



On Nanographene-Reinforced Polyvinylidene Fluoride Composite Matrix for 4D Applications

V. Kumar, R. Singh , I.P.S. Ahuja, and J.P. Davim

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In past two decades, number of studies has been reported on 3D printing of polyvinylidene fluoride (PVDF) composite matrix. But hitherto, little has been reported on 4D applications of graphene(Gr)-reinforced PVDF for maintenance and repair of heritage structures, especially for self-assembly applications. In this work, mechanical blending of Gr (size 5-10 nm)-reinforced PVDF has been reported for 4D applications as possible on-line maintenance tool for heritage structures. The Gr was blended in four different weight proportions in PVDF matrix. The effect of varying Gr proportion was studied on basis of rheological properties (melt flow index (MFI) and viscosity) required for processing on open source fused deposition modeling (FDM) setup. The various proportions/compositions of the composites were also investigated for thermal stability based upon differential scanning calorimetry (DSC) analysis (required for heritage structure). The selected proportion/composition of feed stock filament were processed on twin screw extruder (TSE) followed by mechanical testing on universal testing machine (UTM). The results of the MFI and viscosity outlined that blending of Gr in PVDF decreases the MFI and increases the viscosity of the composite matrix. The DSC testing showed that PVDF-10%Gr composite have heat capacity of -64 J/g (during heating cycle). The maximum peak strength of 43.01 N/mm^2 was observed, while processing at screw temperature $195 \text{ }^\circ\text{C}$ with 0.3 Nm torque for filament wire preparation. Finally the 3D printing of selected composition/ proportion was also successful. The piezoelectric properties of composite were observed after direct current (DC) poling by dielectric constant measurement ($D_{33} = 45 \text{ pC/N}$), which is sufficient for self expansion/contraction properties. The feed stock samples prepared were counter verified by performing morphological analysis. For self-assembly applications, vibration sample magnetometry (VSM) was performed. The results are also supported by Fourier transformed infrared spectroscopy (FTIR) analysis for ascertaining bonding characteristics corresponding to observed mechanical properties.

Keywords 3D printing, graphene, magnetic, piezoelectric, PVDF

1. Introduction

Additive manufacturing (AM) has brought a revolution in engineering of various products (Ref 1). Out of commercially available thermoplastics, many researchers have highlighted use of PVDF for sensors and actuators (because of the existence of four different phases in PVDF) (Ref 2). It has been reported that composite of carbon fiber-reinforced PVDF has good

tribological properties in terms of less wear rate and friction. FDM of such reinforced thermoplastic material has been reported by some researchers in which good mechanical properties were observed (Ref 3, 4). The perfect two dimensional lattices and presence of sp^2 hybridized carbon atoms in Gr gave excellent conducting and thermal properties to it. Some researchers have reported PVDF polymer matrix based composite for super-capacitance applications by using cellulose plastics for reinforcing Gr in it (Ref 5, 6). Cement, PVDF matrix composite and barium titanate-glass based composites have been reported as electrically conductive material for electromagnetic induction, sensing and bone regeneration applications. It has been reported that recycled plastic waste can be used in road construction, which may help in reduction of plastic solid waste (PSW) (Ref 7-9). Also, PVDF has been reported as acceptable material for battery applications due to efficient electro-active and dielectric properties, whereas titanate has been found responsible for imparting piezoelectric property in base polymer matrix (Ref 10-13). The concept of smart materials with one or two way shape memory programming is of great interest in AM these days. Poly-caprolactum, polycarbonate, fiber-reinforced polymer composites and concrete based smart polymers have been investigated by some researchers to ascertain 4D or smart properties in composites for exploring such materials in construction of civil structures (Ref 14-17). The data shown in Table 1 represent the research carried in past 30 years (1990-2020) on PVDF and Gr materials for different engineering applications as per web of science input using VOS viewer open source software.

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V. Kumar, Department of Production Engineering, Guru Nanak Dev Engineering College, Ludhiana, India; and Department of Mechanical Engineering, Punjabi university, Patiala, India; **R. Singh**, Department of Production Engineering, Guru Nanak Dev Engineering College, Ludhiana, India; and Department of Mechanical Engineering, National Institute of Technical Teachers Training and Research, Chandigarh, India; **I.P.S. Ahuja**, Department of Mechanical Engineering, Punjabi university, Patiala, India; and **J.P. Davim**, Department of Mechanical Engineering, University of Aveiro, Aveiro, Portugal. Contact e-mail: rupindersingh78@yahoo.com.

Table 1 Relevance of research of PVDF and graphene

| S. No. | Term | Occurrences | Relevance score |
|--------|--|-------------|-----------------|
| 1 | PVDF matrix | 45 | 0.9469 |
| 2 | PVDF hfp | 23 | 1.1483 |
| 3 | Graphene | 86 | 0.6684 |
| 4 | Graphene nanoplatelet | 16 | 1.1216 |
| 5 | Vinylidene fluoride co hexafluoropropylene | 15 | 0.6277 |
| 6 | Piezoelectric nanogenerator | 18 | 1.6429 |
| 7 | Piezoelectric property | 17 | 0.9898 |
| 8 | Polymer | 81 | 0.5283 |
| 9 | Polymer matrix | 25 | 0.382 |
| 10 | Dielectric permittivity | 14 | 1.4846 |
| 11 | Dielectric property | 40 | 1.5769 |
| 12 | Differential scanning calorimetry | 11 | 1.3281 |
| 13 | Dispersion | 42 | 0.6503 |
| 14 | Dielectric permittivity | 14 | 1.4846 |

Based on the above data, Fig. 1(a) was obtained for clear understanding of relevant research carried in the proposed field. Investigations on PVDF and Gr have been reported for 3D printing of sensors, actuators, superconductors and many other robotic applications. Figure 1(b) shows that less work is reported on 4D capabilities of PVDF-Gr composite for maintenance and repair of cultural heritage structures.

It has been reported that composite of PVDF, polyamide (PA6), acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), etc. having reinforcement of Gr, BaTiO₃, TiO₂, can be used successfully for 3D printing on open source FDM setup with acceptable mechanical properties (Ref 18-27). The literature review reveals that the previous studies on PVDF were focused on increasing mechanical and electrical properties of PVDF for sensor and actuators. But hitherto little has been reported on PVDF-Gr composite for 4D applications such as self-assembly in maintenance and repair of heritage structures. This study reports the investigations on mechanical, thermal, morphological, magnetic and piezoelectric properties of PVDF-Gr composite as customized self-assembly based solution for filling of surface cracks of heritage structures.

2. Experimentation

Mechanical blending of PVDF and Gr nano-particles was performed to investigate rheological, thermal, mechanical, piezoelectric, morphological and 4D properties of the composite. Figure 2 shows the work methodology of the present research work.

2.1 MFI and Viscosity Testing

To investigate the rheological properties of PVDF and its composite, nano sized Gr particles were reinforced in PVDF in four different weight proportions i.e., 2.5, 5.0, 7.5, and 10% by mechanical blending. MFI of each composition/proportion was tested as per ASTM D1238 standard. Table 2 shows the MFI of prepared samples. The wire sample obtained from MFI tester was weighed and volume of each sample was recorded for viscosity calculations as per literature reference (Ref 18). Shear stress and shear rate for each case was recorded as per standard equations. Table 3 shows density and viscosity of each

composition/proportion. The results obtained for rheological and viscosity test were discussed.

