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A Targeted Functional Value Based Nanoclay/PA12 Composite Material Development for Selective Laser Sintering Process

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Abstract

The work presents an evaluation of possibilities of mixing Nanoclay with polyamide (nylon 12 or PA 12) powder in order to enhance fire retarding properties. Further the work deals to estimate making of part which are useful in daily use with Selective Laser Sintering process using the Nanoclay and PA12 mixture. To achieve the identical process condition in order to qualitatively compare the results with that of SLS fabricated parts, a pressure-less casting process is employed to prepare specimen of PA12 based composite powder (containing 0-15 wt % Nanoclay). Surface modified montmorillonite Nanoclay is used for reinforcing the cast parts of PA12. The composite powders are examined by material characterization techniques (SEM, DSC and XRD). The effects of Nanoclay on the thermal (viscosity, melt flow index, molecular weight etc.), and mechanical properties of the casted parts are investigated. The results show that the uniform dispersion of Nanoclay is achieved in the prepared specimen. The composite powder has much high thermal stability than pure PA12 material. On addition of such a small quantity of Nanoclay most of the mechanical properties and flammability properties are improved while elongation at break (%) decreased significantly. The study will be useful in making the value added parts using an alternate material.

Keywords: Value Creation by Sustainable Manufacturing , Nanoclay, PA2200 (PA 12), Selective Laser Sintering, Value Engineering.

1. Introduction

Selective laser sintering (SLS) is a group of automated, highly productive, energy saving and powder based sustainable manufacturing process [1-2]. The acceptance of SLS process (an AM process) in future predicted for value chains are having shorter, smaller, more localized, more concerted, and offer considerable sustainability

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benefits. It is intrinsically less wasteful and it has potentials to overcome social and economic barriers from the environmental impact of business activities. The possible sustainability benefits of this technology are being improved resource efficiency, extended product life etc. These can be achieved through technical approaches such as repair, remanufacture and refurbishment. However, despite these benefits, it could be an enabler and a driving force for enhanced industrial sustainability. The consequences of its execution on the industrial system could bring about another scenario wherein less eco-efficient localized production may be necessary. [2].

SLS process directly forms 3D solid parts of any complexity through selective sintering of successive layers of powdered raw materials using 3D CAD model [2]. Range of materials, such as wax, cermets, ceramic, polymers, metals, metals system, alloys, biomaterial, and etc., can be used as a SLS process material [1-13]. Among these available SLS materials, polymers mainly thermoplastic are preferred over other SLS materials due to their lower cost, low processing temperatures and sintering laser power, etc. [4, 10]. However mechanical properties and fire retardant property of polymers are poor than those of composite materials [2]. Presently, micron size inorganic fillers, such as cement, glass beads, silicon carbide, and aluminum powder have been widely used to reinforce for SLS process [3], [14-17]. Usually these fillers can improve the mechanical properties, such as the modulus, and hardness etc. Improvement is a function of concentration of fillers. Polymer/layered silicate (PLS) nano-composites have excellent combination of mechanical propertiesrelative to virgin polymers for sustainable manufacturing [18-20]. In literature, it has been outlined that addition of clay nanoparticles increases the viscosity of PA6. It has been observed that bed temperature during SLS process and laser power that is required to fabricate the part significantly increases [21].Wang et al. [22] have fabricated functional parts from the blends of PA12 material, and organically modified rectorite clay(OREC) using SLS process. Significant improvement in mechanical properties has been observed for these materials [22]. It has been established that the ultimate tensile strength, elongation at break, and other properties of the PA/clay composite SLS specimens degrade relative to pure PA12. It has also been suggested that the suitable part bed temperature for the part fabrication needs to be optimized for the blended powder to avoid part curling [23]. Nowadays, several methods are available to prepare PLS composite powders, mechanical mixing, grinding, and dissolution-precipitation process [22-25].

