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Recycling potential of MWCNTs/HDPE nanocomposite filament: 3D printing and mechanical characterization

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Abstract

Fused filament fabrication (FFF) based additive manufacturing (AM) process is a widely used and emerging manufacturing process for polymer-based products. The recycled filaments are realized through wastage generated while extruding the constant diameter feedstock filament, which is otherwise dumped in landfills or incinerated, releasing hazardous and toxic gases that influence the ecological environment. The wastage of these filaments can be eliminated by recycling and reusing them, addressing materials circular economy effectively, presented in this paper. The functionalized MWCNT reinforced HDPE (high-density polyethylene) nanocomposite (NC) is realized through a brabender, which is further used for filament extrusion. The waste/unrecycled (W/UR) and the recycled filaments are checked for quality. The density of the recycled filaments increases compared to the W/UR filament in each extrusion pass. The crystallinity and tensile properties of the recycled filaments increase compared to the W/UR filament with each additional extrusion cycle. Further, these filaments are used for 3D printing, and investigated for density, XRD and tensile tests. It is observed that the density, crystallinity and tensile properties of the recycled prints increase compared to the W/UR print. The tensile strength and modulus of $1\times$, $2\times$ and $3\times$ prints are 63.82, 67.11 and 67.76%, and 45.63, 55.34 and 97.81% respectively, higher than those of the W/UR print. The highest tensile strength and modulus are observed for $3\times$ print which is 67.76 and 97.81% respectively, higher than those of the W/UR print. 3D prints exhibited enhanced performance as compared to their respective filaments. Finally, the present tensile results are mapped on a property chart, and compared with the available HDPE composites.

Keywords Recycling · Nanocomposite · MWCNT · HDPE · 3D Printing · Tensile

Abbreviations

ρ_H	: Density of HDPE (kg/m^3)
ρ_{exp}	: Experimental density (kg/m^3)
ρ_{CNT}	: Density of MWCNT (kg/m^3)
ρ_{th}	: Theoretical density (kg/m^3)
ρ_C	: Density of composite (kg/m^3)
W_H	: Weight % of HDPE
W_{CNT}	: Weight % of MWCNT
$\overline{d}$	: Recycled filament diameter (mm)
σ	: Standard deviation (mm)
n	: No. of samples

3D	: Three dimensional
3DP	: 3D printing

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Introduction

As documented by the United Nations high-level panel on challenges, threats and climate change, environmental degradation (depletion of natural resources like water, soil and air, elimination of ecosystems, pollution and extinction of wildlife, which are harmful to the ecosystem) is one of the ten threats affecting the world today [1, 2]. Environmental degradation is mainly due to indiscriminate CO_2 emission. CO_2, a greenhouse gas, is emitted from burning fossil fuels (natural gas, oils, coal), trees, solid waste and other biological waste [3]. Plastic waste is polymer-based products that are carbon-based materials and emit CO_2 into the atmosphere. CO_2 emission leads to global warming, which further leads to climate change resulting in fluctuation in seasons, low rainfall and temperature rise of the environment, causing

low agricultural output and drought globally. Moreover, some effects of climate change are health problems, severe storms, and rising sea levels affecting coastal areas, migration, and the decreasing economy [4]. These concerns are a major challenge for the world, and finding the appropriate solution for decarbonization, i.e., minimizing CO_2 emissions in the atmosphere is crucial for human survival. Scientists/researchers have taken several steps to provide solutions to the climate change issue like the development of different new materials for the storage of CO_2 and the recommendation for shifting toward renewable energy sources [5–7]. Moreover, reducing deforestation and making the environment free from plastic waste can also minimize CO_2 emissions in the atmosphere. The current work focuses on recycling carbon-based nanocomposite products and reusing them to make the desired products. This will help eliminate plastic waste from the environment and thereby help reduce CO_2 emissions to achieve the carbon neutral society.

The most widely consumed polymer, high-density polyethylene, provides various properties such as mechanical, chemical, and corrosion resistance, making them useful for industrial applications such as aeronautical, automotive, agricultural and domestic products manufacturing industries [8]. Nonetheless, these thermoplastic wastes are non-degradable, causing environmental pollution and affecting the ecological balance [9]. Environmental pollution has become a global issue nowadays, and plastic waste is the major contributor to it as plastic material releases toxic gases in post-usage/consumption. These toxic gases are hazardous to plants, animals and human beings. In our day-to-day life, polymers' usage is increasing, hence the associated wastage. Therefore, reducing the plastic waste is crucial to saving environmental pollution, which can be accomplished by adopting a circular materials approach of recycling and reuse. Recycling is a manufacturing process in which waste material is processed and made useful for polymer-related applications [10]. There are different recycling processes such as mechanical, primary, quaternary and chemical. Among them, mechanical recycling is the most commonly used process as it involves reheating the polymers [11]. Most plastic waste comes from the packaging and daily used products such as straws, plastic bottles and carry bags, which are made of thermoplastic polymers such as polypropylene, polyethylene, polycarbonate and polyvinyl chloride. Therefore, recycling thermoplastic polymers and their composites and reusing them to make different functional components can reduce plastic waste to a large extent. Thermoplastic polymers have unique characteristics and reheating capabilities, which can be recycled and reused for different applications. There are different thermoplastic polymers such as polypropylene [12], polycarbonate [13], polyvinyl chloride [14], polylactic acid [15], acrylonitrile butadiene styrene [16], polyethylene terephthalate [17] and

HDPE [18, 19], used as the matrix in thermoplastic polymer composites. Glass microballoons (GMBs) [20, 21], fly ash cenospheres [22, 23], glass fibers [24], carbon fibers [25], carbon black [26], montmorillonite nanoclay [27], graphene [28] and carbon nanotubes [15, 29] are the common filler materials used to reinforce these thermoplastic polymers.

