

3D printed polycarbonate reinforced acrylonitrile–butadiene–styrene composites: Composition effects on mechanical properties, micro-structure and void formation study[†]

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Abstract

3D printing is one of the most popular additive manufacturing technique due to its usage in vast applications. The process of 3D printed polycarbonate (PC) reinforced acrylonitrile-butadiene-styrene (ABS) composite increases the mechanical properties and yields higher strength for 3D printed structures/products. In this paper, a comparative study was conducted on PC/ABS polymer composites developed using fused deposition modeling (FDM) and conventional compression molding (CM). The proposed study aims at analyzing 3D printed PC/ABS in terms of their processibility, microstructure, and mechanical performance. Three different specimens were prepared with weight percentages (10 wt%, 20 wt%, and 30 wt%) of PC reinforcement in ABS. Mechanical properties of the specimens are used to find the best composition of the composite using FDM and CM. Similarly, the microstructure of specimens is studied to identify the variations in the strength of the polymer composites. This study proves the compatibility of the two polymers. With an increase in the PC content in the sample, the hardness and strength are improved and can provide an excellent amount of strength to the product at a required concentration of PC reinforcement. This phenomenon was explained based on changes in the void formation using micro-structural study. Knowing the appropriate polymer composition, it contributes to printing complex 3D printed with better rational, aesthetic and economic benefits for different applications such as automotive, marine, and several other fields.

Keywords: 3D printing; Polycarbonate; Acrylonitrile-butadiene-styrene; Micro-structure; Mechanical properties; Void formation

1. Introduction

Rapid prototyping is an additive manufacturing process, which is the most favorable and quick production technique in manufacturing industry [1]. It differs from conventional manufacturing techniques such as machining and casting for its capability, to produce composite shapes with excellent design flexibility without any waste generation. It improves the time required to develop the product, thereby facilitating mass production. Manufacturing of several products using polycarbonate (PC) and acrylonitrile–butadiene–styrene (ABS) based composite materials are getting popular these days. However, reinforcement of PC into ABS base material increases the mechanical properties and it yields higher strength in 3D printed structures/product.

3D printing helps in creating molds, prototypes, and patterns, as it can create models of any complicated shapes and sizes [2, 3]. 3D printing using fused deposition modeling

(FDM) is an RP method which comes under additive manufacturing, one of the fastest growing methods in the manufacturing industry today [4, 5]. In the conventional process like compression molding (CM), complicated molds are required to develop the PC-ABS structures/products. This process is expensive and time-consuming. Moreover, it is difficult to fabricate complex shapes, which moved our attention to additive manufacturing techniques [6, 7].

Fig. 1 shows a general schematic of the FDM process. It has a nozzle unit, heat bed, build platform, material spool and object/model [8, 9]. Nozzle unit can move in a cartesian three-axis translation along x, y, and z-axes. Nozzle unit has its own heating chamber in order to melt the filament and prepare it for printing. The heat bed is used to maintain a high temperature on the bottom layer of the 3D printed component. It helps the user to remove the printed component easily from the hot-bed.

3D printing is a layer-by-layer addition of the material. Thus, one can follow the desired pattern and can even vary the parameters like layer thickness, air gap, raster angle, build orientation, road width, number of contours while printing the

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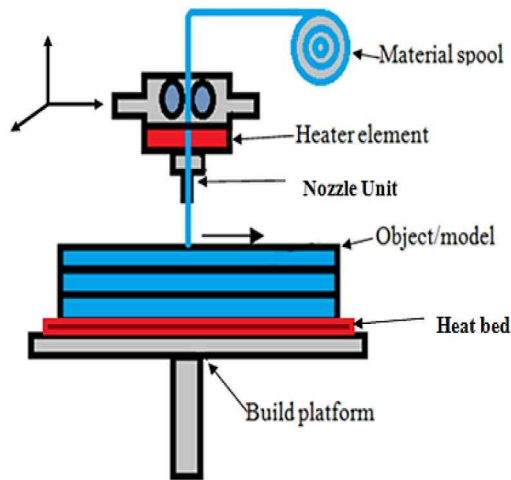


Fig. 1. Schematic of FDM process.

model [10]. However, the use of reinforcements in composite materials and then 3D printed has various benefits, as they improve the mechanical properties such as tensile strength, hardness, bending strength, impact strength, etc. in 3D structures [11, 12]. The strength properties offer an incredible advantage over other material. Considering that, it was only in the past few years that composites became viable in a large-scale performance production line [13, 14].