2. Experimental

The PA12 powder has been used with 56 microns particle size, and surface modified Nanoclay of 6-13 microns particle size. The composite materials are formed by loading the different concentration varying between 5wt% and 15wt% of SMMT Nanoclay filler in PA12. The powders are mechanically mixed using ball milling processes. Pressure less casting is employed to make specimen for i.e. tensile strength, flexural strength and modulus, compressive strength, impact strength, density, and fire retardant properties. The specimen are fabricated in a rich nitrogen environment in case of EOSINTP385 machine, thus, the identical environment has been employed. The SLS system has CO_2 laser (λ=10.6μm) [26].Various tests that have been carried out are given in table 1.

Table 1. Standard testing procedures followed

Test name	Standard	Machine	Description
Tensile test	ISO 527.2	H25KS	Cross head speed 5 mm/min
Three point flexural test	ISO 178	Instron 3345	Speed of 2 mm/min
Compression test	ISO604	Instron 3345	Speed 5 mm/min
Izod impact test	ISO 180	Model IT 504	Unnotched specimen
Flammability test	UL94-V	Flammability tester	Vertical and inclined at 45^{o} test
Microscopic morphology	-	Hitachi-3400N	Resolution 10nm at 30 kV and 300,000X magnification
X-ray diffraction	-	X'Pert PRO diffractometer	λ=0.1540nm,scan0.1^{o}/10 sec
Melting and crystallization	ISO 11357	SDT Q 600	Heating 10℃/min; to 250℃.
Melt flow index	ISO-1133	Melt flow index tester (International Engg.)	Melt temperature of 235℃
Density	ISO 1183-3	Density tester	Electronic measurement

3. Results and discussion

The SEM micrographs of SMMT Nanoclay/PA12 for the 5wt% and 10wt% of SMMT Nanoclay dispersion are shown in Figure 1 and Figure 2 respectively. It has been observed that the powders have irregular shape. The powders with more regular shape and narrower particle size distribution are favourable to distribute powders to shape SLS and casting parts with superior accuracy. The particle size measured from SEM micrographs of SMMT clay 5 wt% and PA12 composite is shown in Figure 3. The measured mean particle size for PA12 based composite containing 5wt% SMMT Nanoclay is about 35.85±sd µm which is quite close to the recommended value by EOS for SLS processing.

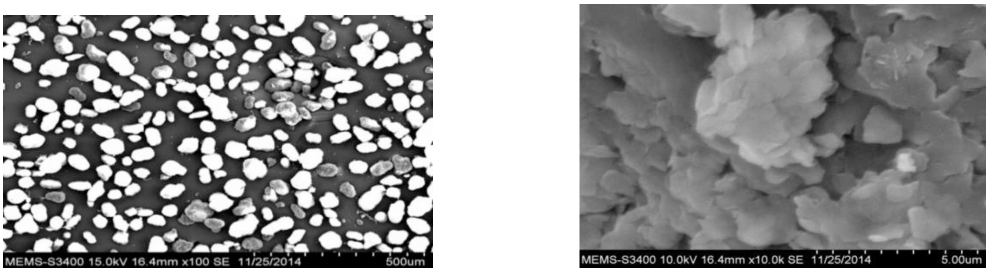


Fig. 1. SEM micrographs for composite containing PA12 based 5wt% SMMT clay.

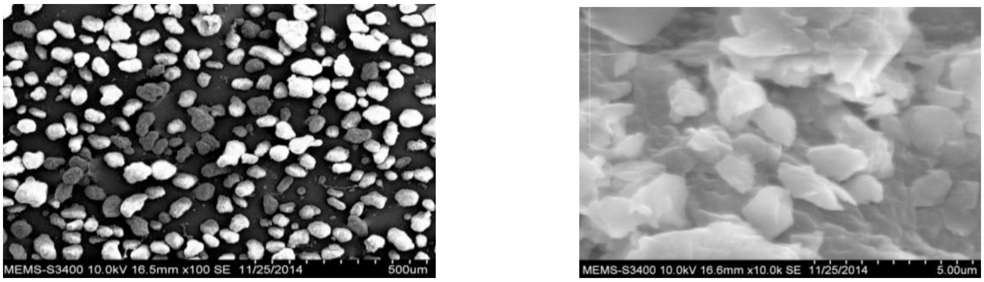


Fig. 2.SEM micrographs for PA12 based composite containing 10wt% SMMT clay.

