



Open  
Access

## Thermal Properties of Polycaprolactone (PCL) Reinforced Montmorillonite (MMT) and Hydroxyapatite (HA) as an Alternate of FDM Composite Filament

Reazul Haq Abdul Haq<sup>1,\*</sup>, Mohd Nasrull Abdol Rahman<sup>1</sup>, Ahmad Mubarak Tajul Arifin<sup>1</sup>, Mohd Fahrul Hassan<sup>1</sup>, Ishkrizat Taib<sup>1</sup>, Mat Uzir Wahit<sup>2</sup>

<sup>1</sup> Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Malaysia, 86400 Batu Pahat, Johor, Malaysia

<sup>2</sup> Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

### ARTICLE INFO

#### Article history:

Received 3 May 2019

Received in revised form 24 August 2019

Accepted 22 September 2019

Available online 24 October 2019

### ABSTRACT

Most of medical parts today are still made by conventional method such as machining and injection moulding which is not economical because it involves in fabricating a mould. With Additive manufacturing (AM) technique all these problems can be overcome as there no needs of mould fabrication and more towards customize medical parts as long as the feeding material are suitable. In this study, thermal properties of polymer nanocomposites filament wire for Fused Deposition Modelling (FDM) was investigated. The Polycaprolactone (PCL) filled with montmorillonite (MMT) and Hydroxyapatite (HA) composites were prepared by melting and compounding using a single screw extruder. The montmorillonite was ranging from 2 to 4 wt% meanwhile hydroxyapatite was fixed at 10 wt%. The thermal properties were studied via differential scanning calorimetry (DSC) and thermogravimetric analyser (TGA). As for the result of Differential scanning calorimeter (DSC) it shows that the addition of MMT shows a minor increment in the melting temperature ( $T_m$ ), heat of fusion ( $\Delta H_f$ ) and degree of crystallinity ( $\chi_c$ ) of PCL/MMT composites compare to pure PCL polymer. On the other hand, the incorporation of HA shows no difference or changes in  $T_m$  of PCL/MMT/HA composites. As for the Thermogravimetric analysis in general, the initial decomposition temperature,  $T_{10\%}$  increased with the increasing of MMT content where the highest temperature recorded for P9M4 is 321.7°C. The same pattern of result is found for the peak decomposition temperature,  $T_p$  as the temperature also increased as the amount of MMT is increased. The remaining char residue weight,  $W_T$  increased as the amount of filler content in the PCL is increased. It can be conclude that the addition of MMT and HA enhanced the thermal stability and the decomposition temperature of the PCL/MMT/HA.

#### Keywords:

PCL; MMT; HA; Thermal; Additive  
Manufacturing; FDM

Copyright © 2019 PENERBIT AKADEMIABARU - All rights reserved

\* Corresponding author.

E-mail address: [reazul@uthm.edu.my](mailto:reazul@uthm.edu.my) (Reazul Haq Abdul Haq)

## 1. Introduction

Fused deposition modelling (FDM) has become a widely used additive manufacturing technology for various applications in engineering. The uniqueness of FDM technique is more economical for small to medium size parts in the shortest lead time. FDM has progressed one step further from fabricating a prototype to a fully functional product. One of the key industries that shows a huge impact in emerging of this technology are medical industries [1-2]. The strongest reason is because of the ease in which 3D medical imaging data can be converted into solid objects. In this way the objects or product can be customized to suit the needs of an individual patient. This eventually led to a reduction in cost of production of an implant and other medical instruments which significantly reduce the cost that have to be charged over most of the patients.

There are a lot of different types of biocompatible polymers nowadays that have been investigated by most of the researcher associate with FDM and one of the most famous biopolymer is Polycaprolactone (PCL) [2]. As the material development effort progresses by time, composites approaches come into action to continue to improve the properties whilst maintaining material characteristics required for producing products [3]. The key 3 development for direct manufacturing of parts from FDM has been the incorporation of additives to polymer matrix material to enhance the mechanical properties of the resulting parts. PNCs have emerged as materials which can show significantly enhanced mechanical properties over those of the base polymer through the addition of relatively small amounts of nano-scale additives. Improvements in strength and modulus of 40-70% have been reported to have arisen as a result of the addition of 2-5wt% of nano clay [4].