2.2 Thermal and Mechanical Characterization

Thermal analysis of each composition/proportion was performed on Mettler Toledo DSC setup. The heat capacity observed for each sample is shown in Table 4. All the proportions were processed on TSE to prepare 3D printer feedstock filament wire. Wires were extruded at screw temperature of 195 °C with 0.3 Nm torque by applying 10 kg load. Mechanical properties of each filament wire were tested on UTM. 3D printing of disk-shaped pallet was performed on FDM based open source printer.

2.3 4D Characterization

The DC poling of 3D printed disk was performed on 5 kV poling unit and dielectric constant (D_{33}) for each composition was measured. After ascertaining piezoelectric properties in PVDF-Gr composite, 4D characteristics of compositions were investigated by performing VSM test. The FTIR of PVDF and its composites was performed to analyze bonding characteristics and effect of Gr reinforcement on mechanical properties. Morphology of each composition/proportion was studied using Tool Maker's and metallurgical microscope.

3. Results and Discussion

3.1 Rheological and Viscosity Analysis

Based upon Tables 2 and 3, MFI and viscosity of PVDF-Gr composite matrix were plotted with common X-axis (Fig. 3). As observed from Fig. 3, PVDF-5%Gr composition/proportion is representing intersection point for MFI and viscosity observations. One of the major outcomes is that beyond this point usually mechanical and thermal properties are improved (which may be counter verified from mechanical and thermal testing). Hence this proportion may be considered as a limiting/ bare minimum proportion for preparing PVDF-Gr composites.

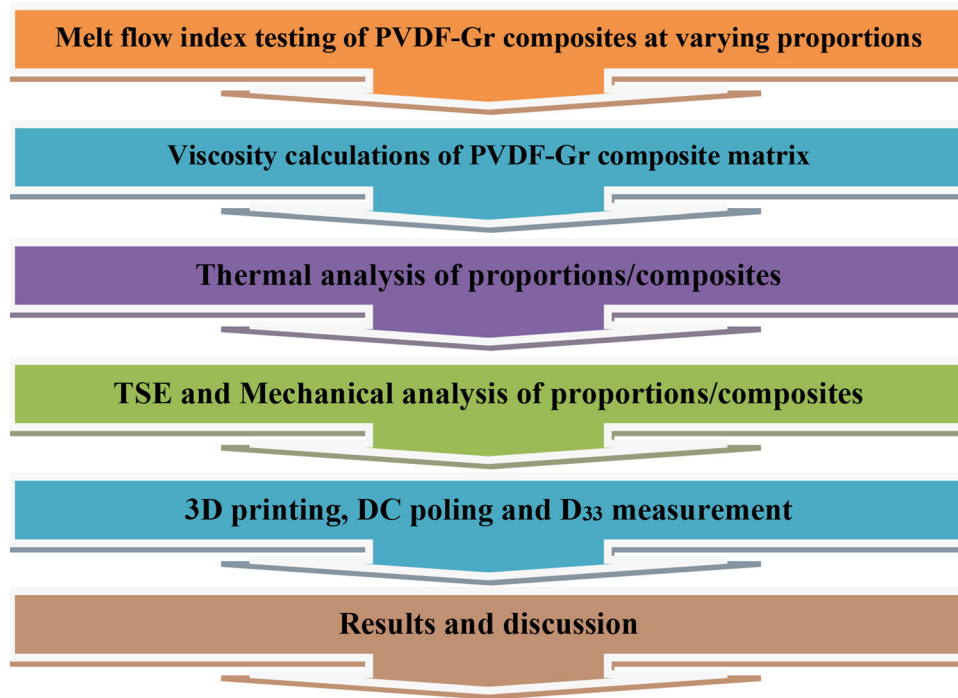


Fig. 2 Process outflow of the proposed work

Table 2 MFI results of PVDF-Gr composites

| S. No. | Composition/proportion | MFI g/(10 min) |
|--------|------------------------|----------------|
| 1. | PVDF | 3.804±0.005 |
| 2. | PVDF + 2.5%Gr | 3.647±0.002 |
| 3. | PVDF + 5%Gr | 3.164±0.004 |
| 4. | PVDF + 7.5%Gr | 2.723±0.003 |
| 5. | PVDF + 10%Gr | 2.451±0.002 |

Table 3 Viscosity of PVDF-Gr composites

| S. No. | Composition | Density, g/cm ³ | Viscosity, Pa-s |
|--------|---------------|----------------------------|-----------------|
| 1. | PVDF | 1.004 | 4014.32 |
| 2. | PVDF + 2.5%Gr | 1.06 | 4194.99 |
| 3. | PVDF + 5%Gr | 1.37 | 4266.13 |
| 4. | PVDF + 7.5%Gr | 1.51 | 4461.84 |
| 5. | PVDF + 10%Gr | 1.83 | 5184.22 |

Table 4 Thermal (heat) capacity of PVDF-Gr composite

| S. No. | Composition/proportion | Thermal (heat) capacity, J/g |
|--------|------------------------|------------------------------|
| 1 | PVDF | – 24 |
| 2 | PVDF + 2.5%Gr | – 26 |
| 3 | PVDF + 5%Gr | – 43 |
| 4 | PVDF + 7.5%Gr | – 52 |
| 5 | PVDF + 10%Gr | – 64 |

3.4 VSM and FTIR Analysis

The results obtained for VSM of PVDF-Gr samples showed that sample 3, 4 and 5 possess acceptable value of magnetization (emu/g), coercivity (Oe) and retentivity (G) for good magnetic properties. Figure 7(a), (b) and (c) shows the hysteresis plots obtained for VSM testing of sample 3, 4 and 5, respectively. Table 6 shows the magnetic characteristics of each tested composite. VSM analysis outlined that composition/proportion of PVDF with 10%Gr can be magnetized up to maximum content with average magnetization of 0.00131×10^{-3} emu/g. This proportion has higher average retentivity and coercivity of 6.16×10^{-3} G and 1660.34 Oe, respectively.

The FTIR analysis of sample 1 and sample 5 (as per Table 2) was conducted to investigate the effect of infra-red (IR) rays intensity on nature of bonding in PVDF due to reinforcement of nanoGr particles. The FTIR of samples shown in Figure 8(a) and (b), respectively, highlighted the FTIR absorption spectrum of virgin PVDF in comparison to PVDF-10%Gr composite. The sharp peaks in FTIR of PVDF-10%Gr show the increase in bond strength of composite that possibly increased the mechanical properties of the composite. The stretch of C-F bond (observed in the range of 830-890 WN) was also confirmed by FTIR. The sharp peaks showing C-O stretch at 1160-1180 WN frequency range show the strong chemical bonding in atoms of sample 5 in comparison to sample 1. The incremental change in bond strength can be seen clearly in sample 5 as the peaks got sharper in comparison to sample 1 at 865 WN for C-F stretch and at 1178 WN for C-O bond stretch. It shows that reinforcement of 10%Gr in PVDF matrix is responsible for bond stretching and increase in bond strength as the absorption of composite increased in sample 5 as compared to PVDF absorption spectra. Further at high WN the absorbance is approaching zero value both for virgin PVDF