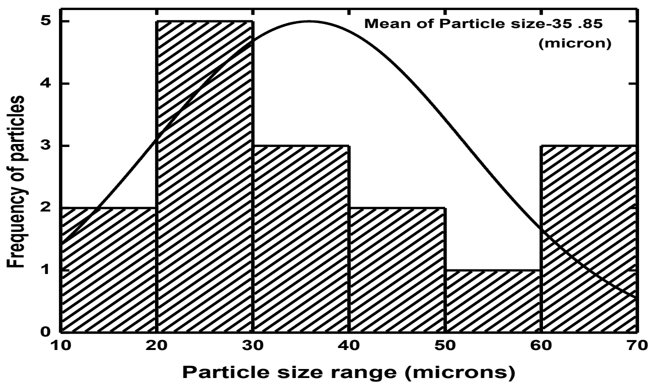
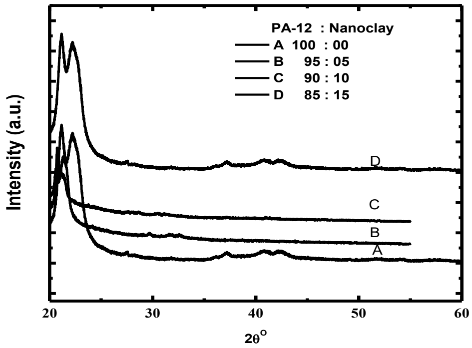


Fig. 3. Particle size histogram plotted using SEM micrograph (PA12- SMMT Nanoclay: 95:5 by wt %).



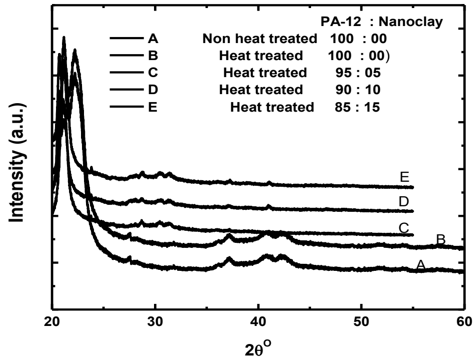
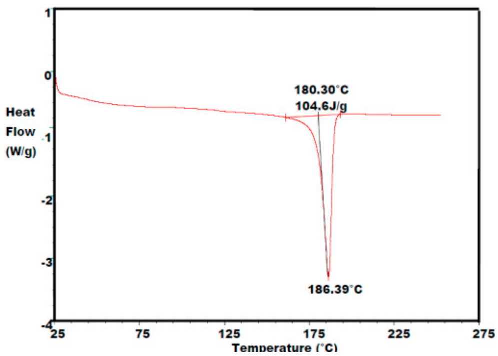


Fig. 4.XRD of SMMTNanoclay/ PA12 composite non heat treated.Fig. 5.XRD of SMMT/ PA12 composite heat treated.

The XRD patterns of SMMT Nanoclay/PA12 composite without any heat treatment are shown in Figure 4. Figure 5 corresponds to the XRD pattern of specimen made of composite, heated for three hours at 175^0C.To find out the optimal values of process parameters for processing the material on SLS machine, the SMMT Nanoclay/PA12 composite material heated at temperatures of 100°C and 180°C for the periods of 25 hours, 50 hours, 75 hours and 100 hours. From the DSC curve, it can be observed that the effect of loading with different concentration of SMMT Nanoclay in PA12 on melting point is negligible, and it remains approximately unaltered. The heating of samples for period of 0-100 hours can increase the value of glass transition temperature, re-crystallization temperature and melting temperature by 3-5℃ [3]. It has also been observed that temperature effects on various factor of material. Higher temperature gives significant variation. Figure 6 and Figure 7 shows the DSC curves of PA12 and SMMT Nanoclay/PA12 composite.