A part from that, material currently available and being investigated by researchers for FDM is only biocompatible, which can only adapt in the human body without regenerating the tissues. Much attention has been paid towards the development of polymer composites with hydroxyapatite (HA) as bioactive material in bone tissue engineering [4, 5]. Applying of HA filler particles to form composites has been shown to enhance bone-bonding rates. The emerging interest of using HA is due to its chemical and structural similarity with natural bone mineral. Due to its bioactive traits, HA has the ability to integrate into bone structures and support bone growth. The addition of Ca-P ceramic to the polymer makes a composite bone analogue and improves the bone bonding behaviour of unfilled polymers [6].

Thus it is important to study the behaviour of PCL polymer blends with nano-filler and HA especially its thermal properties as the process of FDM involves extrusions of composite. This process melts the composite into semi molten solid as it flows through a fine nozzle in order to fabricate products.

## 2. Methodology

### 2.1 Materials

The biodegradable used in this studies was polycaprolactone, medical grade of BGH600C in a pellets form supplied by Shenzhen BrightChina Industrial Co, China. Type of MMT used in this research is Nanomer I.34TCN (modified montmorillonite) nanoclay in a powder form supplied by Nanocor Inc, America. It is specifically designed for extrusion compounding (Table 1). The mineral and resin form a near-molecular blend with enhanced mechanical properties, especially in the area of heat distortion. Hydroxyapatite (HA Fluka,  $3.16 \text{ kg/cm}^3$ ) was purchased from Sigma Aldrich. The specific surface area of the powder, measured by N<sub>2</sub> absorption (according to the Brunauer-Emmet-Teller) method was found to be  $33.05 \text{ m}^2/\text{g}$ , and the particle size is 57.5 nm.

**Table 1**  
Blend formulation of PCL with MMT and HA

Designation	PCL (wt%)	HA(wt%)	MMT (wt%)
P100	100	0	0
P9M2	97	0	2
P9M3	97	0	3
P9M4	94	0	4
P8M2HA10	92	10	2
P8M3HA10	90	10	3
P8M4HA10	88	10	4

## 2.2 Sample Preparation

The PCL which is in resin form are mixed manually with MMT powder and also HA powder. These uniformly dry-mixed batches are melt-blended in a single screw extruder nanomixer (L/D = 26) with a screw speed of 40rpm as in Figure 1. The temperature profile of the extruder is set at 100, 110, 120 and 120°C at the fed zone, metering zone and die, respectively. The extruded blends are cooled in a water bath and subsequently, fed to a pelletizer.



**Fig. 1.** Single screw extruder with special design nano-mixer

## 2.3 Differential Scanning Calorimeter (DSC)

The melting and crystallization behavior testing of the individual components of the nanocomposites are carried out using a Perkin-Elmer DSC 7 instrument. DSC measurements is to determine the melting temperature ( $T_m$ ), heat of fusion ( $\Delta H^o_f$ ) and the degree of crystallinity ( $\chi$ ) in each sample from the cooling and second heating thermograms. Samples of about 5mg are analyzed at heating and cooling rates of 10°C/min under a nitrogen flow of 30mL/min in the temperature range between 0°C and 100°C. The samples are first heat up to 100°C (first scan), held at this temperature for 1min, cooled down to 0°C, and then re-heated (second scan). The enthalpy of 100% crystalline PCL ( $\Delta H^o_f$ ) is estimated to be 139 J/g [7]. The degrees of crystallinity are calculated by the following Eq. (1).  $\Delta H_f$  is the enthalpy of the samples.

$$\chi = \left[ \frac{\Delta H_f}{\Delta H^o_f} \right] \times 100\% \quad (1)$$

Thermogravimetric analysis is one of the techniques most frequently used to study the primary decomposition reactions involving solids, and has been widely used to study the thermal

decomposition of polymers. Generally, thermal stability of each component of the composite is different. In the present work the study of the thermal degradation of PCL and the influence of the addition of fillers has been carried out by comparison of thermal behavior of the pure polymer. First, thermal behavior of individual components of the nanocomposite are measured followed with the PCL composite. The actual MMT and HA content (wt%) in the composite are measured by TGA, which give a weight change during heating. The analysis was conducted from ambient temperature to 600°C at a nitrogen flow rate of 20 cm<sup>3</sup>/min and a uniform heating rate of 10°C/min by using Perkin Elmer-TGA 7. In order to determine the thermal stability of the component, the following temperatures are determined.