Acrylonitrile–butadiene–styrene (ABS) is the most commonly used material in 3D printing. In the composite material, ABS acts as a base material and PC polymer will be a reinforcement [15]. ABS is used for its mechanical properties and molding performance. When compared with other polymers, its low-temperature resistance and mechanical performance may limit its usage [16, 17]. On the other hand, polycarbonate (PC) is a kind of thermoplastic with better properties such as creep resistance, temperature resistance, high impact strength, and good dimensional stability [18, 19].

Blend of PC and ABS materials are the most frequently used plastics in several applications. The success of the PC/ABS blend is due to their properties combination of two materials like high thermal stability and good impact behavior of PC and easy processibility of ABS. Thus, PC reinforced ABS will improve the mechanical behavior of ABS and ultimately will make it a product with excellent mechanical properties [20]. This improvement in PC/ABS blends has been exploited by the industry, especially in automotive, and appliances [21, 22].

Some of the important properties of PC/ABS like impact strength, flexural modulus and hardness are relatively greater than pure PC and ABS materials as shown in Fig. 2. Nowadays, studies related to 3D printed PC/ABS has a lot of scope for research due to its vast applications.

This paper deals with the development of 3D printed PC/ABS (polymer) composites of varying PC content in order to search for best composition from the formulated compositions. The details of the current investigations are presented in

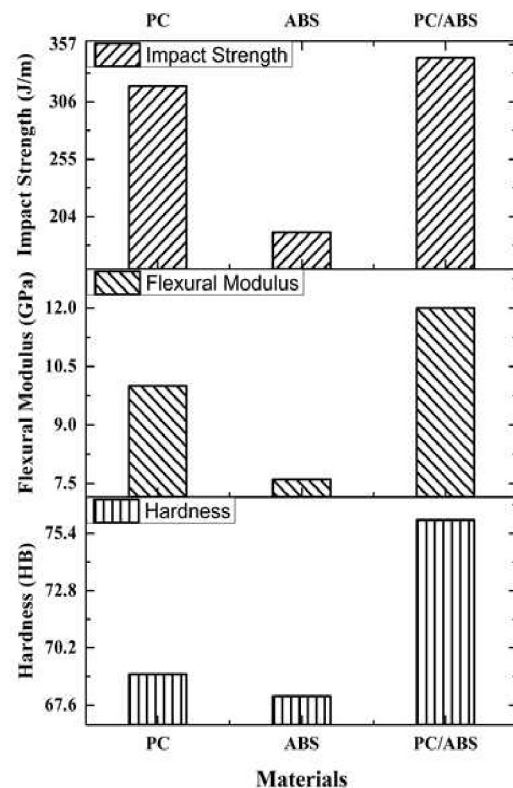


Fig. 2. Mechanical properties of PC, ABS and PC/ABS [7].

the sections that follow: Sec. 2 describes the process flow for preparing PC/ABS blends with varying PC contents, also it discusses the process parameters that are adopted during material preparation and experiments. Sec. 3 explains the effect of PC content on various mechanical properties like hardness, flexural strength, impact strength, also describes the fluctuations that occur in the properties with varying PC content. SEM analysis was conducted on different specimens to notice the changes in the microstructures of the materials with varying PC content. Sec. 4 concludes the investigations conducted on PC/ABS composites with varying PC content and its effect on the properties of a material. It highlights the significance of FDM over the conventional technique.

Although 3D printing has attracted a lot of attention over the past few decades, most of the articles focused on the development of processing techniques and 3D printing of pure polymer materials. However, in recent years, there has been considerable progress in developing printable polymer composites with the improved performance [23, 24]. Therefore, it would be pertinent to present, analyze and summarize information on 3D printing of polymer composites and the effect of their properties with varying PC content.

