Surface enhancement approach for FDM rapid prototypes by organically modified montmorillonite nanoparticles

V Francis* and P K Jain

CAD/CAM lab, Mechanical Engineering Discipline, Indian Institute of Information Technology, Design and Manufacturing, Jabalpur, 482005, India

*Email: f.vishal@iiitdmj.ac.in

Abstract. Fused deposition modelling (FDM) is one of the widely used rapid prototyping techniques for fabricating complex shaped objects from CAD data. Minimum wastage of material, simple manufacturing process and economical desktop like machine have made the technique a major contender in the field of manufacturing. However, due to layered manufacturing process, the surface of FDM parts lacks quality. In the present research work, the FDM built parts were surface treated with organically modified montmorillonite (OMMT) nanoparticles. The post-treated specimens were characterised by XRD, FTIR, SEM and UV-vis analysis which revealed the successful deposition of nanoparticles on the surface of the FDM built specimens. Effect of post-treatment parameters on surface hardness, dimensional accuracy and average surface roughness was investigated using Taguchi technique. It was found that the embedment of OMMT nanoparticles increased the hardness of FDM parts due to its ceramic attributes and the combined effect of nanoparticles/chemicals reduced the surface roughness providing a smooth surface. Moreover, the process does not marred the dimensional accuracy of the fabricated parts. Further, multi objective optimisation technique was used to find the optimum post-treatment parameters. The present approach can be utilised for improving the surface integrity of FDM parts.

1. Introduction

Rapid prototyping (RP)/3D printing has emerged as a promising candidate for fabrication of intricate objects with ease [1]. Initially the technique was used for prototyping purposes, however due to its inevitable advantages various sectors have adopted the technique for fabrication of end use products [2]. FDM is one of the widely utilised RP techniques to fabricate complex parts with polymeric materials [3]. A polymer material generally acrylonitrile butadiene styrene (ABS), in the form of filament is used in FDM process. The filament is heated and extruded through a nozzle on the platform, where it solidifies and bonds with the adjacent deposited raster’s. The process is repeated layer by layer and the final parts is fabricated resembling the computer aided design (CAD) model. The process gives freedom to design any complex shaped structures. However, due to the layered manufacturing, the surface of FDM built parts have inferior surface properties compared to other polymer processing techniques [4, 5]. The surface issues associated with FDM limits its potential for end use applications. To overcome this limitation several attempts have been made to post-treat the FDM built parts. Various techniques such as micro machining, parametric optimisation and chemical treatment have been used for post-treating the FDM parts [4, 6, 7]. Each process has its own benefits and shortcoming. However, there is inadequate literature available reporting the utilisation of nanoparticles for surface
improvement of FDM parts. Utilising nanoparticles for surface treatment can increase the application domain of the FDM process by overcoming the limitation of surface integrity.

In the present research work, the FDM parts were post-treated with OMMT nanoparticles via chemical route. The post-treated specimens were characterised by XRD, FTIR, SEM and UV-vis analysis. The effect of OMMT/nanoclay content, dipping time and layer thickness were investigated using Taguchi technique on the surface properties of FDM parts namely, surface hardness, average surface roughness and variation in dimensional accuracy. It has been found that the proposed methodology can effectively improve the hardness and surface finish of the parts without marring the dimensional accuracy. The experimentation was planned according to $L_{18}$ orthogonal array. Further, multi objective optimisation (grey relational analysis) was carried to optimise the coupled effect of the post-treatment process parameters on all the three responses namely, hardness, average roughness and dimension deviation. The present approach can be utilised for improving the surface integrity of FDM parts.

2. Experimental

2.1. Materials, sample preparation and post-treatment

Acrylonitrile butadiene styrene (ABS) was used to print the specimens using FDM 3D printer. The layer thickness of 0.25 and 0.3 mm was used with 230º C nozzle temperature and 110º C bed temperature. The travel feed rate of 80 mm/sec and 100% infill was used in the investigation. The raster orientation was kept at 0º for all the specimen preparations. For average surface roughness and dimensional analysis, specimens of 25 x 10 x 1.2 mm were fabricated. For hardness testing specimens were prepared according to ASTM D 2240. For post-treatment of the fabricated specimens, first OMMT nanoparticles were dissolved in acetone in varying proportions containing 1, 3 and 5 wt% of OMMT. Further the specimens were dipped in the prepared solution for 30, 50 and 70 seconds. After chemical treatment the specimens were heat treated at 60º C for the removal of the solvent. The experiments were planned according to $L_{18}$ orthogonal array.

