# Preparation and Characterization of Poly(*L*-lactic acid)/Chitosan/Microcrystalline Cellulose Blends

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*Authors' contributions*

*This work was carried out in collaboration between all authors. Authors MSH and MHR designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors MHR and MSH managed the analyses of the study. Authors MHR and MSH managed the literature searches. All authors read and approved the final manuscript.*

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## ABSTRACT

To prepare biodegradable and biocompatible polymer composites with better thermal and mechanical properties, five different Poly(*L*-lactic acid)(PLLA)/Chitosan/ Microcrystalline Cellulose (MCC) blends, with a different ratio, were prepared and characterized. MCC was extracted from jute fiber by conventional acid hydrolysis method with 64 wt% $H_2SO_4$ and chitosan was extracted from shrimp shell by successively carrying out demineralization, decolorization, deproteinization and deacetylation steps. PLLA was blended with a constant percentage (20 percent) of chitosan and a calculated amount of MCC by solution casting method using a suitable solvent for each. Prepared samples were characterized by Fourier-Transform Infrared Spectroscopy (FTIR) for the identification of their compatibility in blends, Wide-Angle X-ray Diffraction (WAXD) for crystalline species and crystallinity analysis, Thermo-Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) for thermal properties measurement. Results from FTIR analysis showed that except hydrogen

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bonding, there are no new characteristic absorption peaks observed in the spectrum of blends and confirm that PLLA, Chitosan, and MCC have better compatibility in blends via intermolecular hydrogen bonding. WAXD profiles data show the variation in crystallinity of different blends. TGA and DTG results indicate that MCC can improve the heat resistivity of the PLLA/Chitosan/MCC blends by the addition up to 5%.

## 1. INTRODUCTION

Last few decades, Poly(*L*-lactide) or Poly(*L*-lactic acid) (PLLA) is attracting much attention in polymeric research because of its degradability at room temperature and neutral pH. It can be hydrolyzed only with moisture without any help of hydrolytic enzymes [1,2,3]. In recent years, this promising polymer has been applied to the medical science for some excellent properties such as non-toxicity and biocompatibility [4]. Degradable sutures, drug releasing particle and porous scaffolds for human body cell can be prepared from PLLA [5]. But to be implanted into the tissue engineering, it must have antibacterial or anti-microbial properties to remove the risk of infection [6]. Some attempts have been taken to improve the antibacterial activity by blending with different anti-bacterial agents like nano-silver [7]. After perceiving about the adverse effects of nano-silver [8], the trend is shifted to the natural product such as Chitosan. Chitosan exhibits some interesting biological properties such as biocompatibility, biodegradability, hemostatic activity etc. It also can prohibit the activity of some bacteria such as *Staphylococcus aureus and Escherichia coli* [9]. PLLA/Chitosan di-blends are being used in tissue engineering fields [10]. But a more extended application of PLLA/Chitosan blends is being restricted to its relatively poor thermal and mechanical properties. In order to resolve the problem, Some researchers prepared blends by PLLA and PDLA, has improved mechanical and thermal properties [11], also PLLA/Chitosan di-blend is being used with some functional additives by fabricating PLLA based composites and tri-blends [12].

Besides of its low cost, bio-degradability & non-toxic property, natural fibers have high mechanical performance. For this reason, Reinforced polymer composites technology has been focused on natural fibers as a reinforcing agent in polymer/fiber composites and blends [13]. These reinforcing agents can provide an increased surface area for better interaction between the matrix and reinforcement which leads to better mechanical property and thermal resistivity [14]. After removing the amorphous regions by 64% $H_2SO_4$ (acid hydrolysis), Micro Crystalline cellulose (MCC) can be a potential reinforcing agent for polymers [15]. MCC fibrils, prepared by acid hydrolysis from jute, can be about 5–10 nm width and from 100 nm to several micrometers long. Comparing with other conventional reinforcing fiber, MCC has high specific surface area [16]. In this research, MCC is been used as a reinforcing agent to develop the thermal properties of PLLA/Chitosan di-blends. The effect of MCC on the PLLA/Chitosan blends has been discussed up to 10%. Specifically, crystallinity and thermal resistivity properties with the addition of MCC were investigated by X-ray diffraction analysis (XRD), Thermo-gravimetric analysis (TGA).