2. Experimental

2.1 Materials and processing

Fig. 3 shows the process adopted for fabricating the materi-

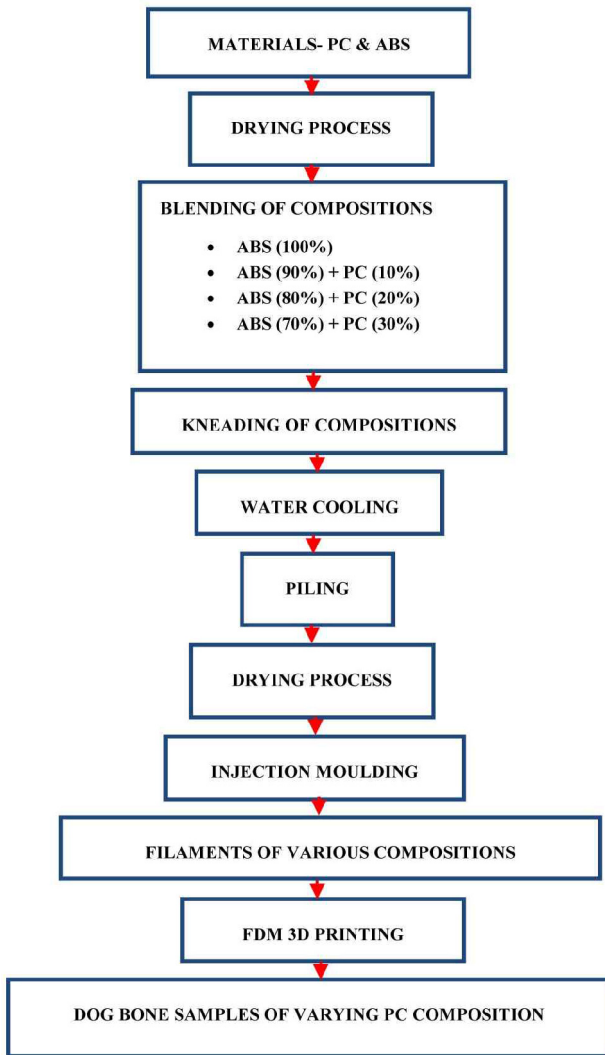


Fig. 3. Material processing flowchart.

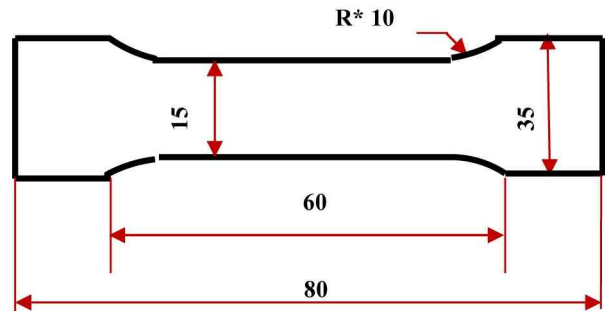
als. Initially, PC and ABS materials need to be dried before use to remove the moisture content. ABS requires about 8 hours of drying at 80 °C and PC requires 12 hours of drying at 120 °C. Different compositions of PC and ABS are blended together as shown in Fig. 3. Blended compositions are kneaded to distribute the PC reinforcement into the ABS matrix. These compositions will be water cooled to remove the heat present in the blend and cool it down for the further process. Piling formation on top of the blend will be removed physically and as well as using water wash. Different blends are made into granules for the extrusion process.

Granules are loaded into the injection molding machine with an extruder of L/D ratio 34:1. After a molten state of the blend is attained, it is passed into the closed mold through the injector. After subsequent cooling and solidifying, it will form filaments of respective polymer compositions. 3.5 mm filaments are fabricated from the different blend and it will be used in a 3D printer.

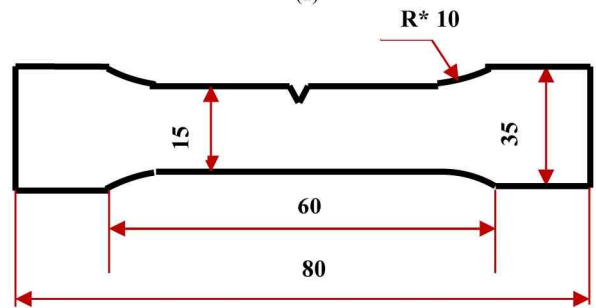
ASTM D628 standard [25] was adapted to construct the

Table 1. 3D printing parameters.