The advanced manufacturing process such as FFF-based 3DP is the most widely used for thermoplastics manufacturing due to its design flexibility, integrated components, a wide range of filament availability and lower lead times. FFF 3DP process is a layered material deposition through G-code created using a stereolithography (.STL) file where input materials are used in filament [30]. 3DP finds applications in different sectors such as automobile [31], aerospace [32], marine [33] and medical [34]. Due to the wide application areas of 3DP, there is increasing thrust for developing different newer filaments. In 3DP thermoplastic polymers and their composites, warpage is the major concern that can be eliminated by embedding thermally stable reinforcements in the polymer matrix [35–37]. Carbon nanotubes (CNTs) are thermally stable and can reinforce polymer matrix to eliminate the warpage issues posed by the semi-crystalline HDPE. Moreover, they have outstanding mechanical and thermal properties. Additionally, they have a higher aspect ratio and surface area [29]. Due to all these reasons, CNTs become a suitable filler material, and are hence chosen as filler in the current work.

The common thermoplastics used with CNTs are polycarbonate and polyurethane [38], polyethylene [39], polystyrene [40], etc. HDPE has a good mechanical, chemical, wear resistance, impact strength, physical and moderate rigidity properties, and is widely utilized in industries [41, 42]. It is used in chemical containers, packaging industries, household products, jugs and many other applications [30, 36]. HDPE is commonly reinforced with GMBs [36], fly ash cenospheres [23], nanoclay [27], carbon [43], wood flour [44], graphite fibers [45], etc. The small addition of CNTs can enhance the modulus and strength of the 3D printed polymer composites [41]. The composites developed using the CNTs reinforcements are called nanocomposites as the CNTs are of nanosize. These NCs are used in several engineering fields such as automobiles, military, aerospace and naval [29, 46].

Ashish Kumar Singh et al. [20] studied the recycling potential of fly ash cenospheres/HDPE foam (HDPE40). The foam density was observed to increase until the 2nd extrusion cycle due to cenospheres breakage and consolidation of porosities. The tensile moduli and yield strengths of HDPE and HDPE40 filaments increased with additional extrusion passes. Rupinder Singh et al. [47] studied the thermal and tensile properties of an energy storage device (ESD) made up of recycled ABS reinforced with different fillers (graphite, MnO_2, $ZnCl_2$, and NH_4Cl) fabricated by

3DP. They observed that the ESD has better tensile properties (modulus, strength), and can work in severe loading conditions. Narinder Singh et al. [48] worked on recycling HDPE and extrusion of filaments by reinforcing SiC/Al$_2$O$_3$ particles. They investigated thermal, MFI and tensile properties, and found no significant effect of reinforcement on thermal and rheological (MFI) properties. Felicia Stan et al. [49] presented the recycling of LDPE/MWCNT composites fabricated by injection molded method, and investigated rheology mechanical and electrical properties. They observed that shear viscosities of neat and recycled composites decrease with increasing shear rates and MWCNT loading. Further, the shear-thinning behavior is prominently exhibited at high shearing rates. The tensile strength and the composite modulus increased with MWCNT loading. The electrical conductivity shows an increasing trend up to 5 wt. %. Changqing Fang et al. [50] studied the effect of MWCNT addition on recycled PET/TPU composite properties. The tensile strength and thermal stability of the CNTs/rPET/TPU composites improved with increasing CNT content. Rupinder Singh et al. [51] extruded recycled HDPE and LDPE filaments reinforced with Fe powder. Reinforced composites exhibited better properties compared to pure materials. The breaking strength and hardness increased with filler loading.

The prevailing literature reveals that the recycling potential of functionalized MWCNTs reinforced HDPE is yet to be explored. The present work studies the recycling potential of functionalized MWCNTs/HDPE NCs. The waste filaments post-extrusion is recycled once (1x), twice (2×) and thrice (3×) by pelletizing them after every extrusion pass. Subsequently, the recycled filaments are tested for density, XRD and tensile properties to check their enhancement and recycling potential. Further, these developed and recycled filaments are utilized in 3D printing of the NCs, and are subsequently tested for density, XRD and tensile responses to check the property enhancement post-printing. Finally, the tensile properties of the printed samples are compared with HDPE composites.

Experimental

Materials and nanocomposite development method

HD50MA180 (HDPE) granules are used as a matrix. Functionalized MWCNTs produced by the carbon vapor deposition process used as filler is procured from Adnano Tech., India. The typical properties of the functionalized MWCNTs and HDPE are presented in Ref. [42]. Due to the higher aspect ratio, small diameters and entwined bundled form of single-walled CNTs, their uniform distribution in the matrix is difficult. In contrast, the MWCNT (non-functionalized) exhibits inferior interfacial bonding between matrix and

filler, limiting their reinforcement potential [46]. The homogeneous mixing of HDPE and the functionalized MWCNTs is achieved by the blending process using a 16CME SPL Brabender. The mixing speed and the temperature are set at 10 rpm and 210 °C, respectively [33]. 1% (wt.) of the functionalized MWCNTs powder is weighed, mixed with HDPE mechanically, and fed to the hopper of the brabender to obtain NC pellets. The developed functionalized MWCNTs/HDPE NC is designated as H1, and the NC pellets are shown in Fig. 1.