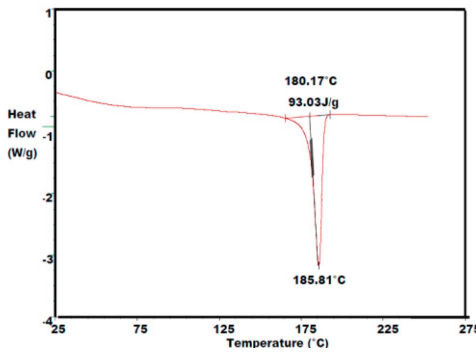


Fig.6.DSC of PA12 ((Non heat treated). Fig. 7. DSC of SMMTNanoclay5wt%/PA12 composite (Non-heat treated).

The material thermal properties values like peak melting temperature (T_{mp}), peak crystallization temperature (T_{cp}), melting enthalpy (ΔH_m) and crystallization enthalpy (ΔH_c) were extracted from the DSC curves. The crystalline index (CI) was calculated using Eq. (1) [18], [21], [25], [27-28].

$$CI = \frac{(\Delta Hm)}{(\Delta Hf \times (1-f))} \times 100 \qquad (1)$$

Where, melting enthalpy is given by ΔH_f for a theoretically 100% crystalline PA12 and ΔH_f value for pure PA12is 209.2 J/g [18], f is the mass portion of the filler (SMMT Nanoclay). It has been observed that there is little difference in the T_{mp} between PA12 and SMMT Nanoclay/PA12, but the $\Delta H_m$of SMMT Nanoclay/ PA12 is 11 % lesser than that of PA12. The composite of SMMT Nanoclay/PA12 requires a less amount of heat for complete melting demonstrating that there are fewer crystals in it. It has been observed that the addition of Nanoclay in PA12 decreases the CI values. Table 2 shows the CI (%) with respect to Nanoclay wt (%) in PA12.

Table 2. CI (%) with respect to Nanoclaywt (%) in PA12.

Sr. No	Wt% of Nanoclay	CI (%)
1	0	50
2	5	46.80

Melt flow index is an important parameter to predict the quality of SLS fabricated parts and to find out suitable amount of virgin powder needed [29].The composite material of different weight proportion of SMMTNanoclay in PA12 was heated at 180°C for the period of 0-100 hours. Figure 8 shows the MFI of the PA12 and SMMTNanoclay/PA12 composite. It has been observed that MFI reduces with increasing filler content of SMMTNanoclay in PA12 and with increasing heating period. With the decrease in MFI the viscosity of the composite material increases. The significant decrease in MFI observed for the powder prepared at 180°C and heat treatment time of 25 hours. Further, it has been observed that heating time also effect the MFI. New powder untreated to temperature has the lowest viscosity and highest MFI, while powder exposed to the temperatures for several hours has the higher viscosity and lower MFI.It is suggestive of the change in processing chamber temperature while fabricating the part by SLS using PA12 material and its parameters keeping rest of the parameters unaltered. The required flow pattern for sintering of material which is pre-requisite may not be achieved, if processing chamber is not modified. Further, poor densification leads to degradation of mechanical properties of composite. Thus, it is suggested that the process chamber temperature may be increased by 2-3 degree.

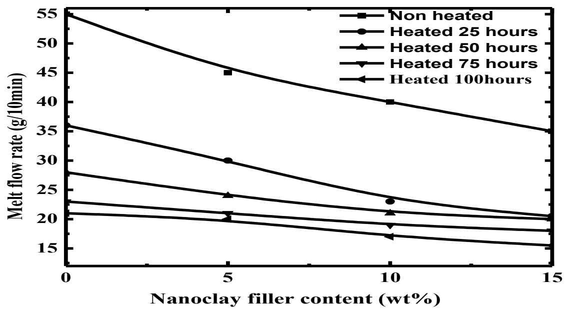


Fig. 8.Melt flow index

The mechanical properties are crucial to find out the functional values of the fabricated part with sustainability. If any part does not fulfil functional aspects of the application, it means that it may not fetch any additional value to the customer also not leads to sustainability[30-31]. The mechanical properties of composite material of SMMT Nanoclay/PA12 were firstly determined by measuring the properties of cast specimen. The tensile strength of SMMT Nanoclay/PA12 composite parts developed using the casting process is provided in Figure 9. From the figure, it has been observed that the tensile strength of the PA12 decreases with the addition of SMMT Nanoclay. Figure 10 shows the tensile modulus of SMMT Nanoclay/PA12 composites for the specimens prepared by casting process. On addition of SMMT Nanoclay in PA12, the tensile modulus decreases.