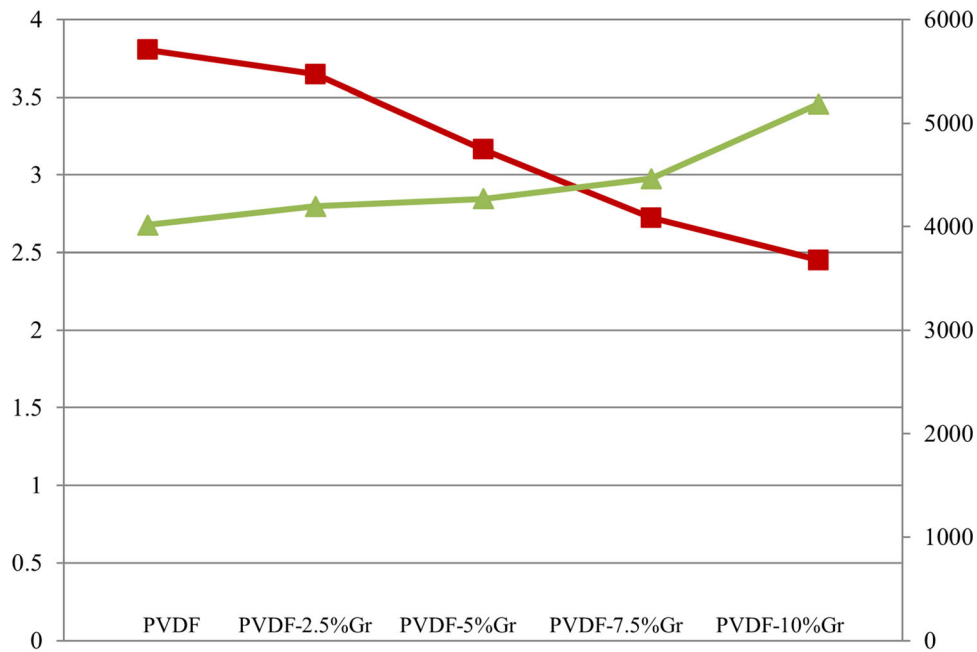


Fig. 3 Correlation graph between MFI and viscosity of PVDF-Gr composite

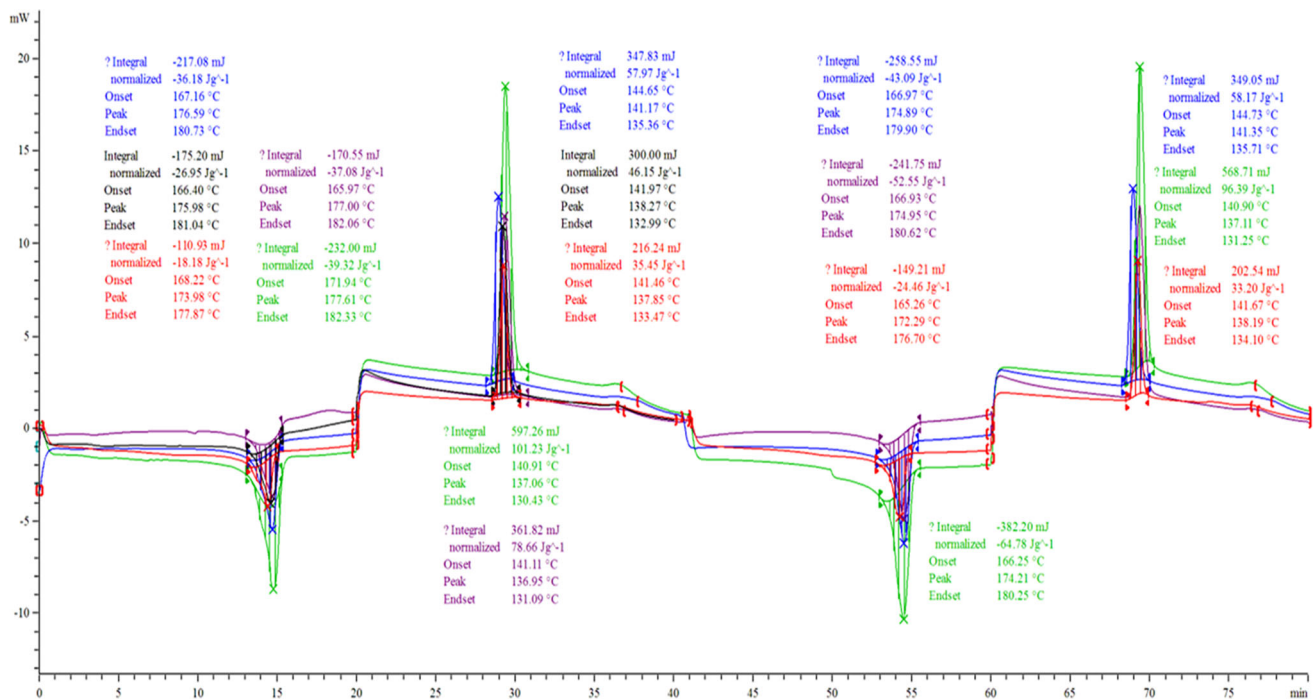


Fig. 4 DSC observations of PVDF-Gr composite

and PVDF-10%Gr matrix; hence the prepared composite may be used as sensor in remote sensing applications.

3.5 Morphological Analysis

Tool Maker's microscopic images obtained at $\times 30$ magnification (Fig. 9) show uniform distribution of nano Gr particles

