Effect of HNT on mechanical and thermal properties of poly(lactic acid)/polypropylene carbonate blends*)

Intan Najwa Humaira Mohamed Haneef[1)] (ORCHID ID: 0000-0003-0516-4525),
Yose Fachmi Buys[2), 3), **)] (0000-0002-4596-751X), Norhashimah Mohd Shaffiar[1)] (0000-0001-7835-8764),
Sharifah Imihezri Syed Shaharuddin[1)] (0000-0002-0333-5346), Abdul Malek Abdul Hamid[1)] (0000-0002-9929-2597),
Mohd Faizul Mohd Sabri[2)] (0000-0001-8096-2709), Amalina Muhammad Afifi[2)] (0000-0003-3964-0171)

Abstract: In this work, the influence of halloysite nanotubes (HNTs) on the mechanical and thermal properties of the poly(lactic acid)/polypropylene carbonate (PLA/PPC 70/30) blend was studied. The HNT was incorporated into the PLA/PPC blend by melt mixing. It was found that addition of 2–6 wt % HNT successfully improved the tensile and flexural strength as well as the flexural and Young's moduli of PLA/PPC blend, due to the reinforcing effect. Although the elongation at break decreases with increasing HNT content, its value is much higher than that of pure PLA. Moreover, the addition of HNT did not affect the miscibility of PLA and PPC, since two glass transition temperatures were observed in the DSC thermograms. However, a higher content of HNT may improve the compatibility between PLA and PPC as evidenced by the lower difference between the glass transition temperature of PPC and PLA and reduced crystallinity resulting in higher tensile strength of nanocomposites.

Keywords: PLA, PPC, HNT, mechanical properties, thermal properties.

Wpływ HNT na właściwości mechaniczne i termiczne mieszaniny poli(kwas mlekowy)/węglan polipropylenu

Streszczenie: W pracy zbadano wpływ nanorurek haloizytowych (HNTs) na właściwości mechaniczne i termiczne mieszaniny poli(kwas mlekowy)/węglan polipropylenu (PLA/PPC 70/30). HNT wprowadzono do PLA/PPC poprzez mieszanie w stanie stopionym. Stwierdzono, że dodatek 2–6% mas. HNT skutecznie poprawił wytrzymałość na rozciąganie i zginanie, a także moduł sprężystości przy zginaniu i moduł Younga mieszaniny PLA/PPC, jako efekt wzmacniający. Pomimo, że wydłużenie przy zerwaniu zmniejsza się wraz ze wzrostem zawartości HNT, to jego wartość jest znacznie większa niż w przypadku czystego PLA. Nie stwierdzono wpływu HNT na mieszalność PLA i PPC, ponieważ na termogramach DSC zaobserwowano dwie temperatury zeszklenia. Jednak większa zawartość HNT może poprawić mieszalność PLA i PPC, o czym świadczy mniejsza różnica między temperaturą zeszklenia PPC i PLA oraz mniejszy stopień krystaliczności, co skutkuje większą wytrzymałościa na rozciaganie nanokompozytów.

Słowa kluczowe: PLA, PPC, HNT, właściwości mechaniczne, właściwości termiczne.

Poly(lactic acid) (PLA) has rapidly become a subject of interest in various areas such as packaging [1] and biomedical applications [2]. It offers biodegradability, biocompatibility, processability, and is eco-friendly compared to other polymers, available in the industry [3]. It also possesses other unique characteristics, such as excellent transparency, high mechanical strength, it is less harmful, and has an excellent barrier properties [4]. PLA,

thanks to its biodegradability, is a promising replacement for the non-degradable engineering polymers such as polyethylene terephthalate (PET) [5].

Malinconico et al. reported many PLA interests in textile, agriculture, packaging, medical and pharmaceutical industry [6]. However, PLA has some disadvantages, and one of its significant problems is a lack of toughness. According to Farah et al., although the mechanical strength of PLA is equal to PET, it has a very low elongation of less than 10 % [7]. Furthermore, its brittle characteristic is one of the problems that hinder PLA in areas that require a flexible application at a higher stress level. Cakir et al. suggested the using of an additive to decrease its brittleness [8].

