomposites [67]. With increasing NC content in the HDPE matrix, MFI decreases, which accounts for 18.04, 17.14, 15.29, and 13.97 gm/10 min, respectively, for H0.5–H5. Pristine HDPE

where, $\Delta H_{\rm m}$ is heat of fusion (J/g) and $\Delta H *$

crystalline HDPE/gram (293 J/g [66]).

is the fusion heat for registered MFI of 23.06 gm/10 min [6]. MFI decreases in the range of 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 $\rho_{th},\,\rho_{exp},\,T_{Cryst},\,\alpha_{Cryst}\,\text{and}\,\,T_{Melt}\,\,\text{estimations of samples}.$

Material	Prnt.		TCryst		αCryst		TMelt	
	ρth	pexp	Flnt	Prnt	Flnt	Prnt	Flnt	Prnt
Н	950.00	948.93 ± 13	108.02	109.05	55.5	57.1	131.07	131.02
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	999.20 ± 11	112.64	112.74	65.8	75.3	131.24	130.29
H5	975.37	999.40 ± 18	112.05	112.40	68.0	77.8	131.26	130.62



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

The densities of prepared filaments and prints are presented in Table 3. The addition of hard and stiff NC into HDPE increases the composite density. Among all the compositions, H5 has shown the highest density as expected. Higher experimental densities, as compared to the respective theoretical ones except H, clearly indicate dense prints and absence of matrix porosity. Uniform distribution of hard and stiff NC particles into HDPE is clearly observed through SEM of representative 3D printed sample (Fig. 2b). Interfacial bonding between NC and HDPE is observed to be poor as constituents materials utilized in the present work are not surface treated. DSC results offilaments and prints are presented inTable 3.Fig. 3 presents the DSC curves of the filament and printed HDPE and their nanocomposites. Compared to HDPE all thefilament and 3D printed samples have shown higherT_{Cryst} temperature indicating strong interaction between HDPE resin and

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	Flnt	Prnt	Flnt	Prnt	Flnt	Prnt	Flnt	Prnt
Н	525 ± 11	874 ± 12	11.1 ± 0.1	13.8 ±	11.4 ± 0.2	13.0 ± 0.2	_	6.0 ± 0.19	_	160.1 ± 3.3
H0.5	677 ± 15	904 ± 13	13.8 ± 0.3	15.0 ±	12.6 ± 0.4	12.1 ± 0.2	9.8 ± 0.12	14.1 ± 0.22	26.1 ± 0.6	19.0 ± 0.6
H1								13.9 ± 0.54		
H2							1.57 ± 0.05	12.0 ± 0.47		
Н5								9.0 ± 0.29		

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 temperature, the melt nucleates on the NC surface leading to the formation of larger thickness crystal lamellas resulting in higher T_{Cryst} [69,70]. 3D prints and filament shows similar T_{Cryst} trend which indicates that the

second material extrusion through printers nozzle has no remarakable impact. No significant difference is observed in T_{Melt} of the filament and prints (Table 3). Polymer chains have a tendency to crystallize by their own (self-nucleation effect) or due to external nucleating agents. In the present nanocomposite filaments and prints, NC has played the role of external nucleating agent enhancing crystallization. The higher percentage of crystallization in 3D prints as against respective filaments is attributed to more aligned martial extrusion and natural cooling of the prints in the printer chamber [71]. Prints cool down by natural convective mode, whereas hot extruded filament is being quenched in a water bath during filament extrusion. Thus the polymer melt has less time to crystallize, enabling the chains to align in random order. Degree of crystallinity increases as nanoclay con—centration increases in filaments and prints. α_{Cryst} increased from 57.1%

to 77.8% for H–H5, respectively, in prints. Higher α_{Cryst} in 3D printed samples as against respective nanocomposite filaments is attributed to the different cooling modes in the respective processing routes [72].

3.3. Tensile testing of filaments and prints

The filament should have sufficient strength and stiffness to be used as feedstock in commercially available 3D printers. It should not rup— ture or buckle while passing through afilament drive mechanism[73]. Filament buckling can be avoided by making it stiffenough such that it will pass through the drive mechanism successfully. Inclusion of NC improves the stiffness of nanocomposite filament. Modulus of nanocomposites filament has increased with NC addition. Among the nanocompositesfilament, H5 has registered the highest modulus 741 MPa (Table 4) and is 41.14% higher compared to H. Filament stiffness is improved by stiff and hard NC additions in compliant HDPE resin. Stress—strain plots for HDPE and the composite filament is plotted in Fig. 4a until 15% strain as neat HDPEfilament exhibits more than 150% strain level. The test is stopped

due to stroke distance and time con—straints. Such a higher strain value signifies the ductile behavior of neat



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

Specific tensile properties of printed H–H5.

Material Sp. Modulus (MPa/kg/m³) Sp. Strength (MPa/kg/m³)× 10⁻³

HDPE. On the contrary, nanocomposite filament elongation decreased severely. The tensile strength of H5 (14.90 MPa) is highest among all the composition, which is ~35% higher compared to neat HDPE filament. Uniform distribution of NC in H for H5 (Fig. 4b) compared H2

(Fig. 4c) might be the reason for such an observation. Further, there may be better molecular level interface inconsonance occurring between the polymer chain and nanoclay at H5. Elongation at UTS is highest for H0.5 in 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.