Filament manufacturing and recycling

The NC pellets obtained from Brabender are used to extrude the filament for a 3D printer. A 25SS/MF/26 single screw extruder is used to extrude the filaments, supplied by Aasabi Machinery Pvt. Ltd., Mumbai, having a 25:1 L/D ratio. The barrel temperatures from the feed-die section are 145–150–155–145 °C. Post-stabilization of the temperatures, the NC pellets/blends are fed to the extruder screw though hopper. The screw (24.8 rpm) and the take-off unit speeds (11.0 rpm) are set up to start the extrusion process, and changed together to obtain the desired diameter of the filament. There is a large amount of filament wastage while selecting/choosing the suitable extrusion parameters setting to obtain the filament's desired diameter. In this work, these waste filaments are recycled to reduce the plastic waste from the environment. The waste filaments are collected, pelletized and pre-heated in an oven at 80 °C for 24 h to avoid moisture content before the extrusion of the recycled filaments. The first-time extruded filament is designated as 1×filament. The 1×filament is pelletized, and fed again to obtain a second-time extruded (2×) filament. The same method is repeated to get the third-time extruded filament, which is further designated as 3×filament. Figure 2 presents

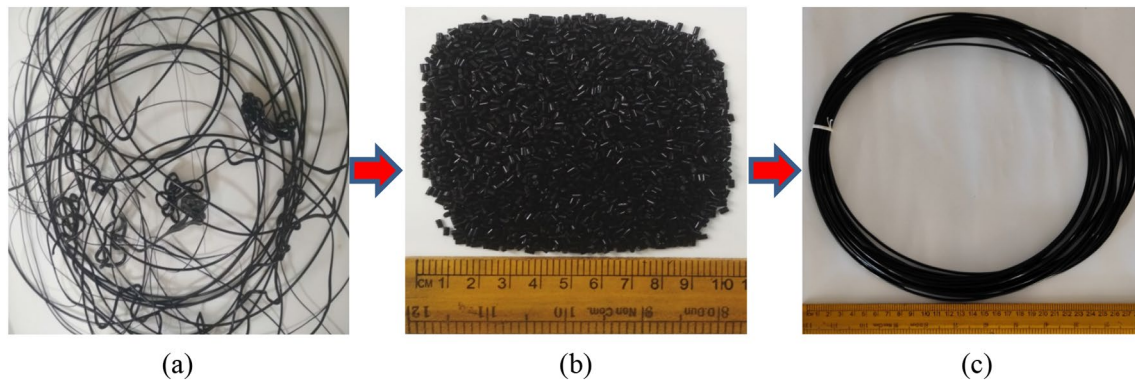**Fig. 1** Representative image of MWCNT/HDPE NC pellets

Fig. 2 Representative images of **a** W/UR filament, **b** pellets of W/UR filaments, and **c** H1-3X recycled filament

the waste extrusion filaments, waste filament pellets and 3×recycled filament having a consistent diameter.

Filament regularity check and density measurement

The regularity of the filament cross-section is checked by measuring its diameter and standard deviation. A minimum of five samples from different filament zones of extruded recycled filaments are taken for diameter measurement. The mean/average diameter ($\bar{d}$) is calculated using [42]

$$\bar{d} = \frac{\sum d_i}{n},\tag{1}$$

and the deviations (σ) are estimated through [42]

$$\sigma = \sqrt{\frac{\sum \left(d_i - \bar{d}\right)^2}{n}}.\tag{2}$$

The measurement of the filament density and the prints are carried out using the ASTM D792-20. The theoretical density of the filaments and the prints are calculated with the help of the rule of mixture [42].

$$\rho_c = \frac{1}{\frac{W_H}{\rho_H} + \frac{W_{CNT}}{\rho_{CNT}}}.\tag{3}$$

XRD of the filaments and prints

The crystallinity of the filaments and the printed samples is measured using Malvern PANalytical, the Netherlands (Model-Empyrean 3rd Gen), fitted out with Cu kα radiation at 40 mA and 45 kV using a Nickel filter. The samples are scanned at a 2°/min speed from 10 to 80 ° (2θ) [52].

Tensile testing of the filaments and prints

The filaments and the prints are tensile tested according to ASTM D638-14 using a Zwick Roell universal testing machine (Z020, load cell: 20 kN, initial load-0.1 MPa) with a 5 mm/min cross-head speed through an extensometer (2-inch gauge length) for strain measurements.

3D Printing of sample

An FFF-based commercial 3D printer supplied by Aha 3D, India (2 nozzles, 0.8 mm diameter), is used to print the samples. The unrecycled and recycled filaments (1×, 2× and 3×) are used to print samples. The NC samples are printed on Kraton™ SEBS FG1901, and left on the build plate to cool to obtain the warpage-free prints [31].