From the TG curves as represent in Figure 2, the following data are measured

- $T_{10\%}$  temperature of initial decomposition, (°C)
- $T_p$  temperature corresponding to x% mass loss, (°C)
- $W_T$  mass loss at a given temperature T, in wt%;

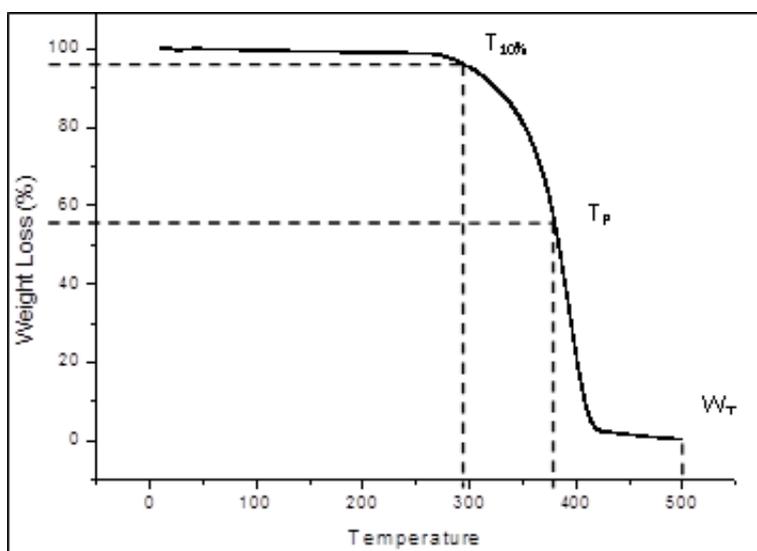


Fig. 2. Data from the thermogravimetric result

### 3. Results and Discussion

#### 3.1 Differential Scanning Calorimetry (DSC) Analysis of PCL/MMT and PCL/MMT/HA Composites

The thermal properties of PCL/MMT and PCL/MMT/HA composites are shown in Table 2. The discussion is focused on the effect of the MMT and HA fillers on melting temperature ( $T_m$ ), Heat Fusion ( $\Delta H_f$ ) and degree of crystallinity ( $\chi$ ). The endotherms obtained indicate that the thermal history may influence the degree of crystallinity of the blends, as indicated by changes in the heat of fusion and melting temperature.

The results show that the addition of MMT shows a minor increment in the  $T_m$ ,  $\Delta H_f$  and  $\chi_c$  of PCL/MMT composites compare to pure PCL polymer. The melting point of P9M4 shows the highest among all as it is increased to 62.8 °C which is almost 4°C from pure PCL. But overall there is no obvious trend or pattern found in the result which indicates that MMT shows a little significant effect. The same pattern of result is also shown by Moussaif *et al.*, [7] who reported that the incorporation of mesoporous silicate (MCM) does not significantly affect the crystallization and the melting behavior of the PCL. There are more studies that reported the same pattern of result on the melting point PCL using various clays [8-10].

**Table 2**

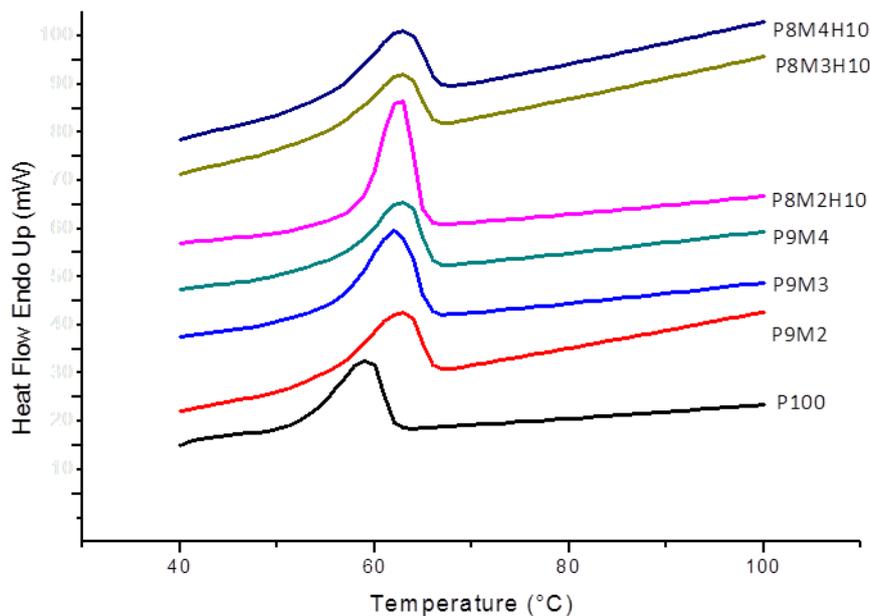
The melting temperature, heat fusion and degree of crystallinity for PCL/MMT and PCL/MMT/HA