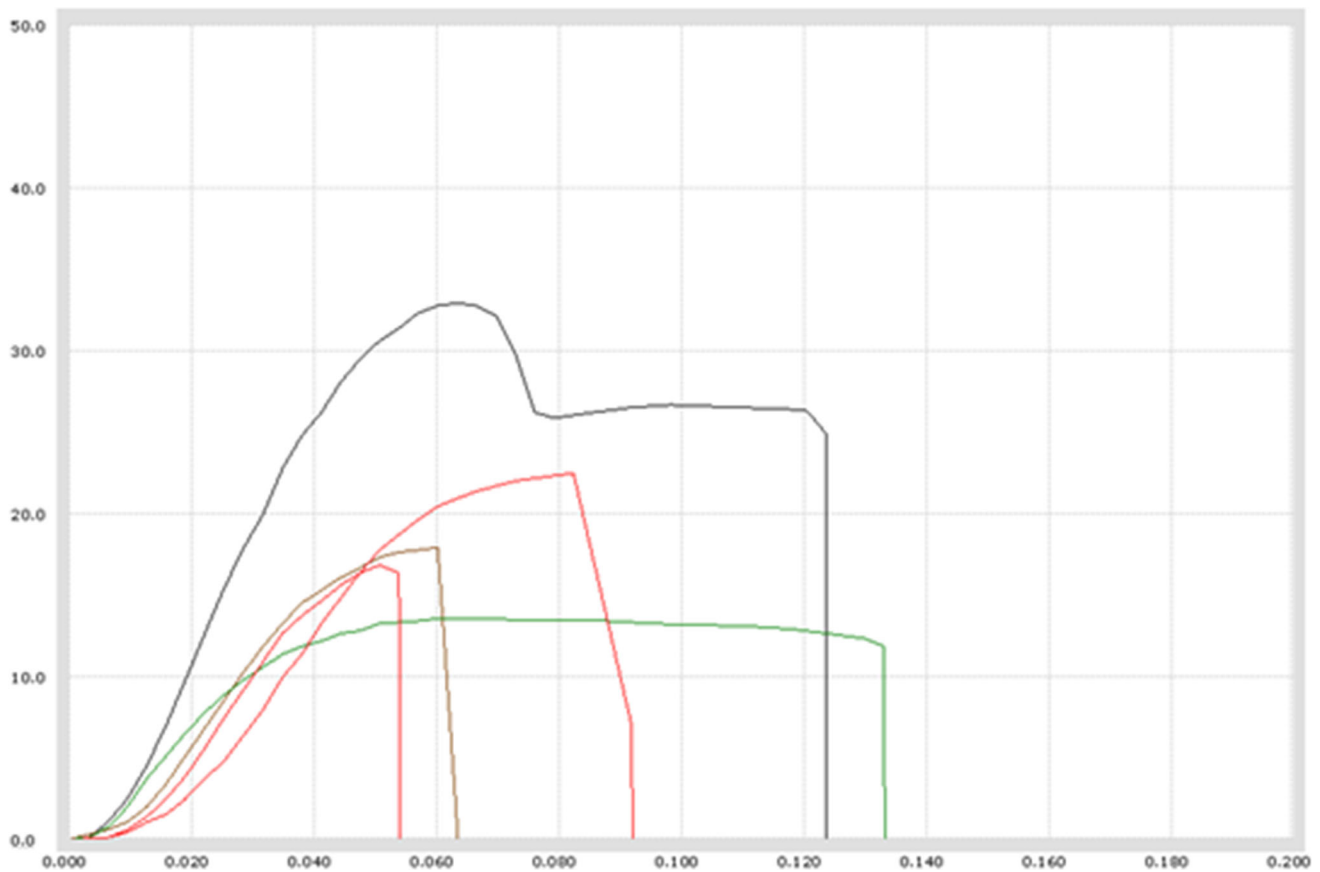
in PVDF matrix due to which acceptable mechanical and 3D/4D properties were obtained. The images show that uniform cross section of feedstock filament wire can be prepared using TSE at proposed processing parameters.

Morphological properties of PVDF-Gr composites were investigated using metallurgical microscope (at $\times 100$ magni-

Table 5 UTM results of PVDF and PVDF-Gr composites

| S. No. | PL, N | BL, N | PS, N/mm ² | BS, N/mm ² | PE, mm | BE, mm | %EP | %EB | SaB, mm | SaP, mm | MoT, N | YM, MPa |
|--------|-------|-------|-----------------------|-----------------------|--------|--------|-----|-----|---------|---------|--------|---------|
| 1 | 52.9 | 47.61 | 22 | 19.80 | 2.85 | 3.23 | 5 | 5 | 0.053 | 0.047 | 0.4080 | 354.736 |
| 2 | 43.15 | 38.79 | 17.92 | 16.13 | 3.99 | 7.98 | 7 | 13 | 0.133 | 0.065 | 0.8212 | 374.615 |
| 3 | 56.3 | 50.67 | 23.41 | 21.07 | 3.42 | 3.8 | 6 | 6 | 0.063 | 0.057 | 0.5111 | 314.561 |
| 4 | 70.6 | 63.54 | 29.36 | 26.43 | 4.75 | 5.51 | 8 | 9 | 0.091 | 0.079 | 0.9293 | 383.957 |
| 5 | 103.4 | 93.06 | 43.01 | 38.71 | 3.61 | 7.41 | 6 | 12 | 0.123 | 0.060 | 1.8302 | 547.313 |

Here, *PL* peak load, *PE* peak elongation, *BL* break load, *BE* break elongation, *PS* peak strength, *BS* break strength, *%EP* percentage elongation (peak) and *%EB* percentage elongation (break), *SaB* strain at break, *SaP* strain at peak, *MoT* modulus of toughness, *YM* Young's Modulus

**Fig. 5** Stress-strain curves for PVDF filament and PVDF-Gr composites

fication) is shown in Fig. 10(a). Images for surface of filament wire along the longitudinal axis and radial axis were captured and processed on metallurgical image analysis software (MIAS) 4.0 to measure the porosity% in the filament wire along its length and cross section. Figure (10b) shows that PVDF-10%Gr possesses lesser porosity% (i.e., 2.93% along longitudinal axis and 2.21% along the radial axis). As regards to better morphological and mechanical properties, this composition/proportion may be considered as the better for required 3D/4D applications.

4. Conclusions

Following conclusions may be drawn from the present study:

- The rheological analysis outlined that blending of Gr in PVDF decreases the MFI and increases the viscosity of the composite matrix. The 5% Gr reinforcement in PVDF resulted into a turning point beyond which better mechanical, thermal and morphological properties were noticed. The thermal testing showed that PVDF-10%Gr composite