## 2. EXPERIMENT

Blend's matrix, PLLA, was collected from Mitsubishi Chemical Corporation, UNITIKA Plastics Division, Japan. By using conventional acid hydrolysis method, Micro Crystalline Cellulose (MCC) was prepared from jute fiber [17]. Tossa jute (*Corchorus olitorius*), as a raw jute, was collected from the southern part of Bangladesh. This species of jute was chosen because it is comparatively softer, silkier and stronger than the other available species like white jute [18]. Chitosan was derived from the partial deacetylation of chitin extracted from chemical treatment of shrimp shell [19,20].

### 2.1 Extraction of Micro Crystalline Cellulose (MCC) from Jute Fiber

Washed and air dried raw jute fibers were cut into a small section of length (approximately 2-3 cm) and bleached with (7 mg/ml) sodium chlorite (NaClO$_2$) solution at pH 4 (with the addition of 2M CH$_3$COOH) [21,22]. Bleaching was conducted at temperature 85°C-90°C for 90 mins with a ratio 1 gm (wt. of fiber):80ml (vol. of bleaching solution). To maintain constant pH

acetic acid and sodium acetate buffer solution was used before bleaching [23]. After washing with distilled water and drying at 105°C for 24 hrs, the bleached fiber was treated with 17.5% NaOH for removing of β and γ cellulose [24]. Remaining NaOH was removed from α-cellulose by washing with distilled $H_2O$ and again dried in the vacuum drier at 75°C for 48 hr.

Micro-crystalline cellulose (MCC) was prepared from aforementioned α-cellulose by well-known acid hydrolysis process. Here 64 wt% $H_2SO_4$ was used to diffuse into the α-cellulose fiber and breaks down glycoside bonds of the cellulose polymeric chain [25]. α-cellulose was treated with 64 wt% $H_2SO_4$ solution at 35-40°C for 25–30 mins with constant stirring. The ratio between α-cellulose and 64 wt% $H_2SO_4$ was maintained at 1 gm:10 ml (w:v). After dissolving all α-cellulose in acid, it was immediately quenched with ice cool de-ionized water to obtain gel type MCC [26]. $H_2SO_4$ was completely removed by washing with distilled $H_2O$ and then $H_2O$ was replaced by acetone by centrifugation.

## 2.2 Extraction of Chitosan from Shrimp Shell

Chitosan was extracted from shrimp shell by a series of chemical treatment. Washed and dried shrimp shell was crushed to reduce its size (approximately 0.25cm×0.5cm). Crushed shell was treated with 1.57M HCl in 1g:10ml (w/v) ratio for 6hrs at room temperature under constant stirring [27]. Demineralized shell was filtered with the aid of a vacuum pump and washed with deionized water. To remove the color from the demineralized shell, it was oxidized with 0.5% $KMnO_4$ in the presence of aq. $H_2C_2O_4$. Decolorization was conducted for 2-3 hrs at 60°C-70°C with a ratio 1 g:15 ml (w:v) [28]. After decolorization, it was treated with 1.25M NaOH at 100°C for 30 mins to separate the chitin from the protein complex [29]. Washed and dried chitin contains acetyl group, should be removed by deacetylation to obtain pure chitosan. Deacetylation process was carried out by 50%

NaOH at 100°C for 4 hours at a ratio of shell to solution is1g:20 ml (w:v) [30].

## 2.3 Preparation of PLLA/Chitosan/MCC Blends

PLLA solution was prepared by dissolving in chloroform [31]. MCC has a hydrophilic property because of –OH group present on its surface which can increase the reactivity. So it was dispersed in a non-aqueous solvent acetone with 90 mins sonication [32]. Chitosan was dissolved in 1-2% acetic acid [33]. The calculated amount of these three solutions were then blended with a magnetic stirrer until homogenous solutions were obtained [34]. Films, obtained on petri dishes by solution casting method, were evaporated at ambient temperature for 3-4 days under vacuum [35]. Sample codes were designed as PCM-X, where P, C and M-X mean PLLA, Chitosan and MCC percentages in the blend respectively, in (Table 1).