2.2. Characterization

The post-treated specimens were characterised using XRD, FTIR, SEM and UV-vis techniques. The morphology of the top surface of treated specimens were investigated using SEM analysis and internal structure of OMMT nanoparticles after treatment was analysed by XRD technique. FTIR was used to investigate molecular components of the post-treated specimens. UV-vis spectroscopy was used to observe the UV absorbance of post-treated ABS specimens in order to see the scope for outdoor applications of ABS specimens which generally undergo photo degradation. The characterisation was performed for specimens treated with 3 wt% OMMT content and subjected to 30 seconds of dipping which was selected randomly to observe the presence of nanoparticles on the post-treated specimens.

2.3. Testing

Hardness testing was done according to shore D scale. First the fabricated samples were tested and hardness values were recorded using a durometer. Then the samples were subjected to post-treatment and again the readings were recorded. Similar methodology was adopted for roughness testing and dimensional analysis. Three readings were taken and the average values were used for analysis purpose. For average roughness ($R_a$) testing 0.8 mm cut off length was used. The dimensional variation was tested in z direction as maximum deviation in FDM prototypes is observed in this direction compared to x and y directions.

2.4. Statistical analysis

Taguchi technique was used to investigate the individual effect of post-treatment parameters on the surface properties of the specimens. Orthogonal array was used to design the experiments. Three levels of nanoparticle content and dipping time were taken and two levels of layer thickness were considered. $L_{18}$ orthogonal array was selected based on the number of factors and their levels. For
optimisation of hardness larger the better type category of S/N ratio was used and for roughness and dimensional deviation smaller the better S/N ratio was used. For multi optimisation of the responses, grey relational analysis was used. The S/N ratios were normalised in the range of 0 to 1. Further the normalised values were used to calculate the grey relational coefficient. These coefficient were further used to calculate the grey relational grade and accordingly the ranks were assigned.

3. Results and discussion
The presence of OMMT nanoparticles on post-treated ABS specimens were observed by XRD results which showed a peak at 4.75° 2θ value. This is the characteristic peak of OMMT nanoparticles [8, 9]. A broad peak was also present around 20° 2θ value which is due to the ABS amorphous structure [10] (Figure 1). However, it was also evident from the figure that no delamination of OMMT platelets occurred since the gallery between the platelets was not increased from 1.85 nm. This signifies that the nanoparticles were embedded between the polymeric chains and not exfoliated. On observing the FTIR data it was confirmed that the nanoparticles were successfully deposited on the polymer (Figure 2). A sharp peak was observed at 1018 cm⁻¹ due to the presence of Si-O-Si bond in the nanoparticle [11]. The presence of organic modifier in the nanoparticles was observed by the peak at 1488 cm⁻¹ which is due to the C-H vibrations of modifier [12]. The band at 702, 918 and 2237 cm⁻¹ were due to the styrene, butadiene and acrylonitrile components of the ABS polymers [13]. The UV-vis spectroscopy of nanocomposite solution used for post-treatment was carried along with the post-treated specimen to identify the UV absorbance for both the cases. Figure 3 demonstrate the UV absorbance graph for both. It can be seen that the absorbance demonstrated by the post treated specimens resembles the absorbance of the solution used for post-treating. Also it was found that the UV absorbance was increased for the post treated specimens compared to the pristine ABS polymer (Figure 4). This can aid in reducing the photo degradation of ABS polymer. On observing the SEM images of the post-treated specimens the platelet structure was evident (Figure 5). The same morphology can be seen in the SEM image of OMMT nanoparticles. It was also clear that the nanoparticles were homogeneously distributed over the observed region. The SEM image of pristine ABS is much smoother.

Figure 1. XRD plot for OMMT, ABS and post-processed specimens.
Figure 2. FTIR data for the post-treated specimens.
Figure 3. UV-vis spectroscopy of nano solution used for post-treatment and post-treated specimens.
Figure 4. UV-Vis data demonstrating UV absorbance of pristine ABS and post-treated specimens.
The characterisation of post-treated specimens revealed that OMMT nanoparticles were present on the surface of the post-treated specimens. This will aid in improving the surface properties of the FDM built parts.