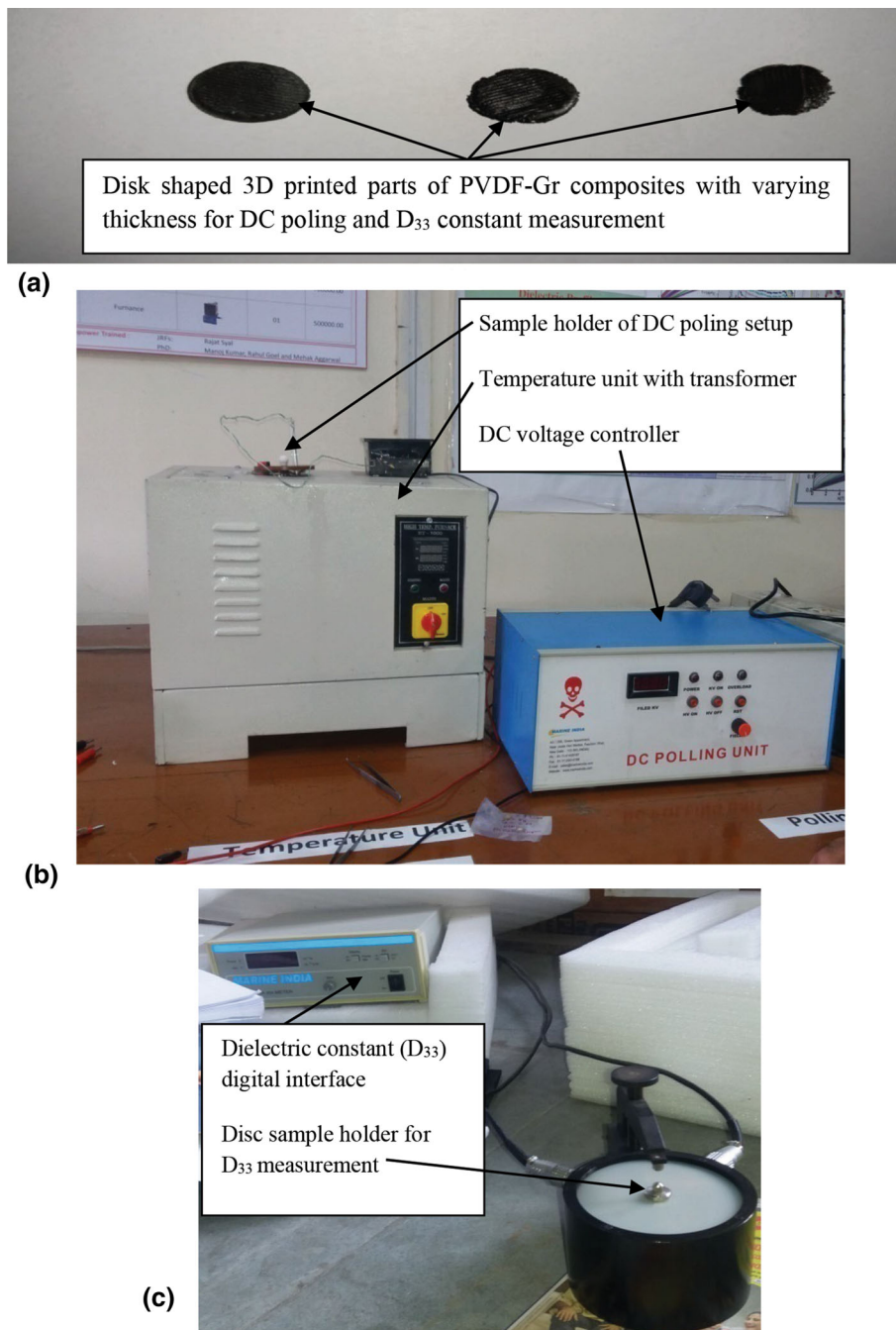


Fig. 6 3D printed disks (a), DC poling setup (b), D₃₃measuring equipment (c)

have highest heat capacity of – 64 J/g (during heating cycle).

- The maximum peak strength of 43.01 N/mm² was observed, while processing at screw temperature 195 °C with 0.3 Nm torque for filament wire preparation of PVDF-10% Gr matrix. Finally the 3D printing of selected composition/ proportion was also successful.
- The piezoelectric properties of composite (PVDF-10% Gr) were observed (after DC poling) by dielectric constant measurement (D₃₃ = 45 pC/N), which is sufficient for self expansion/ contraction properties.
- The feed stock samples prepared were counter checked for morphological testing, which outlined that porosity for

PVDF-10%Gr was observed as minimum (2.93 % for surface along longitudinal axis and 2.21 % for surface along radial axis).

- For self-assembly applications, vibration sample magnetometry (VSM) was performed on PVDF-Gr composite. Finally based upon observed magnetic properties (magnetization 0.00131×10^{-3} emu/g, retentivity 6.16×10^{-3} G and coercivity 1660.34 Oe) and piezoelectric property (45pC/N) of PVDF-10%Gr composite, it may be used as 4D material for self-assembly applications by preparing 3D printed smart fillers for repairing cracks in heritage structures.

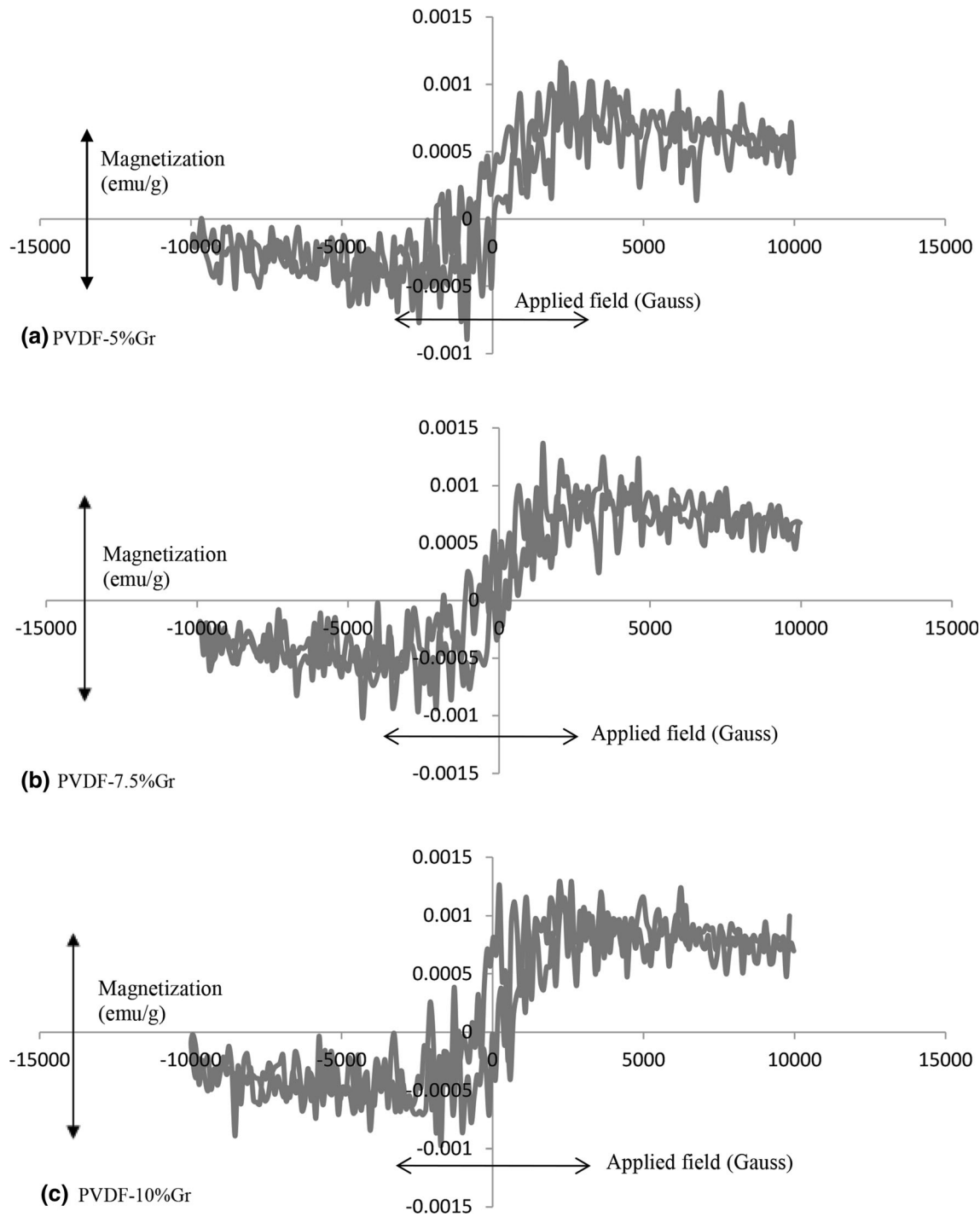


Fig. 7 Hysteresis curve obtained from VSM test for PVDF-Gr specimen

Table 6 Magnetic properties of PVDF-Gr composites

| S. No. | Composition/proportion | Output | | | | | |
|--------|------------------------|----------------|---------|-----------------------|-----------------------|--------------------------|--------------------------|
| | | Coercivity, Oe | | Retentivity, G | | Magnetization, emu/g | |
| | | + | - | + | - | + | - |
| 1 | PVDF + 5%Gr | 584.18 | 546.93 | 4.36×10^{-3} | 3.74×10^{-3} | 0.00122×10^{-3} | 0.00090×10^{-3} |
| 2 | PVDF + 7.5%Gr | 946.56 | 802.23 | 4.91×10^{-3} | 3.82×10^{-3} | 0.00129×10^{-3} | 0.00110×10^{-3} |
| 3 | PVDF + 10%Gr | 1660.34 | 1439.50 | 6.16×10^{-3} | 5.19×10^{-3} | 0.00131×10^{-3} | 0.00124×10^{-3} |