## 2.4 Experimental Measurement

FTIR analysis was carried out on a Shimadzu IR Prestige-21 Fourier Transform Infrared Spectroscopy, Japan, at a resolution of 4 $cm^{-1}$. The samples ware compressed with dry KBr powders for making disks. Thermo-gravimetric analysis (TGA) and Differential thermal analysis (DTA) of the blends were conducted in a TG/DTA (SII-6300 analyzer). Approximately, 10 mg of each sample was heated from 25°C to 580°C at 15°C $min^{-1}$ under a nitrogen atmosphere. X-ray diffraction analysis of different blends and composites were performed at 25°C with a D-8 ADVANCE BRUKER diffractometer operating at 40 kV and 30 mA, using the radiation (λ= 0.1546 nm). The percentage of the crystalline structure of the samples was determined as the ratio of the areas of crystalline reflections to the whole area (after subtraction of background) in the 2θ range [36,37], and can be expressed as follows:

$$\% \text{ of crystalline structure} = \frac{\text{Area of the crystalline peaks}}{\text{Total area}} \times 100$$

**Table 1. Sample code and composition of different blends**

| Sample code | Composition of blend |
|---|---|
| PCM-0 | PLLA 80% + Chitosan 20%+ MCC 0% |
| PCM-1 | PLLA 79% + Chitosan 20%+ MCC 1% |
| PCM-3 | PLLA 77% + Chitosan 20%+ MCC 3% |
| PCM-5 | PLLA 75% + Chitosan 20%+ MCC 5% |
| PCM-10 | PLLA 70% + Chitosan 20%+ MCC 10% |

## 3. RESULTS AND DISCUSSION

### 3.1 FT-IR Spectroscopy Analysis

FTIR is usually used to investigate the intermolecular and intramolecular hydrogen bonding of different blends because it is the most common technique to study inter-molecular and intra-molecular interaction in polymer blends and composites.

The FTIR spectra of Chitosan, PLLA, MCC, PLLA/Chitosan and PLLA/Chitosan/MCC blends are shown in Fig. 1. Compared with the pure PLLA, pure Chitosan and pure MCC, the FTIR spectra in PCM-0 and PCM-5, were shifted slightly (Table 2).
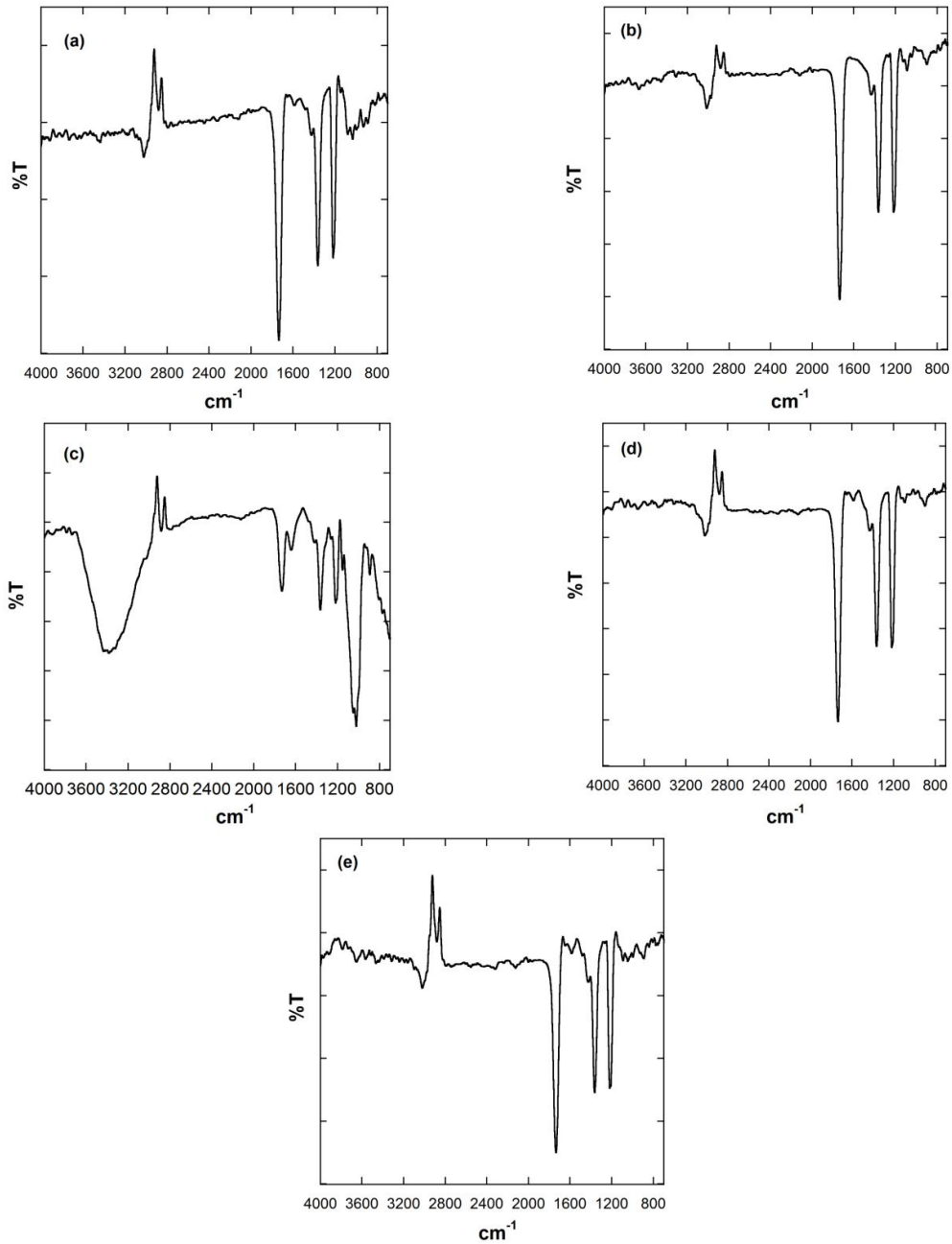