H 0.921 14.58

H_{0.5} 0.906 15.03

H1 0.916 15.12

H2 0.947 15.61

H5 0.950 16.91

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.

Table 6
Flexural properties of prints.

Materia	l Modulus (MPa)	Strength (MPa)	Specific modulus (MPa/kg/m³)	Specific strength (MPa/kg/m ³)× 10 ⁻³
Н	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	0.67	20.83

H2
$$697 \pm 16 \quad {21.50 \pm \atop 0.03} \quad 0.70$$
 21.52

H5
$$735 \pm 13 \quad {22.24 \pm \atop 0.03} \quad 0.74$$
 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 strain though plots in Fig. 5a are graphed until 18% strain. Fig. 5b shows a micrograph of H, which clearly indicates substantial plastic 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.

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 chains realignment and augmented crosslinking in printing. H5 exhibited the highest UTS of 16.9 MPa, which is 22.46% higher as compared to H. Higher surface area rendered by NC might be the reason for effective load transfer between the constituents leading to such an observation. UTS of prints registered better responses compared to their respective filaments. Elongation at UTS decreases with increasing NC content due to the reduction of compliant HDPE content with higher filler loadings. Fracture strength of H5 print is higher by 50% compared to H, while the fracture strain of H5 is substantially lower compared to neat HDPE. Specific mechanical properties are crucial from a structural application perspective. Specific strength of H5 outperformed H by 16% (Table 5).

3.4. Flexural response of prints

Neat HDPE and their nanocomposite prints did not fail until 10% strain (Fig. 6a). Flexural moduli and strength of nanocomposite increase with NC loading (Table 6). The restrictions posed by NC particles effectively hinders the matrix flow. The higher surface area of nanoscale reinforcements might bind the polymer chains together, resulting in the mechanical properties enhancements. Fig. 6b shows H5 micrograph post flexural tests. NC is firmly embedded in the matrix without any signs of locational shifts. This might be due to the enhanced mechanical interlocking between nanoscale NC and polymer chains owing to higher surface area offered by nanoscale reinforcements. Highest flexural modulus and strength are exhibited by H5,

which is 1.12 times respective values of H. H5 registered 1.07 and 1.06 times higher specific modulus and strength respectively compared to their neat counterparts.

Developed NC/HDPE nanocomposite prints reveal superior tensile and flexural properties compared to neat HDPE counterparts. These nanocomposite prints, especially H5, can be a potential candidate material in replacing a few geometrically complex injection and compression molded components. Further, NC addition reduces HDPE consumption to some extent. Nanocompositefilament development and its feasibility in 3D printing, as presented in this work, also widens feedstock filament choices availability for polymer-based additive manufacturing community.

1. Property chart

Tensile andflexural properties are plotted against the density of HDPE composites for different types offiller in Fig. 7[6,46,74–81] and Fig. 8 [74– 76,79,82–86] respectively based on the data extraction from published literature for comparative analysis. It is clearly depicted by these plots, that the solid particle reinforced composites have higher density and modulus as expected. However, printed NC/HDPE nanocomposite exhibits higher density, lower modulus, and higher strength compared to 3D printed fly ash based composites (Fig. 7). Tensile modulus of nanocomposite print is better as compared to lignocellulose, carbon black, wood, cenospheres, CaCO₃, and glass microsphere-based HDPE composites (Fig. 7a). Tensile strength is higher compared to 3D printed, injection and compression molded HDPE base system (Fig. 7b). Theflexural moduli of the nanocomposites are lower as compared to 3D printed, injection and compression molded foam system (Fig. 8a). Printed nanocomposites strength in flexure is higher against wood powder—filled and natural fiber composites, and less compared to compression molded samples as seen from Fig. 8b. Nonetheless, these nanocomposites registered superior performance as compared to 3D printed and injection moldedfly ash based foams. This property chart reveals the potential usage of NC in the HDPE matrix that can be exploited over a wide range of mechanical properties for different functional components.

1. Conclusions

NC/HDPE nanocomposite feedstockfilaments feasibility is successfully demonstrated for commercially available 3D printers. Developed filaments and 3D prints are studied for their thermal and mechanical properties. Observations are listed below as:

NC/HDPE nanocomposites are successfully printed without any warpage.

•

• MFI of nanocomposite blends decrease with increasing NC content, whereas crystallinity is observed to be increasing. H–H5 filaments

crystallinity decreased as against respective prints.

•

Tensile andflexural, modulus and strength are noted to be increased with NC additions in compliant HDPE matrix.

•

H5 is the best composition exhibiting superior mechanical performance.

•

Property map reveals the suitability of NC/HDPE nanocomposite printing with enhanced mechanical properties as compared to other HDPE composites synthesized through conventional and advanced manufacturing technologies.

The aim of the present work is to materialize nanocomposite filaments for 3D printing applications to widen the scope of limited material choices available for the FFF based additive manufacturing community.

CRediT authorship contribution statement

Pavan Beesetty: Methodology, Investigation, Writing - original draft. Aditya kale: Methodology, Investigation, Writing - original draft. Balu Patil: Methodology, Writing - review & editing. Mrityunjay Doddamani: Conceptualization, Writing - review & editing, Visualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competingfinancial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The raw/processed data required to reproduce thesefindings cannot be shared at this time as the data also forms part of an ongoing study.

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