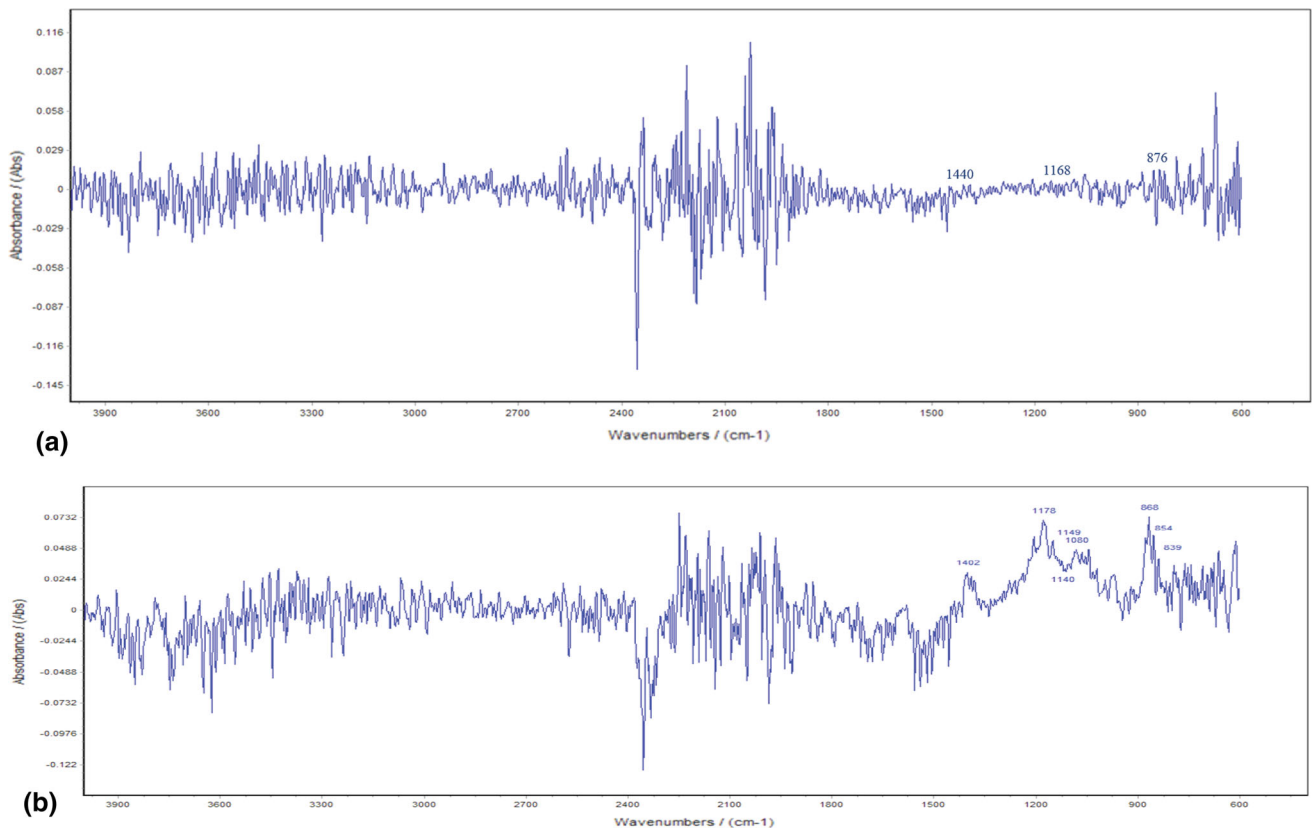


Fig. 8 (a) FTIR absorption spectra of PVDF wire specimen. (b) FTIR absorption spectra of PVDF + 10%Gr

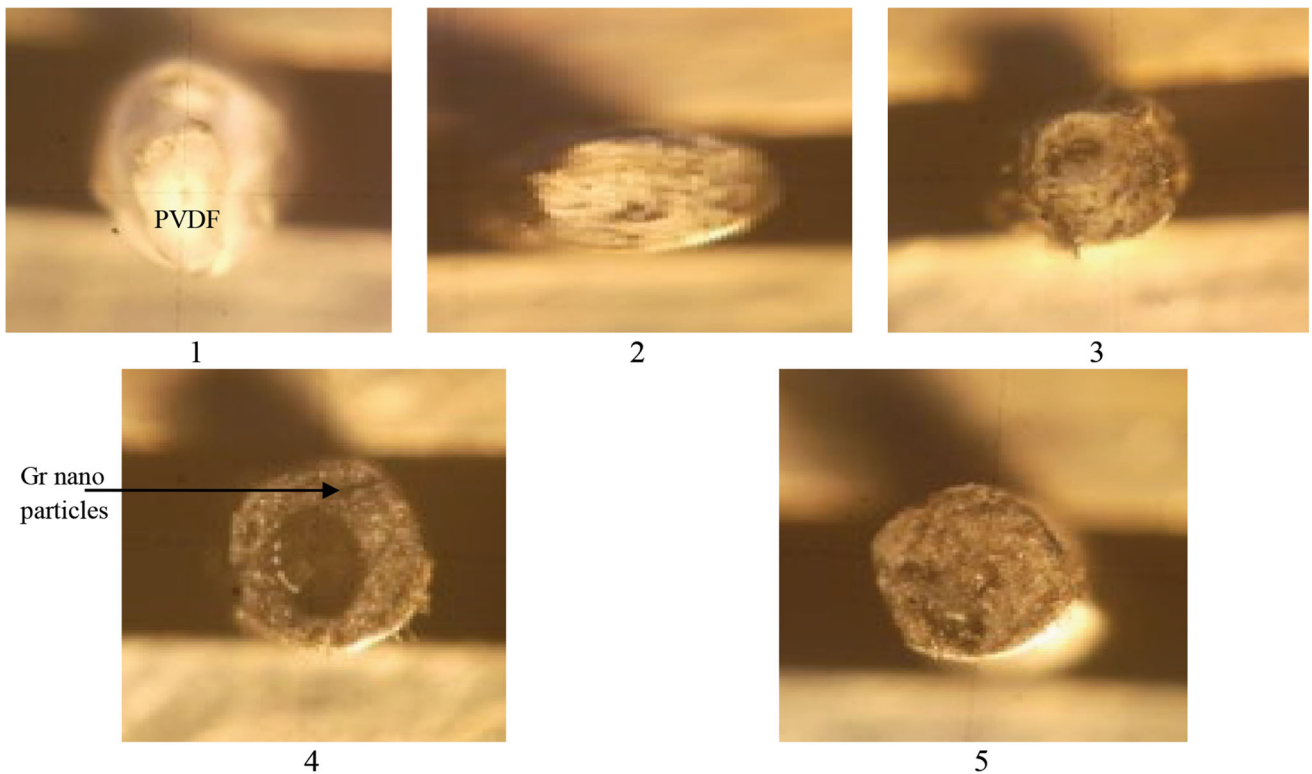


Fig. 9 Tool Maker's microscope images of PVDF-Gr composites (at $\times 30$)