Material	Nozzle diameter (in mm)	Nozzle temperature (°C)	Heating bed temperature (°C)	Layer thickness (in mm)
ABS	0.5	240	80	0.3
ABS-PC	0.4	260	80	0.25



(a) $t^{**}=7\text{ mm}$



(b) $t^{**}=7\text{ mm}$

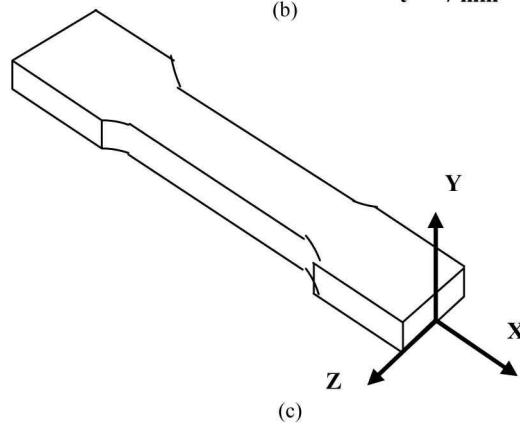


Fig. 4. ASTM D628 standard: (a) Sketch of the dog-bone sample; (b) sketch of the dog-bone sample with a notch; (c) sample orientations.

dog bone shaped 3D Printed PC-ABS material by feeding the extruded PC-ABS filaments into a commercial FDM machine. Similarly, compression molded PC-ABS material was developed for the comparative study using PC/ABS blended granules.

3D printing of PC/ABS material requires printing parameters such as nozzle diameter, layer thickness, printing nozzle temperature, and heating bed temperature. Table 1 shows the

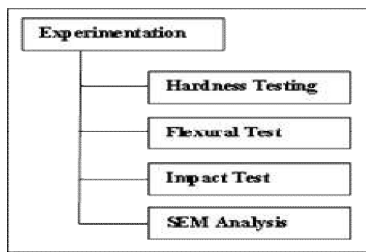


Fig. 5. Test procedure.

process parameters for 3D printing. For pure ABS samples, nozzle diameter of 0.5 mm and for samples of PC and ABS 0.4 mm was taken for developing intricate 3D shapes. Heating bed temperature of 80 °C was maintained for both pure ABS and PC/ABS. Nozzle temperature and layer thickness as mentioned in Table 1 was followed.

As per ASTM D628 standard, the maximum thickness of plastic materials is 14 mm. Authors have maintained 7 mm thickness (0.5 times maximum thickness) of a dog bone shaped specimen and that is below the maximum limit. Other dimensions of the dog-bone specimens are as shown in Figs. 4(a) and (b), Sample orientation direction is as shown in Fig. 4(c).

2.2 Testing and analysis

Mechanical properties of CM and FDM samples are determined by testing dog bone samples of each composition of PC polymer. Fig. 5 shows the mechanical tests performed on the samples.

ASTM E-18 standard was used to test the mechanical properties (hardness, flexural, and impact strength) of the PC/ABS composite with different compositions. The hardness test is performed to reveal the hardness property of different compositions of PC polymer/ABS composite by CM and FDM techniques. It will essentially help in deciding the application of usage of these proposed compositions. Then, the flexural test was performed as per ASTM D-790 standard to calculate the maximum flexural stress before bending and the results were compared. Similarly, the impact strength test was conducted with guidelines of ASTM D-256 standard. SEM analysis was conducted based on an ASTM E-2809 standard for the specimens with different PC contents.