Designation	Melting Point Temperature, $T_m$ (°C)	Heat Fusion, $\Delta H_f$ (J/g)	Crystallinity, $\chi$ (%)
P100	58.7	69.9	50.1
P9M2	62.7	73.3	53.6
P9M3	61.9	70.6	52.2
P9M4	62.8	75.5	56.4
P8M2H10	62.5	65.2	53.1
P8M3H10	62.5	68.4	56.4
P8M4H10	62.5	71.1	59.2

The same trend of result is found in the degree of crystallinity,  $\chi$  as it increases in all loading of MMT and P9M4 again shows the highest value. The previous work of Way *et al.*, [11] indicated that an increase in crystallinity or increase in spherulite size increases the modulus. Significant increase in crystallinity is most likely due to higher nucleation density that induces the clay nanoparticles [12].

Inclusion of MMT with a better dispersion in PCL matrix may provide more nucleation sites to incorporate surrounding the polymers and facilitates the crystallization process. According to Fornes & Paul, [13], the organoclay layers may act as nucleation sites, which subsequently results in higher  $\chi_c$  for composites. The results are consistent the introduction of minute particles into the polymer melt would enhance the nucleation of crystallites in the polymer upon cooling and hence improved the crystallinity of the polymer after cooling [23]. The presence of MMT layers, facilitates the rearrangement of polymer chains during crystallization, hence increased the crystallinity. A similar observation was also reported by Min *et al.*, [14] who studied on the crystallinity and mechanical properties of HDPE/MMT nanocomposite.

On the other hand, the incorporation of HA shows no difference or changes in  $T_m$  of PCL/MMT/HA composites. The melting temperatures are almost the same for all composition. A reverse of trend found in the percentages of crystallinity as it increases. P9M4H10 give the highest value as it marked at 59.28%, which is almost 10% from pure PCL (Figure 3).



**Fig. 3.** The heating curve of PCL/MMT and PCL/MMT/HA composites

The  $T_m$  is known dependence on the lamellar thickness and  $\chi$ . Thus, the lower  $T_m$  is believed to be attributed to thinner lamellar formation as a consequence of faster cooling process. This is in agreement with findings claimed by Lim *et al.*, [15]. The trend of  $T_m$  is consistent with data obtained for  $\chi$  of the composites. The influence of HA on the crystallization kinetics of the matrix is believed to contribute to the results obtained. At this composition, HA acts as an effective nucleating agent of polymer matrix which in turn affects the semicrystalline structure by creating dissimilarities in the semicrystalline structure.

However, further introducing of HA filler compensate the polymer matrix therefore decrease the  $\chi$  of the composites, indicating that the incorporation of the high amount of HA hinders the polymer macromolecules to rearrange regularly to form crystals. It is because increasing of HA particles in the matrix contributes to the higher melt viscosity and therefore retards the crystal formation. This factor is believed to influence the trend observed and the similar reason was also claimed by Zhang *et al.*, [16]. The trend of the results obtained is expected as generally, the  $\Delta H_f$  is proportional to the results of  $\chi$ . In addition, the  $\Delta H_f$  results follow the theory, where the higher the crystallization process, the lower will be the  $\Delta H_f$ .

### 3.2 Thermogravimetric (TG) Analysis of PCL/MMT and PCL/MMT/HA Composites

Thermogravimetric (TG) analysis was carried out to evaluate the effect of blends composition on the thermal stability of the polymers. The weight loss due to the formation of volatile products after degradation at high temperature is monitored as a function of temperature (and/or time). When heating occurs under an inert gas flow, a non-oxidative degradation occurs, while the use of air or oxygen allows oxidative degradation of the samples.

The TG curves of PCL/MMT and PCL/MMT/HA composites are shown in Figure 4(a) and (b) the summary of the thermal degradations results is shown in Table 3. The initial thermal stability is characterized by temperatures at 10% weight loss, which is  $T_{10\%}$ .