Works on diminishing of PLA brittleness have been issued for a couple of years, and it appears to be still an area of active research [9-12]. Recently, the authors have restricted the brittleness of PLA with polypropylene carbonate (PPC) [13, 14]. As a result, the elongation of neat PLA was greatly enhanced with the addition of 30 wt % PPC. However, there is a significant decrease in the tensile strength. This problem is not a new one and has been partly addressed by the previous study by Zou et al. [15]. Hence, maintaining the balance between high tensile strength and high elongation of PLA blends/composites is a difficult task.

Some researchers have suggested a few ways on maintaining a balance between tensile strength and elongation of the PLA/PPC blends, such as the addition of compatibilizer [16-19] and nanoparticles such as coreshell starch [20] and multi-walled carbon nanotubes (MWCNT) [21, 22]. For example, Sun et al. used a compatibilizer in PLA/PPC blends and successfully noted the improvement in mechanical properties [16]. Meanwhile, Yao et al. found that the addition of maleic anhydride (MA) to PLA / PPC blends significantly improved their elongation without losing tensile strength [18].

Halloysite nanotubes (HNT) have recently become a prevalent subject of research [23–25]. It consists of a tubular size varying from 500–1000 nm in length and 15–100 nm in inner diameter. HNT is considered to be the most suitable reinforcing agent compared to other nanotubes because it is biocompatible to the human body [26]. Furthermore, many researchers have proved that HNT could improve the mechanical properties of other polymers such as polycaprolactone/polylactic acid, polyethylene terephthalate/ polypropylene nanocomposites, polyetherimide/silicone rubber, and other PLA nanocomposites [27–30]. For example, Kelnar et al. enhanced the blends' tensile strength at a relatively low content of HNT [27].

Hence, the authors believe that adding HNT to PLA/PPC blends can improve their mechanical properties.To the best of the authors knowledge, no systematic study of PLA/PPC/HNT nanocomposite has been reported yet. Therefore, HNT was used as a reinforcing agent for PLA/PPC 70/30 blend in order to improve the mechanical properties.The effect of HNT content on the mechanical and thermal properties of PLA/PPC/HNT nanocomposites was investigated and critically discussed in this report.

EXPERIMENTAL PART

Materials and preparation of samples

PLA grade 3052D with a molecular weight of 116,000 g/mol was purchased from Nature Works, LLC (USA). PPC with a grade of QPAC 40 and molecular weight of approximately 100,000 – 300,000 g/mol was obtained from Empower Materials, LLC (USA). HNT grade NN-HNT200 with a length range between 500 nm to over 1.2 µm was obtained from Natural Nano, Inc (USA).

PLA is still in its continuous phase when it is melt mixed with less than 30 wt % of PPC [18]. Since this research aims to obtain PLA nanocomposites with balance in mechanical properties, a 70/30 PLA/PPC blend was selected in this study to be incorporated with HNTs. Before blending, PLA and HNTs were dried at 70°C while PPC was dried at 40°C in an oven for at least 24 hours to remove moisture. A specific amount of HNT (2, 4, and 6 wt %) was incorporated into PLA/PPC 70/30 blend at 180°C at a rotation of 50 rpm for 10 minutes using an internal mixer (Haake Polylab System Thermo). After blending, the PLA/PPC/HNT nanocomposites were crushed into smaller pieces using a crusher machine model HITOP, M SY-20. The samples for testing mechanical properties were obtained by compression molding at 185°C using the hot- press machine. The pre-heat time was 7 minutes and a pressing time 3 minutes.

Methods

The tensile mechanical properties of PLA/PPC/HNT nanocomposites were investigated according to ASTM D638 standards. Samples were tested at a 5 mm/min crosshead speed using the Universal Testing Machine model PFG5K (Shimadzu Instrument, Japan). At least five samples of each composition were tested, and average results were reported.