3. Results and discussions

The purpose of this work is to understand the opportunities and challenges of composites by the 3D printing process and to analyze the potential of load-bearing components. Results show that the specific compositions of PC/ABS composites exhibit high specific strength with high specific modulus as shown in Fig. 6. Experimental investigations are required to find an increase in hardness, flexural strength, and impact strength with increase in PC content in the composite. This method leads to better packing of the deposited beads and

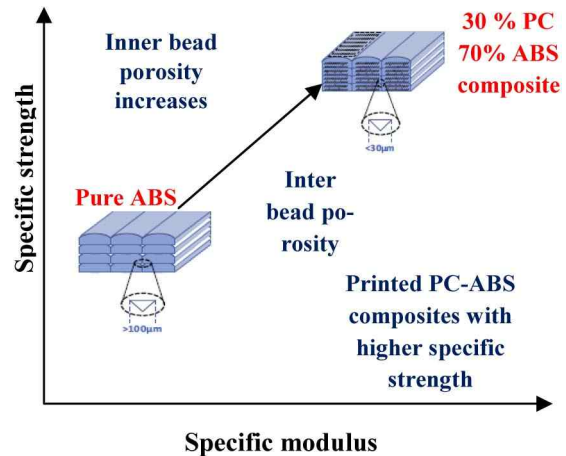


Fig. 6. Schematic presentation of 3D printed composite by FDM.

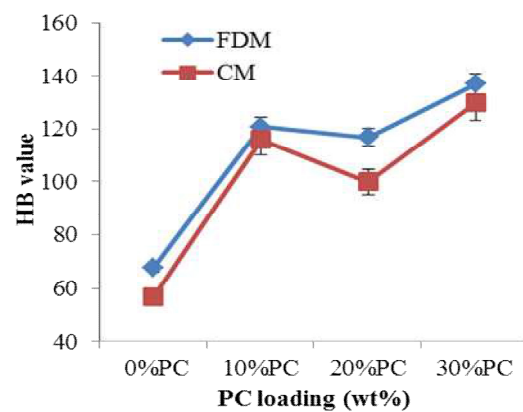


Fig. 7. Effect on the HB value of a change in PC loading wt%.

smaller inter bead voids which increase the specific strength and specific modulus of the material.

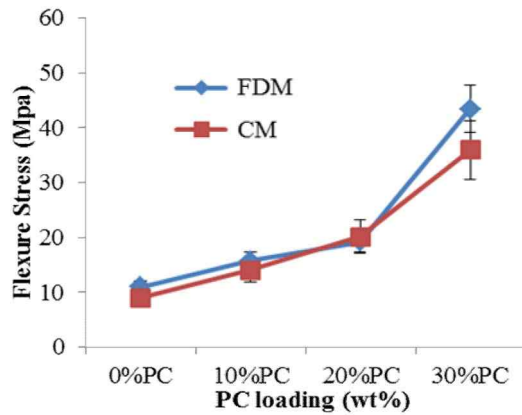
3.1 Effect on the hardness of change in PC wt%

The hardness test results of CM and FDM printed with different PC/ABS compositions are plotted as shown in Fig. 7. It can be observed that the hardness value is highest for the sample with PC 30 wt%. Better results are achieved through a reinforcement of PC polymer than the hardness of the pure ABS specimen. The hardness of 20 wt% PC specimen is lower than that of a specimen with 30 wt% PC and 10 wt% PC.

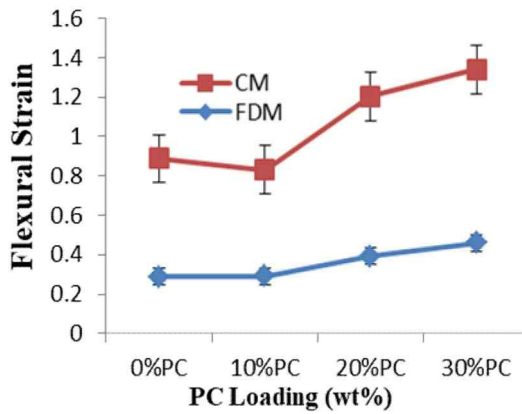
The hardness value of FDM made PC/ABS is relatively higher than CM PC/ABS but the same trend of change in values is seen in both methods. This might be due to improper binding of composite material or void formation. Thus, SEM analysis is necessary to identify the reason for this sudden drop of hardness.

3.2 Effect of flexural strength for change in PC wt%

The flexural strength increases with the increase of PC con-



(a)



(b)

Fig. 8. (a) Effect on flexural stress for change in PC loading wt%; (b) effect on flexural strain for change in PC loading wt%.

tent for both the CM and FDM samples as seen in Figs. 8(a) and (b).