In order to investigate the effect of each parameters on the responses Taguchi technique was used. Table 1 demonstrates the average values of the experimental results obtained. It is clear from the experimental results that the surface hardness enhanced by incorporation of OMMT on the surface of FDM parts. Maximum of 9.7% improvement was observed by the post-treatment compared to untreated specimens. The increase is due to the ceramic attribute of OMMT nanoparticles which resisted indentation compared to pristine polymeric surface. Surface finish was also improved because of the nanoparticle/chemical treatment. Significant reduction in average surface roughness was achieved by the coupled effect of nanoparticles and acetone solvent [14]. Maximum of 94% reduction was observed compared to un-treated specimens. The dimensional variation was marginal compared to the ABS parts without post-treatment. It was found that the dimensional deviation was less than 3% which signifies that the post-treatment approach does not negatively affects the dimension of FDM specimens. However, reduction in thickness was observed after the post-treatment in some cases. The reduction in thickness is favourable as it helps to bring the dimensions closer to the dimension of the CAD model. Since in FDM parts positive deviation is commonly observed in Z height partially because of swelling of the filaments and partially due to the rapid and uneven cooling of the filaments deposited. Also the overlapping of the raster may cause the positive deviation in the z height.

**Table 1.** Results of experimental runs.

| Exp. No. | Layer thickness (mm) | OMMT content (wt %) | Dipping time (sec.) | Hardness (Shore D) | Surface roughness (µm) (Rz) | Dimension (mm) |
|----------|---------------------|---------------------|---------------------|-------------------|----------------------------|----------------|
| 1        | 0.30                | 1                   | 30                  | 69.5              | 0.870                      | 1.31           |
| 2        | 0.30                | 1                   | 50                  | 72.0              | 0.564                      | 1.34           |
| 3        | 0.30                | 1                   | 70                  | 71.0              | 0.647                      | 1.35           |
| 4        | 0.30                | 3                   | 30                  | 73.5              | 0.790                      | 1.31           |
| 5        | 0.30                | 3                   | 50                  | 72.5              | 0.711                      | 1.37           |
| 6        | 0.30                | 3                   | 70                  | 73.0              | 1.346                      | 1.38           |
| 7        | 0.30                | 5                   | 30                  | 71.0              | 1.283                      | 1.33           |
| 8        | 0.30                | 5                   | 50                  | 69.5              | 1.469                      | 1.37           |
| 9        | 0.30                | 5                   | 70                  | 69.0              | 1.403                      | 1.43           |
| 10       | 0.25                | 1                   | 30                  | 75.0              | 1.893                      | 1.47           |
| 11       | 0.25                | 1                   | 50                  | 75.0              | 0.819                      | 1.44           |
| 12       | 0.25                | 1                   | 70                  | 69.5              | 1.113                      | 1.43           |
| 13       | 0.25                | 3                   | 30                  | 75.5              | 1.048                      | 1.45           |
| 14       | 0.25                | 3                   | 50                  | 72.0              | 1.284                      | 1.43           |
| 15       | 0.25                | 3                   | 70                  | 71.0              | 1.102                      | 1.53           |
| 16       | 0.25                | 5                   | 30                  | 73.5              | 1.277                      | 1.51           |
| 17       | 0.25                | 5                   | 50                  | 73.0              | 1.134                      | 1.50           |
| 18       | 0.25                | 5                   | 70                  | 71.5              | 1.679                      | 1.51           |

Un-treated (0.25 mm layer thickness) | 70 | 9.61 | 1.46
Un-treated (0.30 mm layer thickness) | 67 | 11.25 | 1.34
Figure 6 shows the main effect plot for the responses. From the figure the optimal parameters settings can be extracted. For hardness the optimal level setting is 0.25 mm layer thickness, 3 wt% OMMT content and 30 seconds dipping time. The most influential parameter was the dipping time as it governed the amount of OMMT particles deposition. However, on increasing the dipping time surface hardness decreases. This can be due to the clustering effect of nanoclay [15]. For surface roughness the optimal parameters were 0.25 mm layer thickness, 5 wt% OMMT content and 50 seconds dipping time. OMMT content was the most influential parameter for surface roughness. Lower nanoparticle content demonstrated better results. On increasing the nanoparticle content the roughness increased. However, this increase is very insignificant compared to the reduction in roughness obtained in un-treated specimens. The optimal setting for dimensional accuracy is 0.3 mm layer thickness 5 wt% OMMT content and 50 seconds dipping time. Layer thickness was the most influential parameter for marinating the dimensional accuracy compared to the CAD model. Also the dimension (thickness) of CAD model selected plays an important role since during tool path generation for material deposition the thickness in decimal is rounded off towards positive level. Thereby, producing positive deviation in 3D printed model.