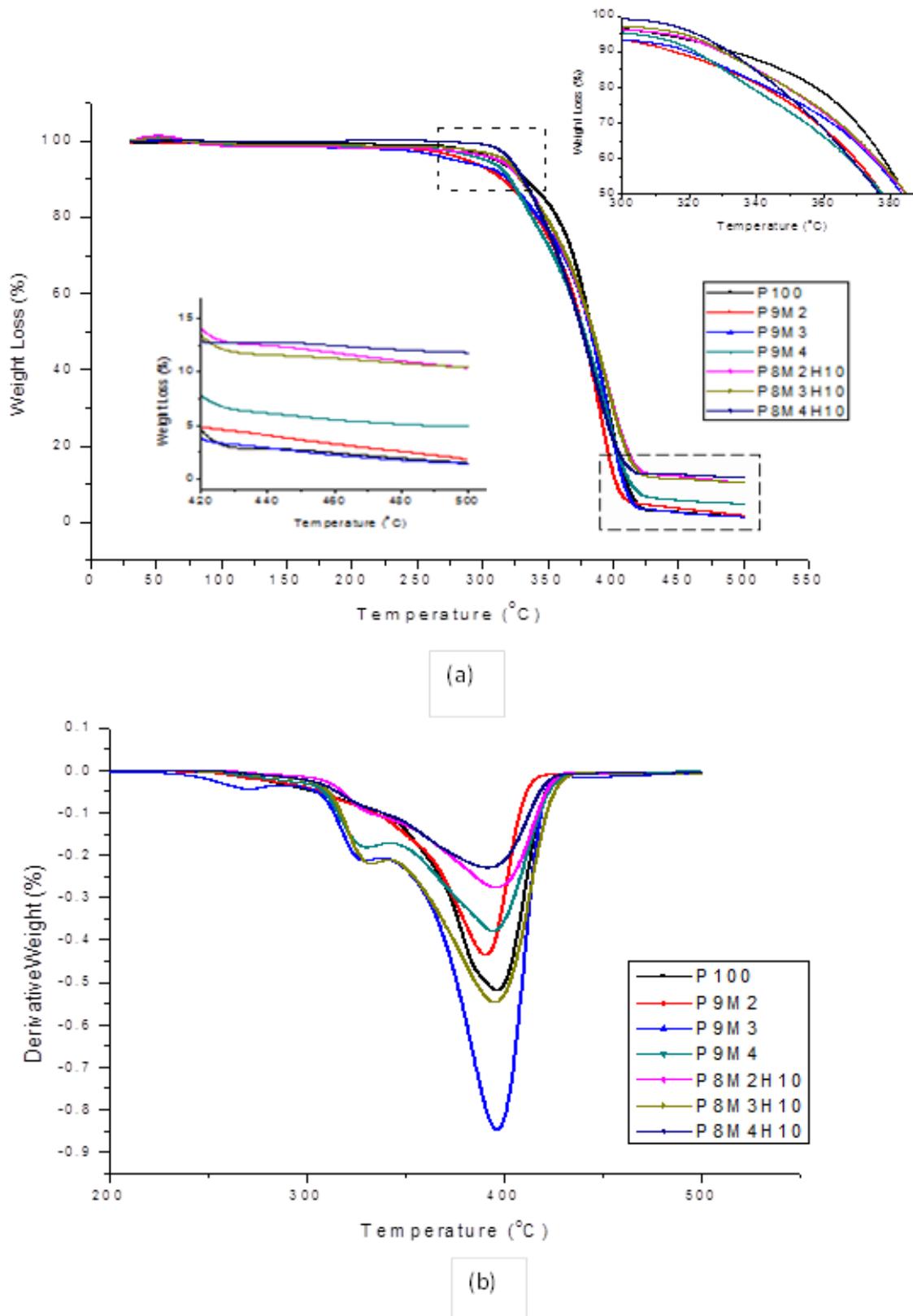
Generally, the incorporation of clay into the polymer matrix was found to enhance thermal stability by acting as a superior insulator and mass transport barriers to the volatile products generated during decomposition, as well as by assisting in the formation of char after thermal decomposition. Vyazovkin *et al.*, [17] who studied PS nanocomposite observed that the virgin polymer degrades without forming any residue, whereas the nanocomposite leaves some residue.

In general, the  $T_{10\%}$  increased with the increasing of MMT content. By increasing the MMT content from 2% to 4 %, the  $T_{10\%}$  shifts to higher values for about 20 °C. The initial decomposition temperature for P9M2 is increased from 310.6°C to 315.6°C. As the amount of MMT content is increased to 3%, the initial decomposition temperature also increased to 319.9°C. The value of  $T_{10\%}$  continues to increase as the amount of MMT is increased to 4% where the temperature recorded for P9M4 is 321.7°C. The presence of MMT in PCL induced better thermal stability and therefore the degradation starting temperature clearly shifted to higher temperature.

The same pattern of result is found for the  $T_p$  as the temperature also increased as the amount of MMT is increased. The peak decomposition temperature of P9M2 increased from 389.7°C to 391.1°C. The temperature continues to increase as the peak decomposition temperature for P9M3 is 396.7°C. But there is slight decreased on the  $T_p$  for P9M4 as the temperature drops to 394.5°C but it is still higher than the neat PCL.