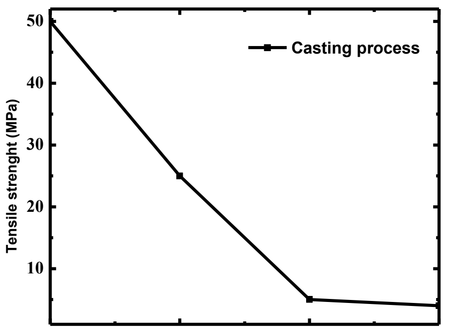


Fig. 9. Tensile strength

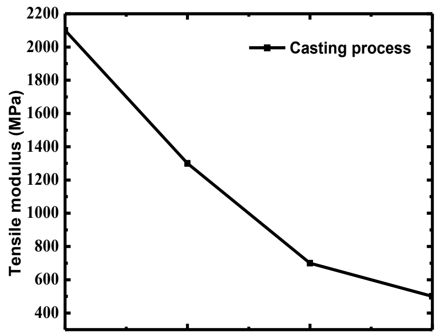


Fig. 10.Tensile modulus

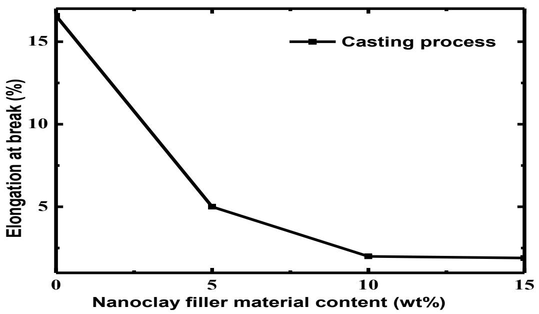


Fig. 11.Elongation at break

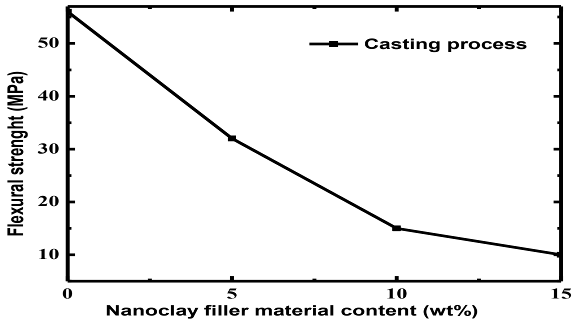


Fig. 12. Flexural strength

Figure 11 shows elongation at break (%) of SMMT Nanoclay/PA12 composite. It seems that elongation at break (%) changes significantly relative as a function of SMMT Nanoclay concentration to the PA12. This may be because of hindering caused by SMMT Nanoclay particles in the progression of polymerization and therefore reducing the length of polymer chain, as a result cast specimens become relatively brittle in nature, which has also been recommended in literature [3] while Figure 12 shows flexural strength of composite.

Figure 13 shows flexural modulus for the same composite as a function of SMMT Nanoclay wt%. Both the flexural strength and modulus decreases linearly with addition of Nanoclay in PA12 up to 10wt% but increasing filler loading after 10wt% it decreases drastically because of being more brittle in nature. Figure 14 shows compressive strength of SMMT Nanoclay /PA12 composite and Figure 15 shows impact strength of SMMT Nanoclay/PA12 composite**.** Due to brittle nature of Nanoclay composite similar results have been also observed for compressive and impact strength of material. From these figures, it has been observed that the mechanical properties of material decreases with addition of SMMT Nanoclay in PA12 base composite specimens prepared by casting process. The intercalation of SMMT in PA12 is only better when adding less than 5wt% of SMMT in nylon and it is expected that addition of lower wt% (2-4wt %) of SMMT Nanoclay may give better mechanical properties [23].