The flexural properties were conducted at a crosshead speed of 5 mm/min according to ASTM D790 using the universal testing machine, model PFG5K from Shimadzu Instrument. The test was conducted to find the samples' flexural strength and flexural modulus with a 3 points bending method. At least five specimens with a dimension of $3.2 \times 12.7 \times 125$ mm were tested, and the average results were calculated.

The impact strength was performed using the Charpy impact test machine (Dynisco Polymer test) with the power of the pendulum set to 75 J at room temperature according to ASTM D256. The notches on each specimen were made using a notch cutter before testing.

The thermal properties were conducted using the differential scanning calorimetry (DSC) machine model Mettler Toledo with a 20 ml/min nitrogen flow rate. The samples were dried at 60°C for 24 h before testing. The specimens weighed between 8 and 12 mg were crimped in the aluminum crucible with an empty crimped aluminum pan used as the reference. The samples were heated from 20°C to 220°C at a rate of 30°C/min to remove the thermal history and then held isothermally for 10 min. Next, the samples were cooled down to -30°C at a rate of 30°C/min. Finally, the samples were heated again from -30°C to 220°C at a rate of 10°C/min. The crystallinity, glass transition temperature and melting temperature of each sample were recorded and analyzed. The crystallinity X_c of the samples were calculated based on Equation 1 [31, 32].

$$X_c = \frac{\Delta H_m^\circ}{(1-\omega_t)\Delta H_m^\circ} \cdot 100 \qquad (1)$$

where: ΔH_m° stands for the theoretical specific melting heat of 100% crystalline sample and ω_t represents the weight fraction of added HNTs. For PLA, ΔH_m° value was taken as 93 J/g [33, 34].

RESULTS AND DISCUSSION

Tensile properies

Figure 1 illustrates the tensile strength and Young's modulus of PLA/PPC 70/30 blend with different HNTs content. As shown in Fig. 1, the tensile strength of PLA/PPC blend is 32 MPa with Young's modulus 1.26 GPa. The tensile strength and Young's modulus of PLA/PPC/HNTs nanocomposites increase with increasing HNTs content to 4 wt %. However, a further increase in the HNT content causes a visible decrease in the tensile strength from 41 to 37 MPa. Simultaneously, Young's modulus also significantly decreases from 1.42 to 1.36 GPa. However, both values are still higher compare to the blend without HNT.
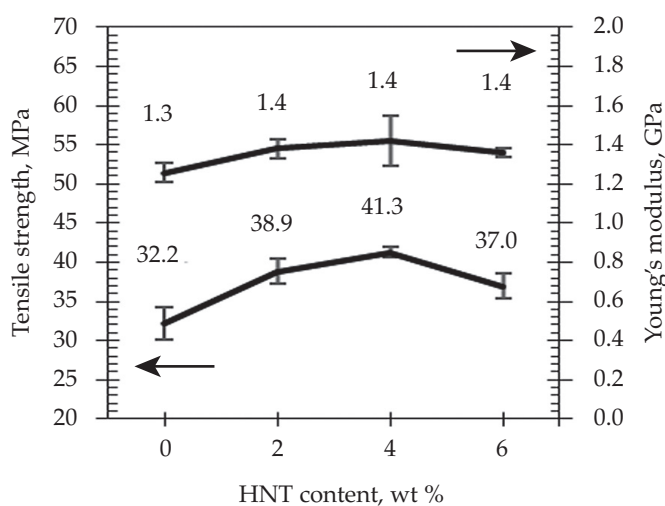

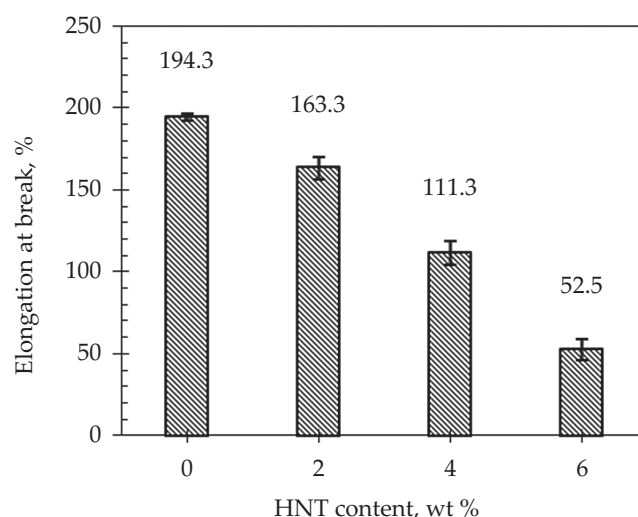**Fig. 1 Tensile strength and Young's modulus of PLA/PPC 70/30 blend with different HNT content**