![Figure 6. Main effect plot for the responses.](image)

It should be important to note that these settings will optimize the responses individually. However, for practical conditions all the responses may come into picture and it is vitally important that all the responses should be considered for optimization. Since Taguchi method is based on the single response criterion. Therefore, grey relational analysis technique is adopted for multi response optimization [4]. The S/N ratio obtained from Taguchi method were normalized between 0 to 1 values for grey relational analysis. Further the normalized values were used to calculate the grey relational coefficient. These coefficient were further used to calculate the grey relational grade and accordingly the ranks were assigned as demonstrated in Table 2. The higher grey relational grade represents that the corresponding experimental result is closer to the ideally normalized value. Ranks are assigned according to the grade. First rank is assigned to the experiment run having highest grade value.
Table 2. Grey relational coefficient with their grades and ranks.

| Exp. No. | Grey Relation coefficient | Grey relation grade | Rank |
|----------|---------------------------|---------------------|------|
|          | Hardness (Shore D) | Surface roughness (µm) ($R_a$) | Dimension (mm) |          |
| 1        | 0.352159618 | 0.437812699 | 0.333333333 | 0.374435217 | 18 |
| 2        | 0.48671024 | 0.333333333 | 0.369236499 | 0.396426691 | 16 |
| 3        | 0.42280863 | 0.360590141 | 0.382774576 | 0.388724449 | 17 |
| 4        | 0.626371866 | 0.409264479 | 0.333333333 | 0.456323226 | 14 |
| 5        | 0.526142252 | 0.380253692 | 0.412703077 | 0.440299673 | 15 |
| 6        | 0.572107997 | 0.639682149 | 0.429303703 | 0.547031283 | 8 |
| 7        | 0.42280863 | 0.608845233 | 0.356530936 | 0.462728266 | 13 |
| 8        | 0.352159618 | 0.704800179 | 0.412703077 | 0.489887624 | 11 |
| 9        | 0.333333333 | 0.668998769 | 0.53452363 | 0.512285244 | 10 |
| 10       | 0.871391954 | 1 | 0.659893509 | 0.843761821 | 1 |
| 11       | 0.871391954 | 0.532697566 | 0.56468379 | 0.67449299 | 7 |
| 12       | 0.352159618 | 0.53269374 | 0.53452363 | 0.47312754 | 12 |
| 13       | 1 | 0.505913467 | 0.591056134 | 0.698989676 | 3 |
| 14       | 0.48671024 | 0.609322832 | 0.53452363 | 0.54351890 | 9 |
| 15       | 0.42280863 | 0.528084438 | 1 | 0.650297689 | 5 |
| 16       | 0.626371866 | 0.605989003 | 0.855052062 | 0.69580431 | 4 |
| 17       | 0.572107997 | 0.541607081 | 0.79673836 | 0.63681781 | 6 |
| 18       | 0.452619392 | 0.834621944 | 0.855052062 | 0.714097799 | 2 |

Since the experimental design is orthogonal, it is then possible to separate out the effect of each process parameter on the grey relational grade at different levels. Table 3 shows the effect of individual parameter based on grey relational grade. The optimal settings was found to be 0.25 m layer thickness, 3 wt% OMMT content and 30 seconds dipping time. Layer thickness is the most influencing factor followed by OMMT content and dipping time.