**Fig. 1. FT-IR spectra (a) Pure Chitosan (b) Pure PLLA (c) Pure MCC (d) PLLA/Chitosan blend (e) PLLA/Chitosan/MCC blends**

**Table 2. Assigned peaks and accounted bonds for Chitosan, PLLA, MCC, PCM-0 & PCM-5**

| Accounted bond for the absorption | 100% Chitosan Assigned Peak(cm$^{-1}$) | 100% PLLA Assigned Peak(cm$^{-1}$) | 100% MCC Assigned Peak(cm$^{-1}$) | PCM-0 Assigned Peak(cm$^{-1}$) | PCM-5 Assigned Peak(cm$^{-1}$) |
|---|---|---|---|---|---|
| -OH stretching | ---------- | --------- | 3383.14 | -------- | 3653.18 |
| -CH stretching (Asymmetric) | 3024.38 | 3016.67 | ---------- | 3018.60 | 3020.53 |
| -CH stretching (symmetric) | 2883.58 | 2883.58 | 2885.51 | 2879.72 | 2881.65 |
| -C=O stretching | 1735.93 | 1739.79 | 1732.08 | 1737.86 | 1735.93 |
| -CH bending | 1365.60 | 1365.60 | 1367.53 | 1365.60 | 1365.60 |
| -C-O- stretching for Acid | 1220.94 | 1219.01 | 1220.94 | 1220.94 | 1211.30 |
| -C-O- stretching for Alcohol | 1035.77 | --------- | 1024.20 | ------- | ------- |

Broad O-H stretching band of MCC at 3383.14 cm$^{-1}$ was observed in PCM-5 to a very small peak at 3653.18 cm$^{-1}$ for overlapping with N-H bond stretching [38]. The C-H stretching peak of PCM-0 shifted to higher wavenumber in PCM-5 from 3018.60 cm$^{-1}$ to 3020.53 cm$^{-1}$ after adding hydroxyl group of MCC. C=O stretching in PLLA shifted from high region 1739.79 cm$^{-1}$ to lower 1737.86 cm$^{-1}$ in PCM-0 and 1735.93 cm$^{-1}$ in PCM-5. It indicates that MCC and Chitosan produce intermolecular hydrogen bond between O-H and C=O group to weaken the C=O in ester group in PLLA. Similarly, other bending peaks shifted to the lower wavenumber for the intermolecular hydrogen bonding. Most of the characteristic absorption peaks of the PLLA/Chitosan/MCC blend shifted from the characteristics absorption peaks of PLLA/Chitosan blend. This can be explained based on a hypothesis that MCC is just combined with PLLA and Chitosan by hydrogen bonding interactions without forming new functional groups. This information can provide a confirmation that PLLA, Chitosan and MCC have better compatibility in blends via intermolecular hydrogen bonding and this supports previously reported result [39].