Results and discussion

Filament regularity and quality check

The uniform regularity in the diameter is crucial for the uniform material flow through the printer nozzles resulting in good-quality prints. The mean diameter and the standard deviation of the W/UR and the recycled filament are listed in Table 1. The mean diameter of each filament is 2.73 mm, which shows the extrusion consistency. The standard

Table 1 Density of the filaments and the prints

| Particulars	$\bar{d}$ with σ (mm)	ρ_{th}(kg/m^3)	ρ_{exp}(kg/m^3)	
			Filaments	Prints
W/UR	2.73 ± 0.03	898.04	901.01 ± 4.20	903.18 ± 3.93
1x	2.73 ± 0.02		948.42 ± 4.40	950.27 ± 2.48
2x	2.73 ± 0.01		983.25 ± 7.48	986.31 ± 4.35
3x	2.73 ± 0.01		985.13 ± 9.61	991.43 ± 5.12

deviation of W/UR filament is higher (0.03 mm) than the recycled filaments (1×, 2× and 3×), which shows that W/UR filament has minor variations in the diameter than the 1×, 2× and 3× filaments. The 2× and 3× (0.01 mm) filament diameter is lower than the 1× filament (0.02 mm), which might be due to the stiffening effect post subsequent thermal cycles. Further, the decrease in standard deviation may be due to the good arrangement of polymer chains and the functionalized MWCNTs in the NCs. There is no change in the standard deviation of 2× and 3× recycled filaments, implying the saturation of polymer chains and the fillers realignment. The higher diameter variations in the W/UR filament compared to the recycled filaments are due to the random alignment of the polymer chains and the functionalized MWCNTs. Further, when the filaments are recycled, the polymer chains and the functionalized MWCNTs undergo thermal processing, where they get aligned. Therefore, the filament cross-section reduces slightly, lowering the standard deviation further. Moreover, the variations in the filament diameter may also be due to matrix porosity. The matrix porosity in the recycled filament reduces the material's tensile strength [36]. The presence of porosity is determined through the density measurement of the sample. The density of the W/UR filament, recycled filament and prints are listed in Table 1. The density of the recycled filaments (1×, 2× and 3×) increases compared to the W/UR filament. It is also observed that the recycled filament density increases with each additional extrusion pass. The maximum density is observed to be for 3× recycled filament. In contrast, the densities of 2× and 3× filaments are approximately the same, showing the delay in the realignment of the polymer chains and the fillers. The same trend is observed for the prints as well. The prints' density is higher than the extruded counterparts, showing the additional alignment of the polymer chains with fibers and the higher time of crystallization in the printing process. The experimental density of the W/UR filament, recycled filament and 3D prints are higher compared to the theoretical density of the H1 nanocomposite,

which shows no air voids/porosity in the sample. This can also be seen in the SEM image of the freeze-fractured H1-3× print. The lower magnification image of H1-3× (Fig. 3a) shows the matrix's air voids/porosity absence. In contrast, the higher magnification image (Fig. 3b) shows the homogeneous dispersion of the functionalized MWCNTs in HDPE.

XRD of the NC filaments and prints

The polymer chains' and fibers' realignment influence the filaments' and prints' crystallinity. The XRD test is performed for the filaments and the prints to check the changes in their crystallinity. The XRD of the developed compositions and associated prints are presented in Fig. 4a and b, respectively, and the corresponding values are presented in Table 2. The peaks intensity of the recycled filaments' increases compared to the W/UR filament. The peak intensity also increases with each extrusion cycle. The peak values (Table 2) show orthorhombic crystal structures at (110) and (200) lattice plane [53]. Similar observations are noted for the prints as well. The highest peak intensity is observed for 3× filament and the print. The sharpness of the peak represents crystallinity. Therefore, the increase in the peak intensity can be correlated to an increase in crystallinity. The degree of crystallinity increases for the filaments and the prints compared to the W/UR filament and the print respectively. It also increases with each extrusion cycle, as clearly evident from Table 2. The increase in the peak intensity and the degree of crystallinity of the filaments and the prints may be due to the realignment of the polymer chains and the fillers while undergoing additional thermal processing. The degree of crystallinity of the prints is higher than the filaments owing to the thermal heating (additional) and the higher time of crystallization in the 3D printing.

Fig. 3 Representative images of 3D printed freeze-fractured H1-3× print at **a** lower and **b** higher magnifications
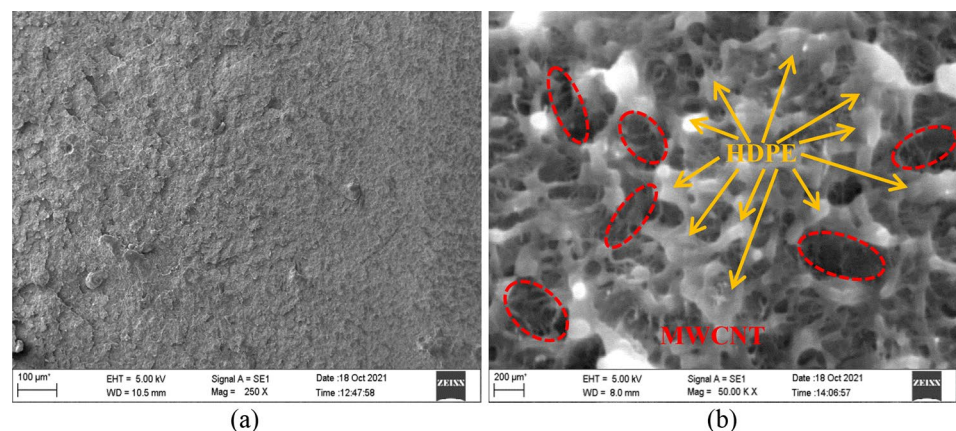
Tensile test of the NC filaments

The increase in the density and the crystallinity of the recycled filaments compared to the W/UR filament influences the mechanical properties. In the present work, the tensile test is performed on the recycled and W/UR filaments to investigate their tensile properties. Moreover, the tensile test of the filaments is crucial to check their strength and stiffness so that they can be further utilized for 3D printing. The tensile responses of the NC filaments are shown in Fig. 5a and Table 3. The modulus of the recycled filaments ($1\times$, $2\times$ and $3\times$) increases compared to the W/UR filament. The modulus of $1\times$, $2\times$ and $3\times$ recycled filaments is 12.74,