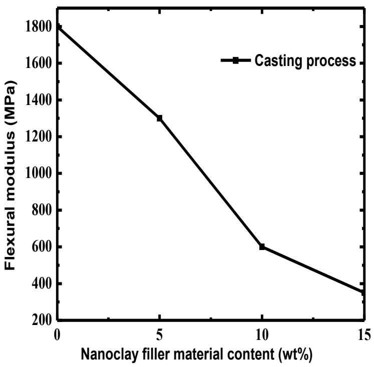


Fig. 13. Flexural modulus

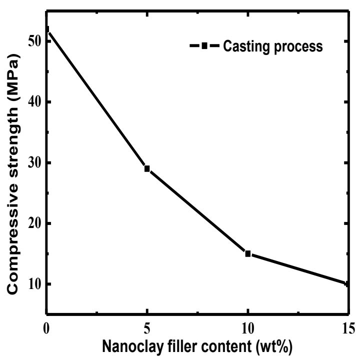


Fig. 14. Compressive strength

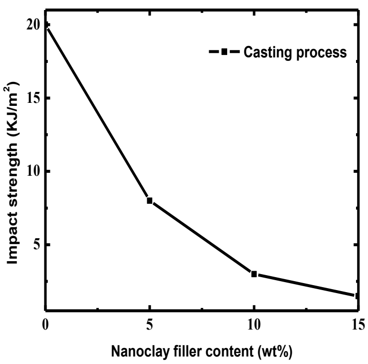
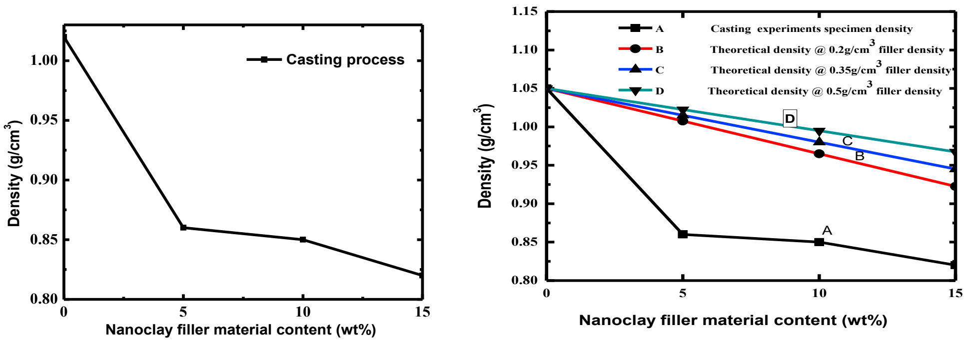


Fig. 15. Impact strength

The density of Nanoclay (0.2-0.5 g/cm^3) is lower than PA12 (1.05 g/cm^3). The loading of SMMT Nanoclay filler content in PA12 show that, density decreases with respect to increasing filler content. The property of low density with considerable strength makes SMMT/PA12 composite more viable for various applications. Figure 16 shows the effect of SMMT Nanoclay filler loading on the density of composite material for casting process.

The fire retardant property is also an important measure to predict the functional value and product sustainability in various applications like, aerospace, electronics items, and household items. The loading of SMMT Nanoclay filler content in PA12 shows significant improvement in fire retardant capability of PA12 in comparison to neat PA12. Flammability grade value with respect to Nanoclay wt (%) in PA12 is shown in Table 3.The experiment result shows that only significant improvement in fire retardant property of composite is achieved at 15wt% addition of SMMT Nanoclay in the PA12 (V1 grade).



(a) Casting Experiments measured (b) Comparison of theoretical and experimental

Fig. 16. Density of SMMT Nanoclay/PA12 composite.

Table 3. Flammability grade value with respect to Nanoclay wt (%) in PA12.