## 3.2 Wide Angle X-ray Diffraction (WAXD) Analysis

The WAXD pattern of the PLLA/Chitosan/MCC blends materials comparing to the PLLA/Chitosan blend as diffractograms are presented in Fig. 2. Here two sharp peaks at *2Θ* = 16.9° and *2Θ* = 19.2° are the characteristics peak for the homo crystalline structure of PLLA [40]. In PCM-0 the amorphous region was increased due to the addition of chitosan.
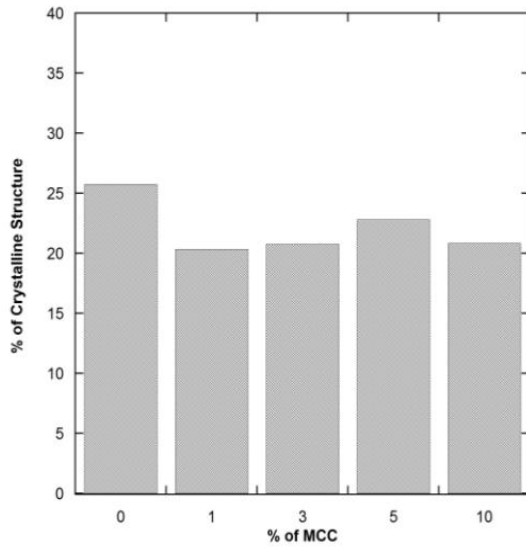
Though chitosan is a crystalline substance, its degree of crystallization decreases after dissolving in chloroform and blended with PLLA. The Interaction between two polymeric chains of PLLA and Chitosan can affect the arrangement of molecules and decrease the degree of crystallinity of both PLLA and Chitosan. With the addition of MCC, the change in the crystalline structure of different blends has been shown in Fig. 3.
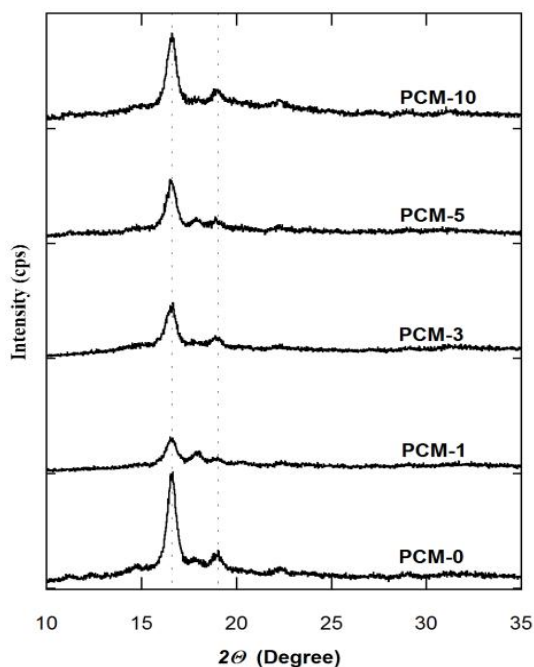


**Fig. 2. WAXD diffractograms of different blends**

1% MCC reduced the crystallinity of PLLA/chitosan blends from nearly 25.75% to 20.34%. Because 1% MCC can also interact with PLLA by the hydrogen bonding and increase the randomness in the chain arrangement of PLLA analogous to the previous research outcome

[41]. But in case of PCM-3 and PCM-5, MCC contains nano-sized particles which can act as a nucleating agent and develop the crystal formation. That is why crystallinity of PLLA was being increased with the increasing of MCC amount up to 5% and PCM-5 showed the maximum crystal structure among those tri-blends [42].

However, in PCM-10, a high percentage of MCC can accumulate to make large particle size unable to act as nucleating agents. So MCC again increases the amorphous portion in PLLA/Chitosan/MCC blends. Therefore it can be concluded, PCM-5 has a better crystalline structure than PCM-10 (Table 3).

## 3.3 Thermal Stability Analysis

Weight loss due to degradation, as a function of temperature, was conducted by Thermogravimetric analysis (TGA) to measure thermal stability of different blends.

Fig. 4 shows the comparison of TGA curves with different compositions. The initial loss of moisture and desorption of gases took place at 80°C to 160°C was followed by major decomposition between 300°C to 390°C.TGA analysis shows a sharp increase of initial degradation point from PCM-0 to PCM-5. In case of PCM-10, each degradation point decreased with the increase of MCC (Table 4).

Fig. 5 showed that Initial degradation point shifted from 305.2°C to 305.9°C, 311.2°C and 336.2°C for PCM-1, PCM-3 and PCM-5 respectively because MCC acts as a filler in the PLLA/chitosan matrix and it holds polymeric chain tightly, [43] which results in a more compact composite structure with better heat