20.30 and 23.12%, respectively, higher than the modulus of the W/UR filament. The polymer chains and the functionalized MWCNTs get realigned through the extrusion process, enhancing the adhesion between the filler and matrix, resulting in a higher modulus. The modulus of the recycled filaments also increases with each extrusion pass up to the 3rd; after that, no significant change is observed. The modulus of $2\times$ and $3\times$ filaments is 6.70 and 9.20%, respectively, higher than that of the $1\times$ filament, while the modulus of the $3\times$ filament is 2.34% higher than the modulus of $2\times$ filament, showing the property enhancement saturation. The highest modulus is observed for $3\times$ filament, 23.12% higher than that of the W/UR filament. The increased modulus in

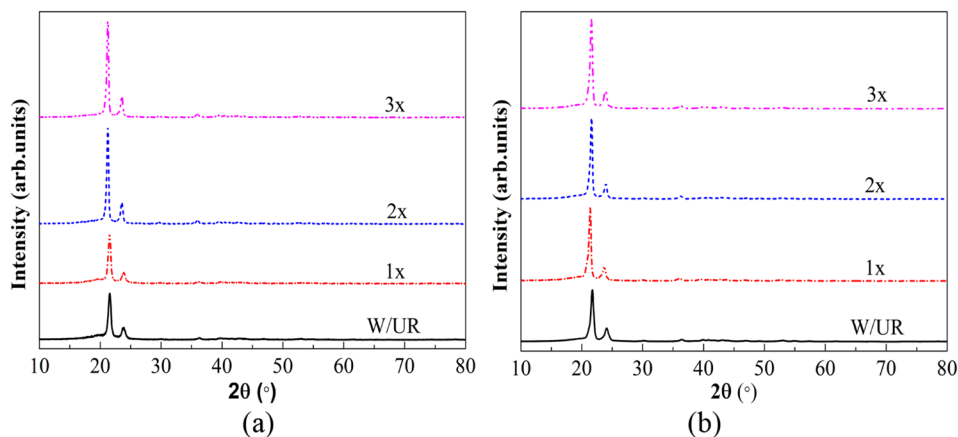**Fig. 4** The XRD pattern of NC **a** filaments and **b** prints

Table 2 The XRD responses of filaments and prints

Particulars	Filament peak position 2θ (°)		3D prints peak position 2θ (°)		Degree of crystallinity (%)	
	1st peak	2nd peak	1st peak	2nd peak	Filaments	3D Prints
W/UR	21.23	23.63	21.32	23.42	59.04	68.35
1x	21.53	23.81	21.48	23.79	61.21	71.42
2x	21.15	23.52	21.51	23.91	62.89	73.33
3x	21.53	23.80	21.26	23.52	65.67	75.46

Fig. 5 Representative **a** tensile stress–strain plot of the NC filaments and **b** SEM image of H1-3×recycled filament
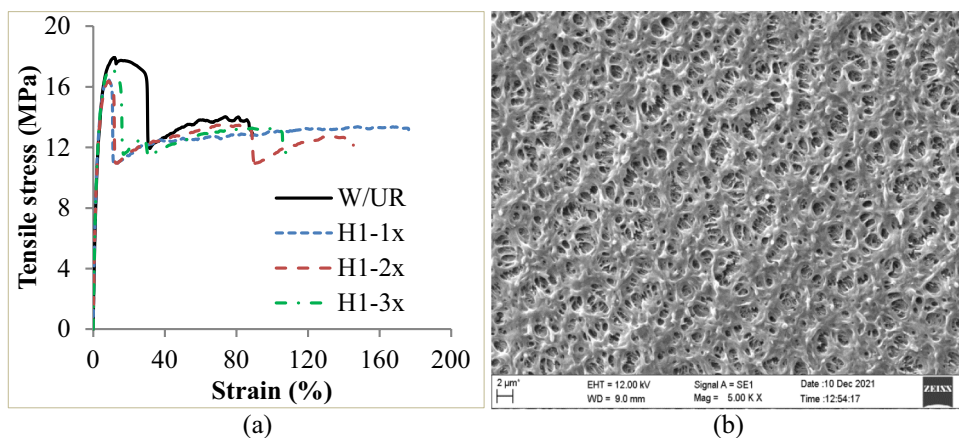
Table 3 Tensile responses of filaments and prints

Number of cycles	Modulus (MPa)		Yield strength (MPa)		UTS (MPa)		Fracture strength (MPa)		Fracture strain (%)	
	Flmt	Print	Flmt	Print	Flmt	Print	Flmt	Print	Flmt	Print
W/UR	675 ±19	824 ±26	15.9 ±0.6	7.86 ±0.4	15.9 ±0.6	15.2 ±0.5	12.87 ±0.6	15.0 ±0.9	89.22 ±0.6	7.64 ±3.31
1x	761 ±12	1200 ±13	16.5 ±0.1	12.7 ±0.3	16.5 ±0.1	24.9 ±0.7	12.94 ±0.3	24.5 ±0.5	176.38 ±3.21	12.17 ±2.23
2x	812 ±17	1280 ±16	17.2 ±0.3	10.37 ±0.2	17.2 ±0.3	25.4 ±0.4	12.15 ±0.2	25.03 ±0.6	145.36 ±4.33	5.07 ±1.04
3x	831 ±15	1630 ±23	17.4 ±0.2	11.71 ±0.3	17.4 ±0.2	25.5 ±0.3	11.35 ±0.5	24.87 ±0.2	108.42 ±3.94	4.70 ±2.06