Fig. 2. Elongation at break of PLA/PPC blend with different HNT content

Contrary to the tensile strength and Young's modulus of PLA/PPC/HNT nanocomposites shown in Figure 1, the elongation at break gradually decreases with increasing HNT's content (Fig. 2). However, the elongation of the composites is much higher than the neat PLA. This behavior was expected because HNT acts as a reinforcing agent and improves the PLA/PPC's stiffness, resulting in a lower elongation at break. A significant decrease in elongation (about 73%) was observed at 6 wt % HNT content, which can be explained by nanofiller agglomeration, as reported by Eryildiz *et al*. [35].

Figure 3 illustrates the stress-strain curves of the nanocomposites. The PLA/PPC blend has the lowest tensile strength of 32 MPa with the highest elongation at break of around 190%. The tensile strength increases to 39 MPa with the incorporation of 4 wt % HNT. The elongation at break, however, gradually decreases with the increase of HNT. Nevertheless, the decrease of elongation at break does not affect the mechanical properties since the value is still much higher than neat PLA reported in previous research [13].

Flexural properties

Figure 4 represents the flexural strength and flexural modulus of PLA/PPC blend with different amounts of HNT. Initially, the flexural modulus decreases from 1.70 to 1.46 GPa when 2 wt % of HNT is added. However, when the HNT content increases to 4 wt %, the flexural modulus increases to 1.76 GPa. On the other hand, the flexural strength increases steadily from 48 to 55 MPa as the amount of HNT increases to 4 wt %. However, there is a slight decrease in flexural strength and flexural modulus from 55 MPa and 1.76 GPa to 54 MPa and 1.74 GPa as the HNT increases from 4 to 6 wt %. It should be emphasized that the values are still much higher compared to the PLA/PPC blend.
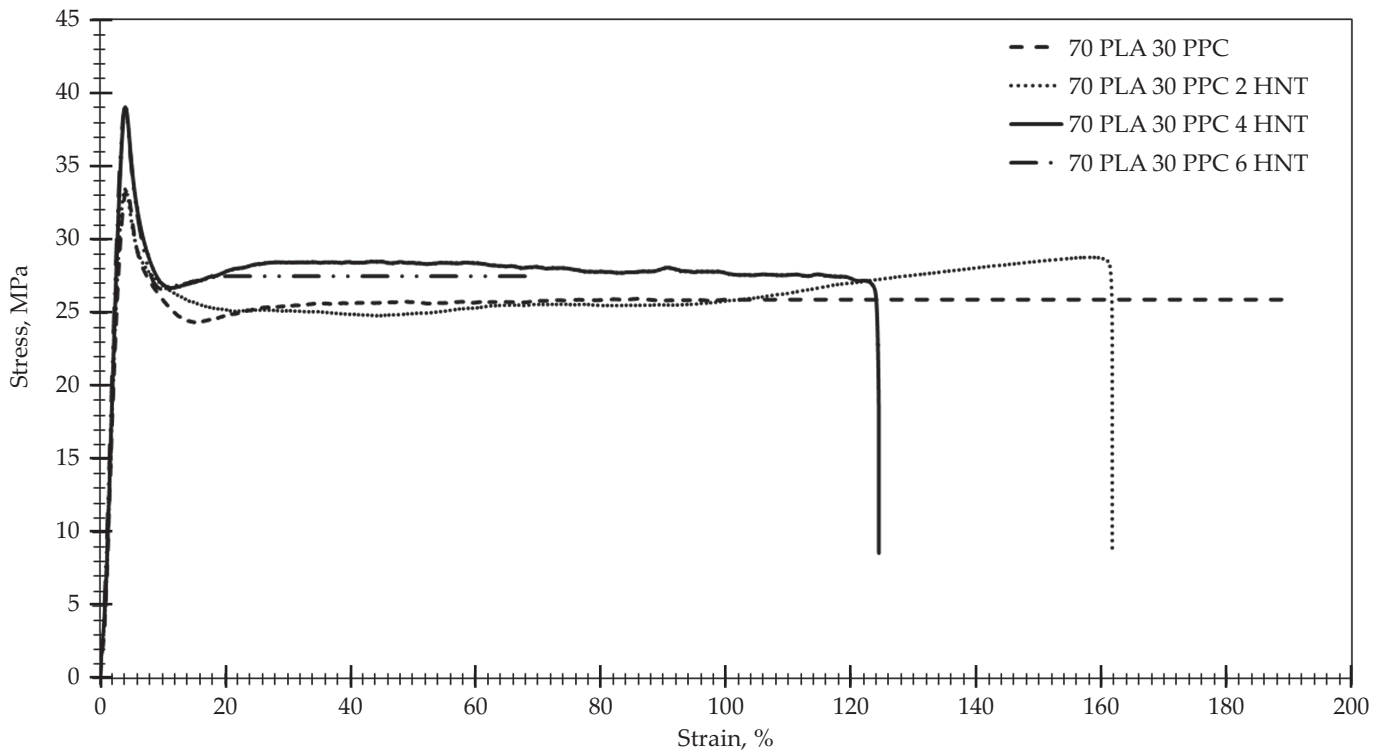
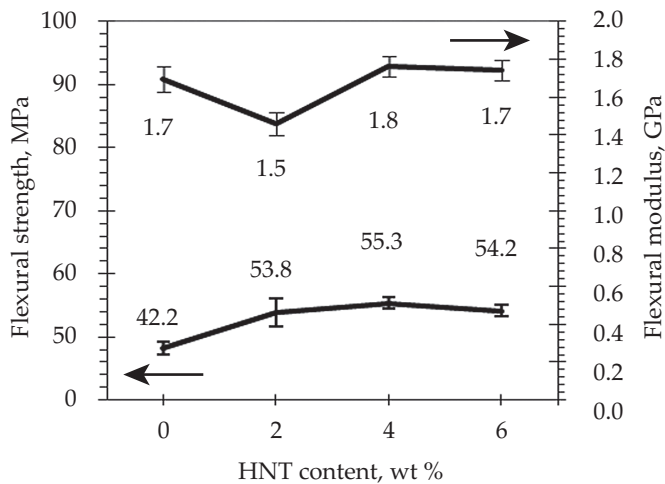**Fig. 3. Stress-strain curves of PLA/PPC blend with different HNT content**

Fig. 4. Flexural strength and modulus of 70/30 PLA/PPC with different HNT content

Fig. 5. Impact strength of PLA/PPC 70/30 with different HNT content

Impact test

Figure 5 displays the impact strength of PLA/PPC with different HNT content. As can be seen there are no significant differences in the impact strength as HNT content increases to 4 wt %. However, the impact strength decreases from 8.7 to 7.7 kJ/m² as the HNT content increases from 4 to 6 wt %, and is lower than without the addition of HNT.