Table 3. Effect of individual parameter based on grey relational grade.

| Factors       | Level 1          | Level 2          | Level 3          | Main effect | Rank |
|---------------|------------------|------------------|------------------|-------------|------|
| Layer thickness | 0.452015742     | 0.652651671*     | -                | 0.20063593 | 1    |
| OMMT content  | 0.51565417      | 0.556076773      | 0.585270176*     | 0.069616007 | 2    |
| Dipping time  | 0.588673784*    | 0.520733333      | 0.547594001      | 0.067940451 | 3    |

Total mean value of grey relational grade 0.552333706

*Optimal levels by grey relational grades

4. Conclusions
OMMT nanoparticles were successfully embedded on the surface of FDM specimens. The approach presented provides an efficient way to enhance the surface properties of the FDM parts which can increasing their application domain. XRD, FTIR and SEM analysis showed the presence of embedded
nanoparticles. UV-vis spectroscopy demonstrated that post-treatment can improve the UV absorbance of FDM built ABS polymer. 9.7% increase in surface hardness was achieved along with 94% reduction in surface roughness. Dimensional deviation of less than 3 % was achieved. The effect of parameters on individual responses according to Taguchi technique showed that dipping time, OMMMT content and layer thickness were the most influential parameters for surface hardness, surface roughness and dimensional accuracy respectively. Further multi objective optimization revealed that layer thickness is the most influential parameter followed by OMMMT content and dipping time. The optimal parametric values were 0.25 mm layer thickness, 5 wt % OMMMT content and 30 seconds dipping time.

References
[1] Chua CK, Leong KF, Lim CS. Rapid Prototyping: principles and applications. Rapid prototyping. 2003
[2] Guo N, Leu MC. Additive manufacturing: Technology, applications and research needs. Front Mech Eng. 2013;8(3): pp 215-43
[3] Ning F, Cong W, Qiu J, Wei J, Wang S. Additive manufacturing of carbon fiber reinforced thermoplastic composites using fused deposition modeling. Compos Part B. 2015;80: pp 369-78
[4] Sood AK, Ohdar RK, Mahapatra SS. Improving dimensional accuracy of Fused Deposition Modelling processed part using grey Taguchi method. Mater Des. 2009;30(10): pp 4243-52
[5] Taufik M, Jain PK. A Study of Build Edge Profile for Prediction of Surface Roughness in Fused Deposition Modeling. J Manuf Sci Eng. 2016;138(6): p 61002
[6] Galantucci LM, Lavecchia F, Percoco G. Quantitative analysis of a chemical treatment to reduce roughness of parts fabricated using fused deposition modeling. CIRP Ann - Manuf Technol. 2010;59(1): pp 247-50
[7] Kuo CC, Mao RC. Development of a Precision Surface Polishing System for Parts Fabricated by Fused Deposition Modeling. Mater Manuf Process. 2016 Jun 10;31(8):pp 1113-18
[8] Sinha Ray S, Okamoto M. Polymer/layered silicate nanocomposites: A review from preparation to processing. Prog Polym Sci. 2003;28(11): pp 1539-641
[9] Francis V, Jain PK. Experimental investigations on fused deposition modelling of polymer-layered silicate nanocomposite. Virtual Phys Prototyp. 2016;11(2): pp 109-21
[10] Wang Z, Wang J, Li M, Sun K, Liu C. Three-dimensional Printed Acrylonitrile Butadiene Styrene Framework Coated with Cu-BTC Metal-organic Frameworks for the Removal of Methylene Blue. Sci Rep. 2014;4(5939): pp 1-7
[11] Pourabas B, Raeesi V. Preparation of ABS/montmorillonite nanocomposite using a solvent/non-solvent method. Polymer. 2005;46(15): pp 5533-40
[12] Bhagabati P, Chaki TK, Khashtri G. Panoptically exfoliated morphology of chlorinated polyethylene (CPE)/ethylene methacrylate copolymer (EMA)/layered silicate nanocomposites by novel in situ covalent modification using poly(e-caprolactone). RSC adv.2015;5(48): pp 38209-22
[13] Skorski MR, Esenther JM, Ahmed Z, Miller AE, Hartings MR. The chemical, mechanical, and physical properties of 3D printed materials composed of TiO2-ABS nanocomposites. Sci Technol Adv Mater. 2016;17(1): pp 89-97
[14] Cunico MWM, Cunico MM, Cavaleiro PM, Carvalho J de. Investigation of additive manufacturing surface smoothing process. Rapid Prototyp J. 2017;23(1): pp 201-08
[15] Lam CK, Cheung HY, Lau KT, Zhou LM, Ho MW, Hui D. Cluster size effect in hardness of nanoclay/epoxy composites. Compos Part B Eng. 2005;36(3): pp 263-69