the recycled filaments with each extrusion pass is due to an additional realignment of the polymer chains due to further thermal processing. The yield strength (YS) and the ultimate tensile strength (UTS) of the recycled filaments are the same, and higher than those of the W/UR filament. The YS and UTS of $1\times$, $2\times$ and $3\times$ recycled filaments are 3.77, 8.17 and 9.43%, respectively, higher than those of the W/UR filament. The recycled filaments' YS and UTS also increase with each extrusion pass. The YS of the $2\times$ and $3\times$ filaments is 4.24 and 5.45%, respectively, higher than that of $1\times$ filament, while the YS of the $3\times$ filament is 1.16% higher than the YS of the $2\times$ filament. The highest YS and UTS are observed for $3\times$ filament (9.43% higher than W/UR filament). YS increases due to the increased crystallinity (as observed in XRD discussions), further increasing the filaments' elasticity (elastic region). The rise in UTS is due to the cross-linking of the polymer chains, which enhances the load transfer capability. The SEM image of the $3\times$ recycled tensile-tested filament is shown in Fig. 5b, showing the cross-linking and the good distribution of the functionalized MWCNTs, and the better bonding between the constituents. The fracture strength of the $1\times$ filament is observed to be the highest. The fracture strain of the recycled filaments ($1\times$, $2\times$ and $3\times$) is higher than that of the W/UR filament, showing the increased ductility (due to more elongation) of the recycled filaments as compared to the W/UR filament. It can also be observed that the fracture strain of the recycled ($1\times$, $2\times$ and $3\times$) filaments is reducing with each extrusion pass. This is due to increased brittleness in the recycled filaments while going through each extrusion pass. Overall, the tensile responses show the enhancement in modulus and the strength of the recycled filaments compared to the W/UR filament, which indicates that these filaments can be utilized in 3D printer for components manufacturing for different applications.
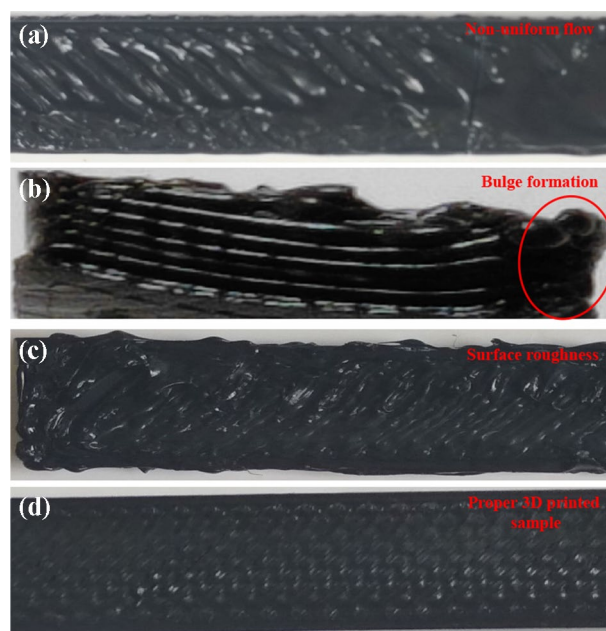
3D printing

Suitable 3D printing parameters are required for good-quality prints. The suitable 3D printing parameters are

Table 4 Suitable 3D printing parameters used in the current work [42, 52]

Parameters	Values
Extrusion multiplier	0.90–1.0 [0.95]
Layer height (mm)	0.30–0.50 [0.50]
Nozzle temperature (°C)	190–220 [200]
Printing speed (mm/s)	25–35 [30]

*Values in the square bracket = Suitable 3D printing parameters

Fig. 6 Challenges encountered in 3DP of recycled filaments

obtained through the pilot studies shown in Table 4 [42, 52], which are set for 3D printing. The samples 3D printed at respective extrusion multipliers of 0.90 and 1.0 showed the non-uniform flow of the material (Fig. 6a). Bulge formation (Fig. 6b) was observed when the samples were printed with layer heights between 0.30 and 0.50 mm. The proper

clearance must be between the two layers to obtain bulge-free samples. Printing temperature is also very crucial for good-quality prints. A higher printing temperature (220 °C) leads to overheating of the samples, and a lower printing temperature (190 °C) leads to improper flow of materials, which further influences the quality of the prints. The samples printed at a higher speed (35 mm/s) increased the surface roughness (Fig. 6c). The samples printed using the suitable parameters showed a good-quality print (Fig. 6d). The W/UR and the recycled filaments (1×, 2× and 3×) are used as feedstock filaments to print samples. The samples printed with W/UR filament are named as waste/unrecycled (W/UR) print, whereas the samples printed with the recycled filaments, 1×, 2× and 3×, are designated as 1×, 2× and 3× prints (recycled prints), respectively. After printing, the samples are tested for density, XRD and tensile properties.