This finding agrees with some other researcher such as Pramoda *et al.*, [18] observed that the degradation onset temperature is 12 °C higher for PA6 with 2.5% clay loading than that of virgin PA6 and that the onset temperature for the higher clay loading remained unchanged. Dutta *et al.*, [19] has studied the effect of clay concentration on the thermal stability of EVA-based nanocomposites

and found that the thermal stability of EVA-12 (12wt. % VA) increases with the introduction of o-MMT. With an increase in the o-MMT loading over 2wt. %, however, the hybrids show a decreasing trend in their initial thermal decomposition temperature.



**Fig. 4.** Thermograms (a) and derivatives thermogram (b) of PCL/MMT and PCL/MMT/HA composites

**Table 3**

The degradation temperature obtained from the TG and DTG curves for PCL/MMT and PCL/MMT/HA

Designation	Initial Decomposition Temperature, $T_{10\%}$ (°C)	Peak of Decomposition Temperature, $T_p$ (°C)	Weight of Residue (wt%)
P100	310.6	389.7	1.5
P9M2	315.6	391.1	1.9
P9M3	319.9	396.7	1.5
P9M4	321.7	394.5	4.9
P8M2H10	329.6	396.1	10.4
IP8M3H10	330.1	395.7	10.4
P8M4H10	331.8	384.6	11.8

It is also suggested that when a low clay fraction is added to the polymer, the clay disperses well and the barrier effect is predominant, but with increasing loading, the catalyzing effect rapidly increases and becomes dominant, so that the thermal stability of the nanocomposite decreases. This explains why the  $T_p$  of P9M4 decreased as the content of MMT is higher.

The weight loss profiles of PCL/MMT composites can be seen in Figure 4(a). The remaining char residue weight increased as the amount of filler content in the PCL is increased. These findings were attributed to the fact that, at low filler contents homogenous exfoliation and random dispersion of clay is achieved on a nanometer level, whereas the higher filler loading destabilizes the matrix, because of the aggregation of silicate layers. This agrees with Chen *et al.*, [20] in his worked PCL/multi-walled carbon nanotube as they found that the residual weight of 1 wt% PCL/MWNT nanocomposites is higher than that of PCL.

This was attributed to the fact that the exfoliated structure formed at low clay content is probably not enough to trigger the thermal and gas barrier properties effectively in the matrix, because of the short tortuous path formed. This result is consistent with reports claiming that optimum thermal stability is usually achieved for clay loadings between 2.5 and 5wt. %. For lower clay fractions, exfoliated morphology dominates, but this low clay content does not enable the barrier effect. At much higher clay content, on the other hand, particle agglomeration occurs. Therefore, intercalated and exfoliated structures usually coexist, which again does not allow maximization of the tortuous path.

Meanwhile by incorporating HA into the composites does actually shows an increased in the initial decomposition temperature  $T_{10\%}$  but decreased the peak decomposition temperature  $T_p$ . From the Table 3 it can be seen that the  $T_{10\%}$  for P8M2H10 is 329.6°C and it rose to 330.1°C for P8M3H10 and continues to rise until 331.8°C for P8M4H10. It shows that the thermal stability of PCL/MMT/HA is higher than the PCL/MMT. This is probably attributed from the higher thermal stability of HA which consist of two elements in HA, which is calcium (Ca) and phosphorus (P) which have a higher decomposition temperature.

The reverse pattern of result is found for the  $T_p$  for PCL/MMT/HA as the peak decomposition temperature decreased. The peak degradation temperature of P8M2H10 drops to 396.1°C. The temperature continues to decrease as the peak degradation temperature for P8M3H10 recorded is 395.7°C and continues to drop as the temperature for P8M4H10 is 384.6°C which is the lowest among all except from the neat PCL.

This may due to the agglomeration of HA particles is which is expected to reduce the degradation temperature of the composites. The agglomeration reduces the surface area available for kinetic effects and fastens the degradation reactions, thus decreasing the  $T_p$ . In a reverse case, it was proven that as the less agglomerates and better dispersion of HA particles are observed in the morphology of the composites the more thermally stable composites produced. These findings are similar to the

findings reported by Albano *et al.*, [21] who discussed in detail on the thermo degradation of HDPE/HA composites reported that the morphology of the composite strongly influenced the mechanism of the degradation process. They found that composites with the presence of agglomerates, results in less stable composites as compared to composites with more homogenous distribution of HA. They also claimed that the decomposition process is through the nucleation and nucleus growth kinetic models.