The results show a strengthening effect of HNT due to better tensile and flexural strength and modulus of the PLA/PPC/HNT composites. It is believed that the enhancement of mechanical properties is due to the fine dispersion of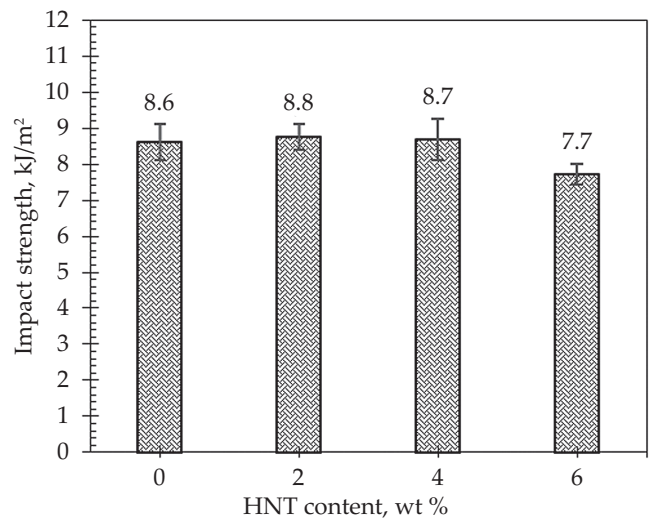 intercalated HNT within PLA/PPC matrix. A similar trend is also reported by Erpek *et al.* for PLA/HNT composites [36]. Moreover, HNT has a tubular nanostructure with a large aspect ratio, consists of an alumine network at the inner surface and a siloxane network on the outer surface. It is believed that during melt-mixing, the polymer chain diffuse from the bulk polymers melt into the interlayer of these nanotubes, resulting in a well-ordered multilayer with alternating polymer, siloxane, and alumine network layer of HNT. This behavior is in accordance with the theory of polymer blends with nanocomposites reported in the literature [37].

Meanwhile, for the elongation at break of PLA/PPC/HNT nanocomposites, there is a noticeable

T a b l e 1. **Mechanical properties of neat PLA and PLA/PPC blend**

Sample	Tensile strength, MPa	Tensile modulus, GPa	Elongation at break, %	Flexural strength, MPa	Flexural modulus, GPa	Impact strength, kJ/m²
Neat PLA	68±1	2.23± 0.06	3.8±0.4	64±5	2.33±0.01	5.5 ± 0.3
PLA/PPC 70/30	32±3	1.26±0.02	194±1	48±2	1.70±0.02	8.6±0.04

T a b l e 2. **Thermal properties of PLA/PPC/HNT nanocomposites determined by the DSC method**

PLA/PPC/ HNT	T_g PPC, °C	T_g PLA, °C	ΔT_g, °C	T_c, °C	T_{m1}, °C	T_{m2}, °C	ΔH_c J/g	ΔH_m, J/g	X_c, %
100/0/0	-	48	-	111	145	151	17.29	15.44	16.60
70/30/0	29	54	25	106	146	154	17.20	18.12	19.50
70/30/2	23	47	24	103	143	152	21.05	17.35	19.04
70/30/4	25	49	24	104	144	153	15.44	16.64	18.64
70/30/6	32	55	23	117	–	152	14.65	14.86	17.00

reduction as a function of HNT. To support the current investigation, the authors performed mechanical tests on neat PLA. As shown in Table 1, neat PLA has a low elongation at break of only about 3% with tensile strength of 68 MPa. The addition of 30 wt % of PPC changed neat PLA from brittle to ductile. However, the tensile strength decreased by 53% of its initial value (neat PLA). An addition of only 2 wt %. HNT increased the tensile strength by about 28%. Although the elongation at break decreased with the addition of HNT, the values were still much higher compared to neat PLA.

Interestingly, an overloading amount of HNT could reduce PLA/PPC blend properties. Deterioration of tensile and flexural properties as well as in impact strength at HNT higher content (6 wt %) is illustrated in Figs. 1, 4 and 5. It is believed that with a high content of HNT, aggregates may be formed, leading to deterioration of the mechanical properties. Further structural research is required to confirm this conclusion (SEM, TEM).

Thermal properties

The thermal behavior of PLA/PPC/HNT nanocomposites was determined by DSC method. The glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), cold crystallization enthalpy (ΔH_c), the heat of melting (ΔH_m), and crystallization degree of PLA/PPC blend reinforced with different HNT amounts is presented in Table 2. Figure 6 illustrates the DSC thermograms of PLA/PPC/HNT nanocomposites.