It can be observed that flexural stress of FDM printed PC/ABS is relatively higher than CM PC/ABS at 30 wt% PC. At the same time, flexural strain remains relatively high for wt% samples. Fig. 9 shows the increase of flexural modulus with a rise in PC wt%. This indicates that the rigidity is greatly improved by rising PC content in the composite material. Flexural strength of PC/ABS is a linear function of PC content. It is evident that the flexural strength of FDM PC/ABS is higher than the CM made PC/ABS composite.

3.3 Effect on impact strength for change in PC wt%

Fig. 10 shows the trend of impact strength Vs. PC wt%. The test results show that the impact strength initially decreases when the reinforcement wt% was increased. Then, after a certain composition, strength rises again. It reaches a maximum value at 30 wt% PC composition (without considering pure ABS). The impact strength will keep rising with an increase in a composition of polycarbonate beyond 30 wt% PC. But, there is a limitation for the increase of wt% PC since beyond a point, it will exhibit more characteristics of PC ma-

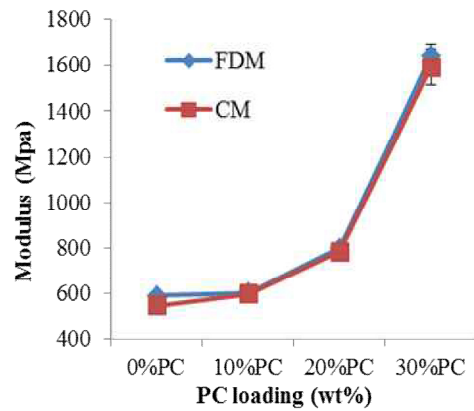


Fig. 9. Effect on flexural modulus of change in PC loading wt%.

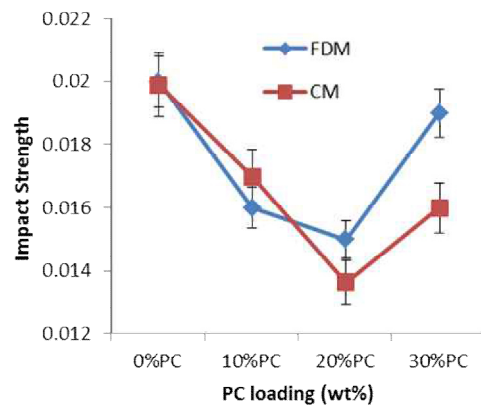


Fig. 10. Effect on Impact strength for change in PC loading wt%.

terial. This will eventually limit its usage in specific applications.

The decisive change occurs when the PC composition is at 20 wt%, and above 30 wt%, which can improve the impact durability of the polymer composite. The impact strength of the mixture was vastly increased when the PC content is more than 20 wt% as shown in Fig. 10. FDM printed PC/ABS exhibits higher impact resistance or strength when compared to CM PC/ABS at 30 wt% PC. However, the impact strength of FDM printed PC/ABS is lower than CM at 10 wt% PC. This drop in impact strength of PC/ABS depends on: 1) Intrinsic factors such as molecular structure, molecular distribution, cohesive energy and morphology of material structure. 2) Extrinsic factors such as temperature, impact speed, shape and weight of the striker, specimen geometry, and notch size and shape affect impact strength. High molecular weight and narrow molecular weight distribution generally improve impact resistance. Where as, an increase in crystalline nature and voids will lower the impact resistance. Hence, a study on void formation has been conducted to analyze the drop in impact strength at 10 wt% and 20 wt% of PC content.

3.4 Void formation

SEM analysis justifies the results of tests performed. It also

Table 2. Void formation table.