Other than that, according to Bryk [22] incorporation of filler causes a reduction in polymer chain mobility in the adsorption and boundary layers. This led to a decreased in the tension induced to the C-C chain by thermal excitation and majority of bond breakings are through this mode, thus less degradation occurs, and improved the thermal stability of the composites. Chen *et al.*, [20] agreed that HA delayed the thermal degradation of composites due to barrier effect. They claimed that the barrier effect on the decomposition is attributed to obstruction of the well-dispersed nano-HA in poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) to the permeability of the volatile degradation products out of the materials. The weight loss profiles of PCL/MMT/HA do shows that the remaining char residue weight increased as the amount of filler content in the PCL is increased.

#### 4. Conclusions

From this research, it can be concluded that by incorporation of Montmorillonite (MMT) and Hydroxyapatite (HA), the thermal properties of Polycaprolactone (PCL) are successfully enhanced. The Differential scanning calorimeter (DSC) result shows that the addition of MMT shows a minor increment in the melting temperature ( $T_m$ ), heat of fusion ( $\Delta H_f$ ) and degree of crystallinity ( $\chi_c$ ) of PCL/MMT composites compare to pure PCL polymer. However, the incorporation of HA shows no difference or changes in melting temperature of PCL/MMT/HA composites but there were increment in heat of fusion for PCL/MMT/HA composites. As for the Thermogravimetric analysis, in general, the initial decomposition temperature,  $T_{10\%}$  increased with the increasing of MMT content where the highest temperature recorded for P9M4 is 321.7°C. The same pattern of result is found for the peak decomposition temperature,  $T_p$  as the temperature also increased as the amount of MMT is increased. The remaining char residue weight  $W_T$  increased as the amount of filler content in the PCL is increased. Inclusion of HA results in significant enhancement on the degradation temperature of the composites due to the higher thermal stability of HA. Overall this study shows promising result that's helps in fabricating feeding material for FDM to produce implants or other medical applications.

#### Acknowledgement

The authors wish to thank the Universiti Tun Hussein Onn Malaysia (UTHM) for the financial support to this work.

#### References

- [1] Haq, R. H. Abdul, M. S. Wahab, and M. U. Wahid. "Fused Deposition Modeling of PCL/HA/MMT Biocompatible Polymer Nano-composites." In *Machining, Joining and Modifications of Advanced Materials*, pp. 23-32. Springer, Singapore, 2016.
- [2] Marwah, O. M. F., M. S. Shukri, E. J. Mohamad, M. A. Johar, R. H. A. Haq, and R. K. Khairuddin. "Direct Investment Casting For Pattern Developed By Desktop 3D Printer." In *MATEC Web of Conferences*, vol. 135, p. 00036. EDP Sciences, 2017.
- [3] Sa'ude, N., M. Ibrahim, M. H. I. Ibrahim, M. S. Wahab, R. Haq, O. M. F. Marwah, and R. K. Khairuddin. "Additive Manufacturing of Copper-ABS Filament by Fused Deposition Modeling (FDM)." *Journal of Mechanical Engineering* SI 5, no. 4 (2018): 23-32.