(a)

(b)

Fig. 7 Tensile-tested samples showing **a** brittle failure and **b** fractured surfaces in brittle mode

Tensile test of the 3D printed samples

The printability of the W/UR and the recycled filaments is assured through the tensile testing of the filaments, and then used to print tensile samples to check their property enhancement potential. The tensile-tested samples exhibiting the brittle failure (Fig. 7a) and the close-up image of the fractured surface (Fig. 7b) are presented. The tensile responses of the prints are shown in Fig. 8a, and the corresponding values are given in Table 3. The modulus of the recycled printed samples increases compared to the W/UR printed samples. The modulus of 1×, 2× and 3× printed samples is 45.63, 55.34 and 97.81%, respectively, higher than that of the W/UR printed sample. The increase in modulus is due to the higher crystallinity and the constituent elements interfacial bonding enhancement. The modulus of 2× and 3× prints is 6.67 and 35.83%, respectively, higher compared to 1× print, while the modulus of the 3× print is 27.34% higher than the modulus of 2× print. The highest modulus is noted for 3× print, 97.81% higher than that of the W/UR print. The modulus of the printed samples has been observed to be higher with respect to the corresponding modulus of the filaments. The modulus of W/UR, 1×, 2× and 3× prints has been increased by 22.07, 57.69, 57.63 and 96.15%, respectively, compared to the modulus of the respective filaments. This is due to the additional thermal processing of the filaments in the 3D printing process, where the polymer chains are again aligned in addition to the filler functionalization. The recycled printed samples' YS are higher than the W/UR prints. The highest YS is observed for 1× print, and is 61.58% higher than that of the W/UR print. No significant effect in the YS of the printed samples is observed compared to the YS of the respective filaments. The UTS of the recycled prints (1×, 2× and 3× prints) also increases compared to the UTS of the W/UR print. The UTS of 1×, 2× and 3× prints is 63.82, 67.11 and 67.76%, respectively, higher as compared to the W/UR print. The highest UTS is observed for 3× print, 67.76%, which is higher than
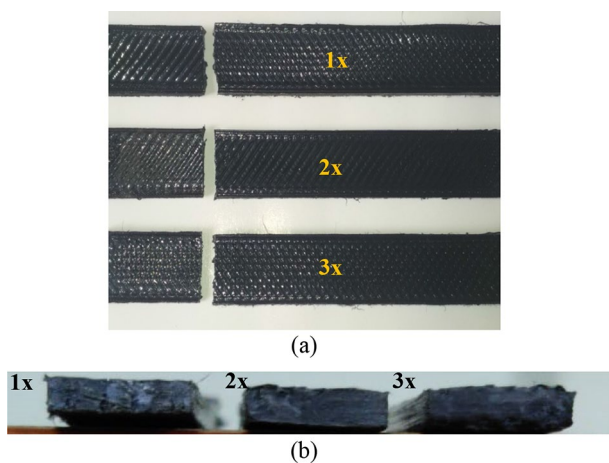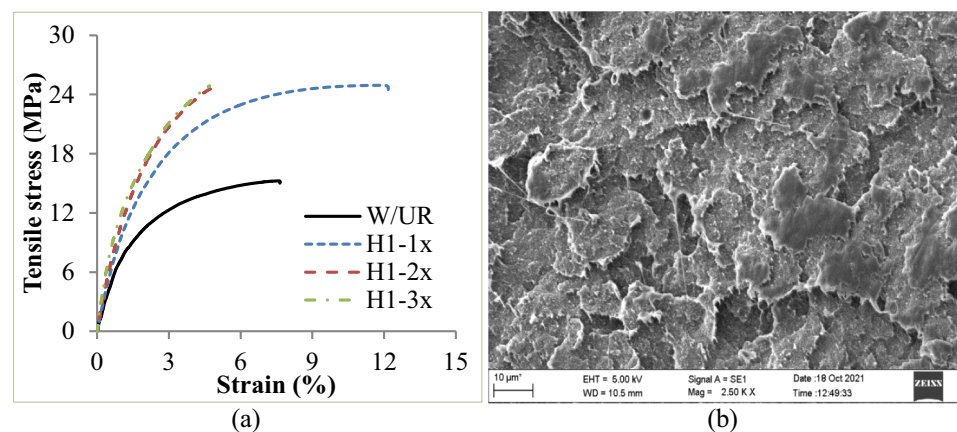
Fig. 8 Representative **a** tensile stress–strain graph of the printed samples and **b** SEM image of tensile-tested H1-3× printed sample

(a)

(b)

Legend (a):
Patil B, 2019 H20-75 µm
Patil B, 2019 H40-75 µm
Patil B, 2019 H60-75 µm
Beesetty, 2020 H0.5
Beesetty, 2020 H1
Beesetty, 2020 H3
Beesetty, 2020 H5
Bharath, 2016 HDPE-20-98 µm
Bharath, 2016 HDPE-40-98 µm
Bharath, 2016 HDPE-60-98 µm
Jayavardhan, 2017 H200-20 53 µm
Jayavardhan, 2017 H200-40 53 µm
Jayavardhan, 2017 H200-60 53 µm
Jayavardhan, 2017 H270-20 50 µm
Jayavardhan, 2017 H270-40 50 µm
Jayavardhan, 2017 H270-60 50 µm
Jayavardhan, 2017 H350-20 45 µm
Jayavardhan, 2017 H350-40 45 µm
Jayavardhan, 2017 H350-60 45 µm
Bharath, 2020 H20-15.3 µm
Bharath, 2020 H40-15.3 µm
Bharath, 2020 H60-15.3 µm
Adhikary, 2011 WF 100 µm
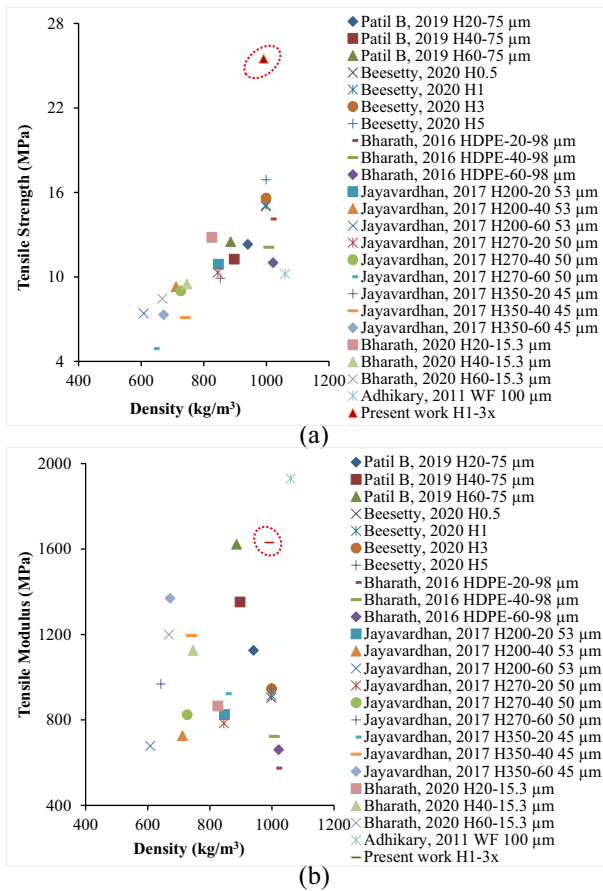Present work H1-3x