Material	No of voids/ μm	Voids formation %
FDM printed pure ABS	3	0.21
FDM printed 10 wt% PC loading	5	0.46
FDM printed 20 wt% PC loading	7	0.93
FDM printed 30 wt% PC loading	3	0.17

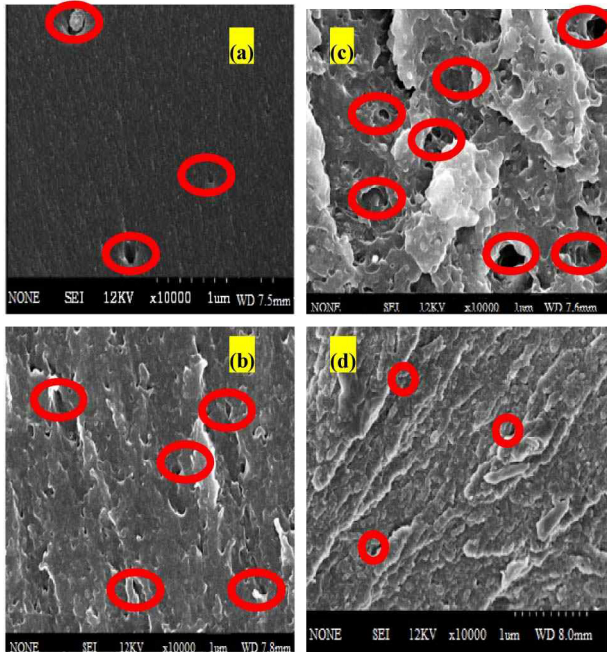


Fig. 11. Micro graphs on the polished surfaces of the dog-bone slices: (a) FDM printed pure ABS; (b) FDM printed 10 wt% PC loading; (c) FDM printed 20 wt% PC loading; (d) FDM printed 30 wt% PC loading.

proves the compatibility of the two polymers. SEM images of polished surfaces of the dog bone samples are shown in Fig. 11.

The increase in PC content leads to better packing of the deposited beads and thus creates a smaller inter-bead void which provides better mechanical properties for the material. The pure ABS sample shows no visible void content. However, FDM samples show significant pore formation.

Fig. 11(a) shows the porosity in the 3D printed pure ABS sample, which of course has no fiber effect and contains relatively large voids. These voids are gaps between beads at the time of printing and voids inside the beads will create stress concentration points. This makes the sample to fail at lower stresses. On the other hand, SEM image of the polished gauge sections of FDM printed 10 wt% PC and 20 wt% PC are shown in Figs. 11(b) and (c), respectively. It shows that the void fraction formation fluctuates between 10 weight% and 20 wt% PC polymer samples independent of PC content. These fluctuations in void formations attributed to the effect of a change in large voids among the bead and smaller voids in the beads with an increase in PC content.

Quantitative analysis of the void formation of surfaces with varying PC content is tabulated in Table 2. In pure ABS material, the percentage of void formation was 0.21 % and the size of voids are relatively larger than the rest of the samples. Similarly, 0.46 % of void formation was traced in 10 wt% of PC content. With the increase in PC content to 20 wt%, the void formation percentage was 0.93 % and this is the reason for the sudden fall in impact strength. However, void formation decreased by 0.76 % for further increase in PC content to 30 wt%. The void formation was reduced to 0.17 %. Therefore, 30 wt% PC content leads to better-deposited beads and smaller inter bead void formation during printing as shown in Fig. 11(d). This causes an increase in the mechanical properties of the material with 30 wt% PC which is revealed from the SEM results.

4. Conclusions

PC with ABS resin feedstock at different PC loadings (10 wt%, 20 wt%, and 30 wt %) was prepared, and these materials were used to successfully fabricate composite specimens by a 3D printing technique. This study shows that PC/ABS composite samples have better mechanical properties than pure ABS samples. The comparative study between FDM and CM was conducted and mechanical properties are revealed to find the best composition and exhibit the compatibility of the two polymers. This study proves that, with an increase in the PC content in the sample, there will be a corresponding sign which will enhance the strength of the product as per requirement.

SEM analysis justifies the results with microstructure and it helps us understand the variations in the strength of the polymer composites. Void formation study was conducted to investigate the reason behind the increase of strength. It is evident that the process with its controlled orientation and good spreading capabilities, with the use of PC reinforced material, enables the manufacturing of superior quality composite that can withstand higher loads. During 3D printing, care has to be taken to avoid pores and cracks during compounding. It is better to enhance interfacial bonding between the reinforcement and the base surface through necessary modifications. Future scope of work can be testing dynamic mechanical behavior and glass transition temperature of the PC/ABS material.

Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Nomenclature

R* : Radius
 Wt% : Weight percentage
 t** : Thickness

°C : Degree celsius
mm : Millimeters

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