Based on the observation, two T_g in the PLA/PPC blend show that the blend is partially miscible. The addition of 2 wt % of HNT has practically no effect on the miscibility of PLA/PPC, as the nanocomposite still has two T_g. When the amount of HNT increases to 6 wt %, the T_g of PPC and the T_g of PLA tend to move towards each other, while the crystallinity continues to decline. Therefore, it is believed that higher HNT content may result in partial miscibility of PLA and PPC, which is associated with higher tensile strength of nanocomposites shown in Figs. 1 and 3. The incorporation of 2 wt % of HNT in PLA/PPC blend

resulted in a T_g decrease, from 29°C and 54°C to 23°C and 47°C, respectively. The T_g of the PLA/PPC/HNT increased from 23°C and 47°C to 32°C and 55°C when the amount of HNT was up to 6 wt %.

The same trend was also seen for the T_c, which increased from 106°C to 117°C. This result was in contrast with Kaygusuz and Kaynak [33]. The decreased T_c showed that HNT acted as a nucleating agent, which improved the polymer flexibility. In this case, adding of HNT resulted in an apparent shift of T_c from 103°C to 117°C. Therefore, it can be concluded that the increase of HNT restricted the blend's molecular entanglement, thus reducing PLA/PPC flexibility explained by Fig. 3. The higher the amount of HNT incorporated into PLA/PPC, the lower elongation of the PLA/PPC/HNT nanocomposites.

Double T_m were recorded for all nanocomposites. The double melting temperature refers to the melt recrystallization mechanism of PLA during the second heating cycle. In the process of this heating, the less perfect PLA crystals have gained enough time to melt and formed more perfect crystals. Later, it melted again creating a higher melting temperature [38]. The incorporation of
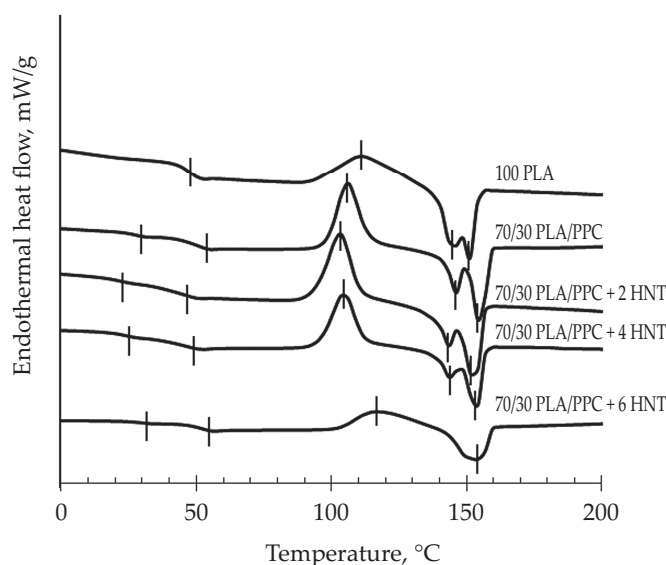
Fig. 6. DCS thermograms of PLA/PPC/HNT nanocomposites

6 wt % HNTs resulted in single T_m. There is only a slight decrease in T_m as the amount of HNT increases. This shows that the HNT amount does not significantly influence the T_m of nanocomposites. Meanwhile, the crystallinity of the nanocomposites gradually decreased as the HNT amount increased. This may be due to rigid filler HNT, which disrupts the PLA/PPC matrix's continuity that causes a decreased flexibility [38].

CONCLUSIONS

The new reinforced PLA/PPC/HNT nanocomposites differing in HNT content (0 wt % to 6 wt %) were obtained by melt mixing. HNT could improve the tensile, impact, and flexural strength of PLA/PPC 70/30 blend. Besides, the stiffness was remarkably improved as Young's modulus of the nanocomposites increased with increasing HNT content. Thermal properties determined by DSC method showed that HNT did not significantly affect the phase transition temperatures of nanocomposites (T_g, T_c and T_m). In addition, HNT limited the flexibility of PLA/PPC/HNT nanocomposites due to the greater stiffness that limited the mobility of the PLA/PPC chains. The lower flexibility is associated with a gradual decrease in crystallinity, suggesting better miscibility.

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