Sr. No	wt% of Nanoclay	Flammability Grade
1	0	V2
2	5	V2
3	10	V2
4	15	V1

Figure 17 shows the PA12 material properties comparison between specimens fabricated by SLS process [23] and prepared by casting process. Figure 18 shows PA12/Nanoclay 5wt% material properties comparison for SLS process [23] and Casting process fabricated specimens. From figure 17 it has been observed that the young modulus of neat PA12 is better as comparison to SLS process where as elongation at break (%) and ultimate tensile strength for casting process is closed with SLS process results and lies in between SLS process maximum value and minimum value. The result reported in figure 18 for the mixture of 5wt% SMMT Nanoclay and PA12 shows that young modulus is obtained improved by casting process as comparison to SLS process where as elongation at break (%) and ultimate tensile strength for casting process is closed with SLS process results and lies in between SLS process maximum value and minimum value.

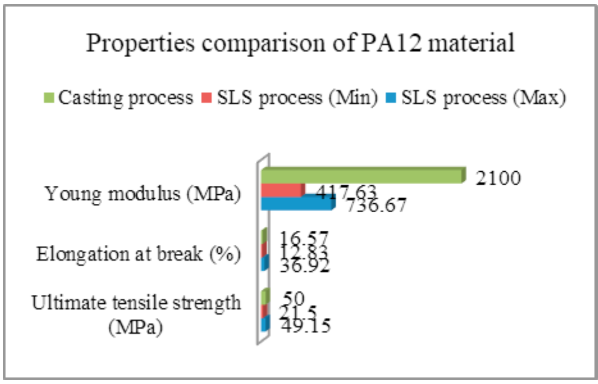


Fig. 17. PA12 material properties comparison between specimens fabricated by SLS process [23] and prepared by casting process.

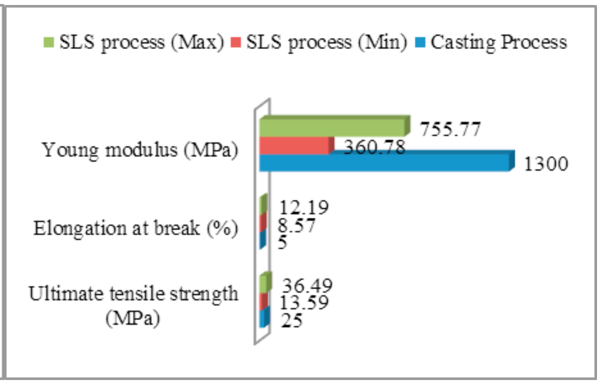


Fig. 18. PA12/Nanoclay5wt% material properties comparison for SLS process [23] and Casting process fabricated specimens.

4. Conclusions

SMMT Nanoclay is used to reinforce PA12 cast parts. From SEM results it is depicted that the SMMT Nanoclay/PA12 powder has a smaller average particle size and a narrower particle size distribution. XRD results confirm that the interlayer spacing of the SMMT Nanoclay is enlarged in the preparation process of the composite powder, representing that PA12 material molecular chains intercalate the SMMT Nanoclay layers, and SEM micrograph shows that the SMMT Nanoclay is homogeneously dispersed in the PA12 matrix. The material DSC analysis shows that the SMMT Nanoclay has small effect on melting temperature of PA12 material but addition of SMMT Nanoclay in PA12 causes to decreases melting enthalpy, relative crystalline content and crystallization temperature of composite materials. Tensile strength, tensile modulus, flexural strength, flexural modulus, elongation at break, compressive strength and impact strength of the cast specimens made from SMMT Nanoclay/PA12 composite powder are less than those of PA12 cast specimens in greater (more than 5 wt%) concentration of SMMT Nanoclay. By addition of SMMT Nanoclay in PA12, flame retardant property is improved as comparison to virgin PA12. Tensile strength, tensile modulus and elongation at break (%) of the cast specimens made from PA12 and of 5wt% SMMT Nanoclay/PA12 composite powder is perfectly matching with the result of SLS process made specimens. Intercalation of SMMT Nanoclay in PA12 is good in less than 10wt%. It is expected that better properties can be achieved by addition of less than 5wt% SMMT Nanoclay in PA12 with using SMMT Nanoclay particle size less than 100 nm.

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