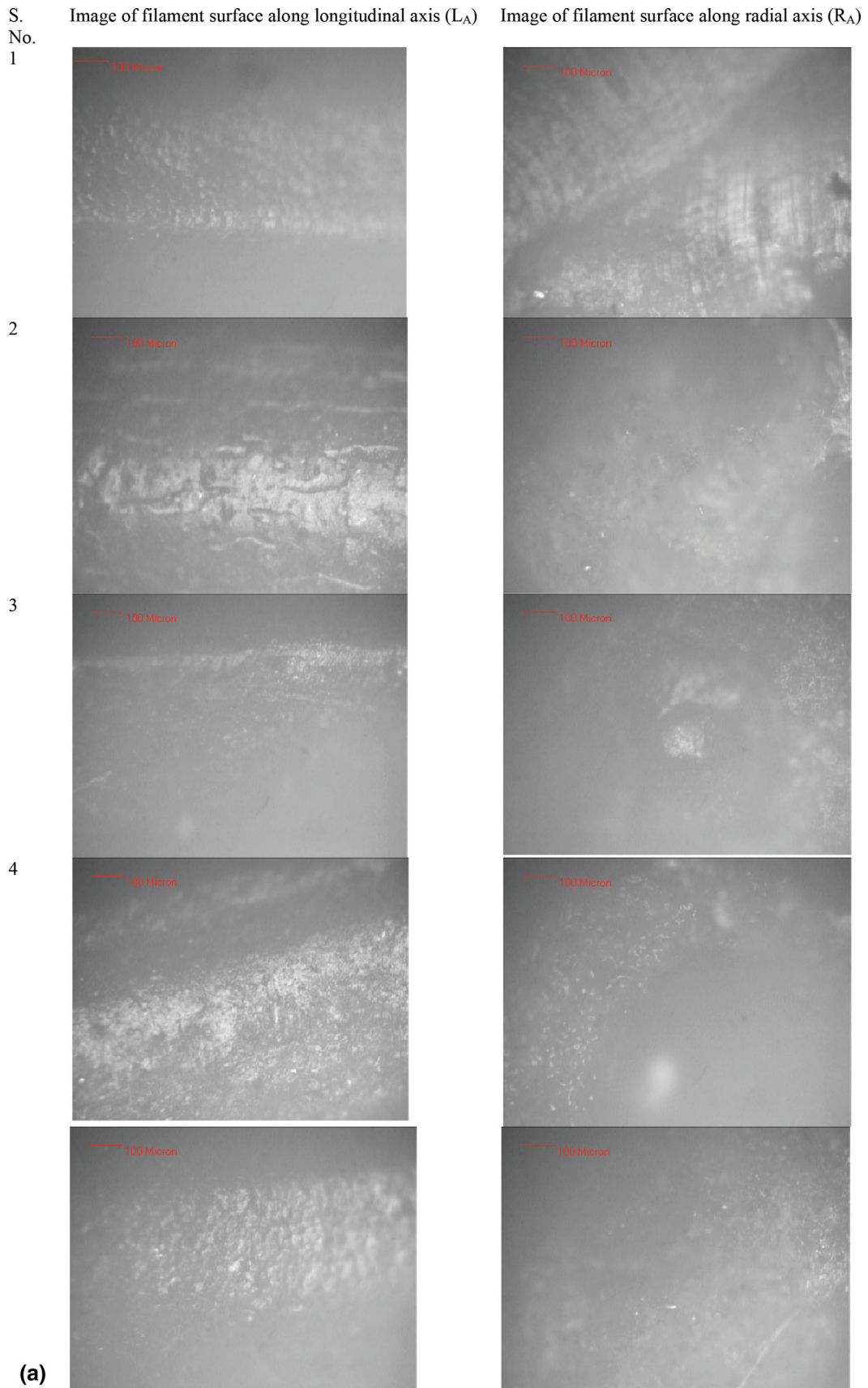
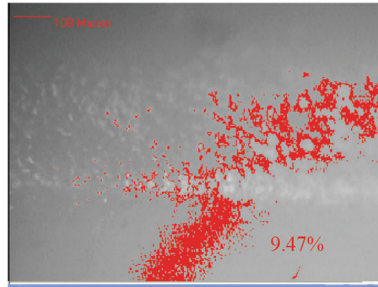


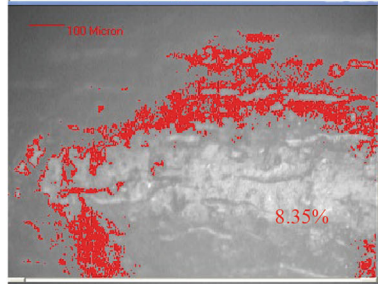
Fig. 10 (a) Optical photo micrographic images (at x100 magnification). (b) Porosity% images (at x100 magnification)

S.No. Porosity % in filament wire along L_A

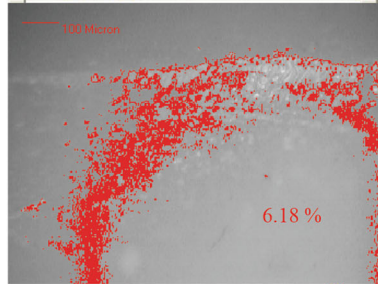
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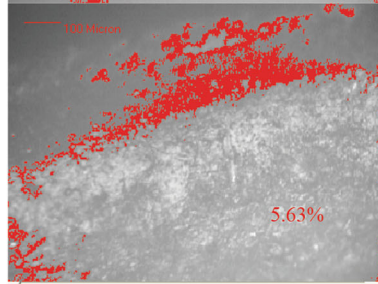
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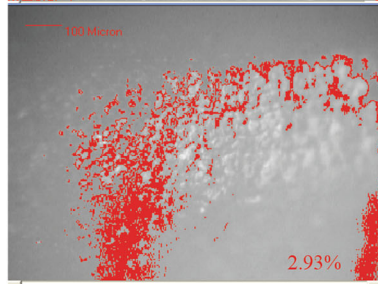
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(b)

Porosity % in filament wire along R_A

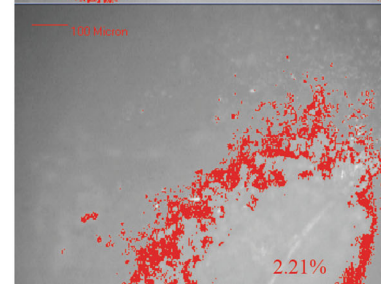
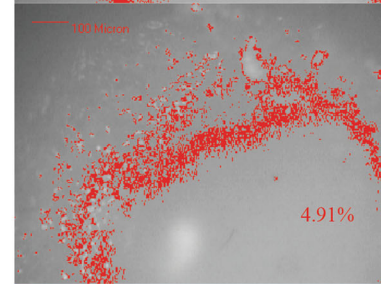
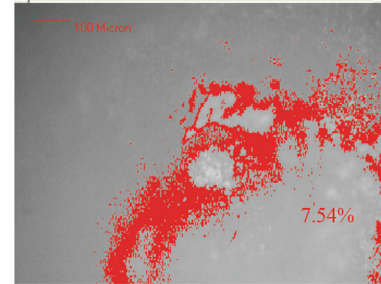
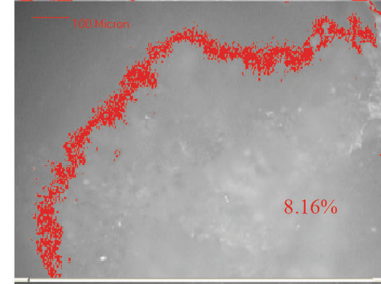
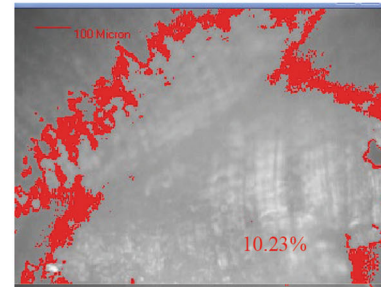