- [4] Pavlidou, S., and C. D. Papaspyrides. "A review on polymer-layered silicate nanocomposites." *Progress in polymer science* 33, no. 12 (2008): 1119-1198.
- [5] Wang, M. "Hydroxyapatite-polyethylene composites for bone substitution: effects of hydrostatic extrusion." In *Proc 11th Int Conf Composite Materials. Gold Coast, Australia, July 1997*, vol. 1, pp. 488-495. Woodhead Publishing, 1997.
- [6] Haq, Reazul Haq Abdul, Bin Wahab, Mohd Saidin, and Mat Uzir Wahit. "Impact Test and Bioactivity Properties of Polycaprolactone (PCL) by Addition of Nano-Montmorillonite (MMT) and Hydroxyapatite (HA)." In *Applied Mechanics and Materials*, vol. 446, pp. 1129-1133. Trans Tech Publications, 2014.
- [7] Pitt, C. G., F. I. Chasalow, Y. M. Hibionada, D. M. Klimas, and A. Schindler. "Aliphatic polyesters. I. The degradation of poly ( $\epsilon$ -caprolactone) in vivo." *Journal of Applied Polymer Science* 26, no. 11 (1981): 3779-3787.
- [8] Moussaif, N., C. Crespo, J. G. Meier, and M. A. Jimenez. "Synergistic reinforcement of nanoclay and mesoporous silicate fillers in polycaprolactone: the effect of nanoclay on the compatibility of the components." *Polymer* 53, no. 17 (2012): 3741-3748.
- [9] Di, Yingwei, Salvatore Iannace, Ernesto Di Maio, and Luigi Nicolais. "Nanocomposites by melt intercalation based on polycaprolactone and organoclay." *Journal of Polymer Science Part B: Polymer Physics* 41, no. 7 (2003): 670-678.
- [10] Labidi, Sami, Nathalie Azema, Didier Perrin, and José-Marie Lopez-Cuesta. "Organo-modified montmorillonite/poly ( $\epsilon$ -caprolactone) nanocomposites prepared by melt intercalation in a twin-screw extruder." *Polymer Degradation and Stability* 95, no. 3 (2010): 382-388.
- [11] Ludueña, Leandro Nicolás, J. M. Kenny, Analía Vázquez, and Vera Alejandra Alvarez. "Effect of clay organic modifier on the final performance of PCL/clay nanocomposites." *Materials Science and Engineering: A* 529 (2011): 215-223.
- [12] Way, J. L., J. R. Atkinson, and J. Nutting. "The effect of spherulite size on the fracture morphology of polypropylene." *Journal of Materials Science* 9, no. 2 (1974): 293-299.
- [13] Tanniru, M., Q. Yuan, and R. D. K. Misra. "On significant retention of impact strength in clay-reinforced high-density polyethylene (HDPE) nanocomposites." *Polymer* 47, no. 6 (2006): 2133-2146.
- [14] Fornes, T. D., and Donald R. Paul. "Crystallization behavior of nylon 6 nanocomposites." *Polymer* 44, no. 14 (2003): 3945-3961.
- [15] Min, Kyung Dae, Min Young Kim, Kil-Yeong Choi, Jae Heung Lee, and Sung-Goo Lee. "Effect of layered silicates on the crystallinity and mechanical properties of HDPE/MMT nanocomposite blown films." *Polymer Bulletin* 57, no. 1 (2006): 101-108.
- [16] Lim, K. L. K., ZA Mohd Ishak, U. S. Ishiaku, A. M. Y. Fuad, A. H. Yusof, T. Czigany, B. Pukanzsky, and D. S. Ogunniyi. "High density polyethylene/ultra high molecular weight polyethylene blend. II. Effect of hydroxyapatite on processing, thermal, and mechanical properties." *Journal of applied polymer science* 100, no. 5 (2006): 3931-3942.
- [17] Zhang, Xiang, Yubao Li, Guoyu Lv, Yi Zuo, and Yuanhua Mu. "Thermal and crystallization studies of nano-hydroxyapatite reinforced polyamide 66 biocomposites." *Polymer degradation and stability* 91, no. 5 (2006): 1202-1207.
- [18] Vyazovkin, Sergey, Ion Dranca, Xiaowu Fan, and Rigoberto Advincula. "Kinetics of the thermal and thermo-oxidative degradation of a polystyrene-clay nanocomposite." *Macromolecular rapid communications* 25, no. 3 (2004): 498-503.
- [19] Pramoda, K. P., Tianxi Liu, Zhehui Liu, Chaobin He, and Hung-Jue Sue. "Thermal degradation behavior of polyamide 6/clay nanocomposites." *Polymer degradation and Stability* 81, no. 1 (2003): 47-56.
- [20] Chen, D. Z., C. Y. Tang, K. C. Chan, C. P. Tsui, H. F. Peter, Mason CP Leung, and P. S. Uskokovic. "Dynamic mechanical properties and in vitro bioactivity of PHBHV/HA nanocomposite." *Composites Science and Technology* 67, no. 7-8 (2007): 1617-1626.
- [21] Albano, C., R. Perera, L. Cataño, S. Alvarez, A. Karam, and G. González. "Compatibilization of polyolefin/hydroxyapatite composites using grafted polymers." *Polymer-Plastics Technology and Engineering* 49, no. 4 (2010): 341-346.
- [22] Bryk, Mikhail Teodorovich. *Degradation of filled polymers: high temperature and thermo-oxidative processes*. Ellis Horwood Ltd, 1991.
- [23] Dzun N. Jimat., Faridah Ariffin., Maimunah Asem, and Sarina Sulaiman. "Characterization of Biodegradable composite based on polycaprolactone/starch reinforced with sugarcane bagasse microfibrillated cellulose." *Journal of Advanced Research in Materials Science* 39, no. 1 (2017): 32-39.