(a)

(b)

Fig. 9 Comparison of tensile **a** strength and **b** modulus of different HDPE composites with H1-3×composite ([22, 27, 33, 36, 44, 54])

that of the W/UR print. There is no significant change in the UTS of the W/UR filament and the print, whereas the UTS of the recycled prints is observed to be increasing compared to the recycled filaments. The UTS of the 1×, 2× and 3×prints is 50.91, 47.67 and 46.55%, respectively, higher than that of the 1×, 2× and 3×filaments. The increase in UTS may be attributed to the rise in load transfer capability due to additional cross-linking of the polymer chains when it undergoes recycling. The fracture strength of the recycled print is higher in comparison to W/UR print. The fracture strength of the prints is higher than that of the filaments, 16.55, 89.33, 106.01 and 119.12% higher for W/UR, 1×, 2× and 3×prints, respectively, for their respective filaments. The highest fracture strength and strain are observed for 2×and 1×print, 66.87 and 59.29%, respectively, higher than that of the W/UR print. The printed samples undergo the additional extrusion recycling cycle when printed using a 3D printer, where they get more aligned and cross-linked, thereby enhancing the modulus and strength. It is observed that the 3×print is the best sample having the highest modulus, YS, UTS and fracture strength. The SEM image of the tensile-tested 3×printed sample is shown in Fig. 8b.

Property map

The tensile modulus and the strength [22, 27, 33, 36, 44, 54] of the H1-3×printed sample (which is an HDPE-based composite) of the present study have been compared with different HDPE-based composites reinforced with various filler materials and manufactured by different methods against the density of the composites. The tensile modulus and the strength are presented in Fig. 9. The density of the H1-3×printed sample is lower than the nanoclay/HDPE composites [27] and fly ash cenospheres/HDPE composites [33]. The H1-3×print exhibited the highest modulus (Fig. 9a), except for the solid particle-filled HDPE composite. This highest modulus of the H1-3×sample may be due to the good distribution of the functionalized MWCNTs in HDPE and the enhanced interfacial bonding between HDPE and the functionalized MWCNTs. The highest tensile strength (Fig. 9b) is observed for the H1-3×printed sample compared to the other HDPE composites. The highest tensile strength shows that the functionalized MWCNTs are well oriented in HDPE, helping in the effective (highest) load transition from HDPE to the functionalized MWCNTs. The property plot shows that the H1-3×print has more strength than other HDPE composites filled with fillers, like nano-clay, GMB, fly ash cenospheres and wood flour. Moreover, the H1-3×printed sample shows a superior tensile modulus than HDPE composites with GMB, nanoclay and fly ash cenospheres. Thus, the study of the property map reveals that the functionalized MWCNTs/HDPE NCs recyclability potential can be effectively and efficiently exploited through 3D printing method to achieve a wider range of tailored physical and mechanical responses for various applications.

Conclusions

The waste filaments of the functionalized MWCNTs/HDPE NCs are successfully utilized to obtain the recycled filaments, and tested for density, crystallinity and tensile properties. The W/UR and the recycled filaments are used for 3D printing of the samples. The printed samples are subjected to density, XRD and tensile tests. The results are summarized below:

- The density of the recycled filaments and the prints rises compared to the W/UR filament and print respectively.
- The crystallinity of the recycled filaments and the prints increases compared to the W/UR filament and print respectively.
- The tensile strength and modulus of the recycled filaments increases compared to the W/UR filament. The highest tensile strength and modulus are found for H1-3×recycled filament.

- The tensile strength and modulus of the recycled prints increase compared to the W/UR printed sample. The highest tensile strength and modulus are observed for the H1-3× print.
- The H1-3× print has exhibited superior tensile strength and modulus among all the recycled prints.

The present work successfully illustrated the recycling of nanocomposite waste filaments to minimize plastic waste. Through such an approach, as presented as part of this paper, the environmental pollution due to plastic waste generated by 3D printing industries can be substantially lowered in addition to expanding the filament material options for the FFF community. The H1 NCs have been printed without any warpage using suitable 3D printing parameters. Therefore, a similar route can be explored for other NCs (0.5, 1, 3 and 5 wt. % of the functionalized MWCNTs in the HDPE matrix), increasing the applications across various engineering fields such as structural, marine, aerospace and automobile.

Data availability Data is a part of the ongoing research work.

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