Fig. 10 continued

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References

1. C. Walde, D. Cote, V. Champagne and R. Sisson, Characterizing the effect of thermal processing on feedstock Al alloy powder for additive

- manufacturing applications, *J. Mater. Eng. Perform.*, 2019, **28**(2), p 601–610
2. N. Yamada and G. Murasawa, Film fabrication using poly (vinylidene fluoride) solution droplet, *J. Mater. Eng. Perform.*, 2017, **26**(5), p 2072–2078
3. J. Li and X.Z. Li, Evaluation of the tribological properties of carbon fiber reinforced poly (vinylidene fluoride) composites, *J. Mater. Eng. Perform.*, 2010, **19**(7), p 1025–1030
4. P. Bettini, G. Alitta, G. Sala and L. Di Landro, Fused deposition technique for continuous fiber reinforced thermoplastic, *J. Mater. Eng. Perform.*, 2017, **26**(2), p 843–848

5. J. Li, X. Chen, W. Li, K. Zhang, F. Ma, S. Fu and L. Zhao, In situ synthesis of 3D interconnected graphene-reinforced copper composites, *J. Mater. Eng. Perform.*, 2019, **28**(7), p 4265–4274
6. H. Pal, S. Bhubna, P. Kumar, R. Mahapatra and S. Chatterjee, Synthesis of flexible graphene/polymer composites for supercapacitor applications, *J. Mater. Eng. Perform.*, 2018, **27**(6), p 2668–2672
7. D.D.L. Chung, Electrical conduction behavior of cement-matrix composites, *J. Mater. Eng. Perform.*, 2002, **11**(2), p 194–204
8. B. Saeidi, M.R. Derakhshandeh, M.D. Chermahini and A. Doostmohammadi, Novel porous barium titanate/nano-bioactive glass composite with high piezoelectric coefficient for bone regeneration applications, *J. Mater. Eng. Perform.*, 2020, **29**(8), p 5420–5427
9. K. MacBain and M.A. Saadeghvaziri, Analytical modeling of the mechanical properties of recycled plastics, *J. Mater. Eng. Perform.*, 1999, **8**(3), p 339–346
10. R. Singh, S. Janakiraman, M. Khalifa, S. Anandhan, S. Ghosh, A. Venimadhav and K. Biswas, An electroactive β -phase polyvinylidene fluoride as gel polymer electrolyte for magnesium-ion battery application, *J. Electroanal. Chem.*, 2019, **851**, p 113417
11. H. Kim, J. Johnson, L.A. Chavez, C.A.G. Rosales, T.L.B. Tseng and Y. Lin, Enhanced dielectric properties of three phase dielectric MWCNTs/BaTiO₃/PVDF nanocomposites for energy storage using fused deposition modeling 3D printing, *Ceram. Int.*, 2018, **44**(8), p 9037–9044
12. Q. Guo, G.Z. Cao and I.Y. Shen, Measurements of piezoelectric coefficient d₃₃ of lead zirconate titanate thin films using a mini force hammer, *J. Vib. Acoust.*, 2013 <https://doi.org/10.1115/1.4006881>
13. Bryant, R.G., Effinger IV, R.T., Aranda Jr, I., Copeland Jr, B.M. and Covington III, E.W., 2002, July. Active piezoelectric diaphragms. In *Smart Structures and Materials 2002: Active Materials: Behavior and Mechanics* (Vol. 4699, pp. 303-314). International Society for Optics and Photonics
14. Y. Yao, T. Zhou, J. Wang, Z. Li, H. Lu, Y. Liu and J. Leng, 'Two way' shape memory composites based on electroactive polymer and thermoplastic membrane, *Compos. A Appl. Sci. Manuf.*, 2016, **90**, p 502–509
15. W. Wang, Y. Liu and J. Leng, Recent developments in shape memory polymer nanocomposites: actuation methods and mechanisms, *Coord. Chem. Rev.*, 2016, **320**, p 38–52
16. A. Biswal and S.K. Swain, Smart composite materials for civil engineering applications, *Polymer Nanocomposite-Based Smart Materials*. Woodhead Publishing, Cambridge, 2020, p 197–210
17. Y. Ding, Y. Yang, R.G. Liu, T. Xiao and J.H. Tian, Study on pressure sensitivity of smart polymer concrete based on steel slag, *Measurement*, 2019, **140**, p 14–21
18. R. Sharma, R. Singh, and A. Batish, On effect of chemical-assisted mechanical blending of barium titanate and graphene in PVDF for 3D printing applications. *J. Thermoplast. Compos. Mater.* p. 0892705720945377 (2020)
19. V. Kumar, R. Singh, R. and Ahuja, I.P.S., 2020. Secondary recycled acrylonitrile-butadiene-styrene and graphene composite for 3D/4D applications: Rheological, thermal, magnetometric, and mechanical analyses. *J. Thermoplast. Compos. Mater.* p. 0892705720925114 (2020)
20. R. Singh, R. Kumar, I. Mascolo and M. Modano, On the applicability of composite PA6-TiO₂ filaments for the rapid prototyping of innovative materials and structures, *Compos. B Eng.*, 2018, **143**, p 132–140
21. S. Kumar, R. Singh, M. Singh, T.P. Singh and A. Batish, Multi material 3D printing of PLA-PA6/TiO₂ polymeric matrix: flexural, wear and morphological properties. *J. Thermoplast. Compos. Mater.* p. 0892705720953193 (2020)
22. R. Singh and N. Ranjan, Experimental investigations for preparation of biocompatible feedstock filament of fused deposition modeling (FDM) using twin screw extrusion process, *J. Thermoplast. Compos. Mater.*, 2018, **31**(11), p 1455–1469
23. V. Kumar, R. Singh, I.P.S. Ahuja and M.J. Hashmi, On technological solutions for repair and rehabilitation of heritage sites: a review, *Adv. Mater. Process. Technol.*, 2020, **6**(1), p 146–166
24. R. Kumar, R. Singh, D. Hui, L. Feo and F. Fraternali, Graphene as biomedical sensing element: state of art review and potential engineering applications, *Compos. B Eng.*, 2018, **134**, p 193–206
25. N. Ranjan, R. Singh, I.S. Ahuja and J. Singh, Fabrication of PLA-HAP-CS based biocompatible and biodegradable feedstock filament using twin screw extrusion, *Additive Manufacturing of Emerging Materials*. Springer, Cham, 2019, p 325–345
26. L. Lu, W. Ding, J. Liu and B. Yang, Flexible PVDF based piezoelectric nanogenerators, *Nano Energy*, 2020, **78**, p 105251
27. R. Sharma, R. Singh, and A. Batish, Study on barium titanate and graphene reinforced PVDF matrix for 4D applications. *J. Thermoplast. Compos. Mater.* 0892705719865004 (2019)

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