**Fig. 3. Relation between % of MCC and % of the crystalline structure**
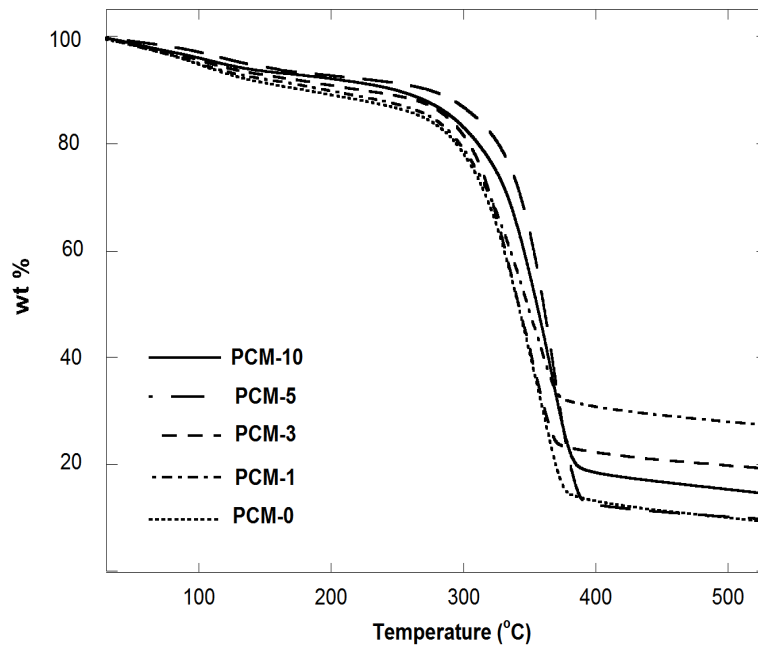
**Fig. 4. Comparison between TGA curves of different blends**

**Table 3. Wt. of crystalline region, amorphous region, total area & % of crystallinity**

| Sample | wt. of crystalline region (gm) | wt. of amorphous region (gm) | wt. of total area (gm) | % of crystallinity |
|---|---|---|---|---|
| PCM-0 | 0.0137 | 0.0395 | 0.0532 | 25.75 ± 1 |
| PCM-1 | 0.0056 | 0.0219 | 0.0275 | 20.34 ± 1 |
| PCM-3 | 0.0071 | 0.0271 | 0.0342 | 20.76 ± 1 |
| PCM-5 | 0.0089 | 0.0301 | 0.0390 | 22.82 ± 1 |
| PCM-10 | 0.0123 | 0.0467 | 0.0590 | 20.84 ± 1 |

**Table 4. Initial, half and final degradation points of different blends**

| Blend name | Initial degradation point (°C) | Half degradation point (°C) | Final degradation point (°C) |
|---|---|---|---|
| PCM-0 | 305.2 | 336.8 | 368.4 |
| PCM-1 | 305.9 | 338.2 | 371.2 |
| PCM-3 | 311.2 | 342.6 | 374.7 |
| PCM-5 | 336.2 | 360.7 | 384.6 |
| PCM-10 | 325.3 | 353.1 | 381.8 |
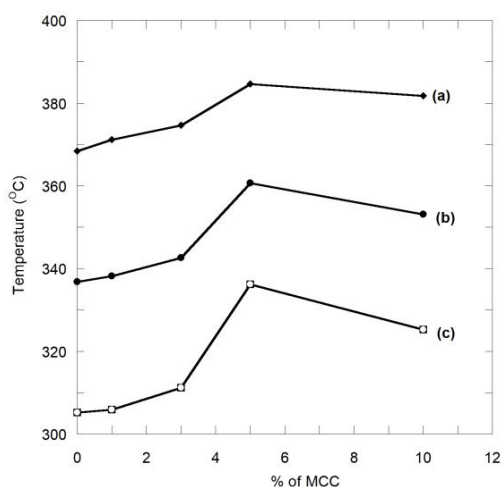


**Fig. 5. Relation between % of MCC and degradation point (a) Final degradation point (b) Half degradation point (c) Initial degradation point**

resistivity. In case of PCM-10, MCC has a tendency to accumulate by hydrogen bonding in a higher percentage cause sudden drop in heat degradation point to 325.3$^{o}$C [44]. Half degradation and final degradation point indicated the same trend. After complete degradation, 10-30% residue had been found and among them, PCM-0 and PCM-5 left a nearly same amount of residue approximately 10% and PCM-1 left the maximum residue approximately 30%.

Fig. 6 shows the change in melting point ($T_m$) of different blends depending upon the DTA curves. DTA data shows a similar trend in shifting of $T_m$ with the addition of MCC into the blends. In PCM-0, $T_m$ 162.6°C shifted gradually up to 165.2°C in PCM-5 and then similarly dropped down to 164.9°C.

The increase in the $T_m$ with the introduction of MCC into the PLLA/Chitosan blends can be ascribed based on their intermolecular attraction between chitosan and cellulose. Due to the formation of hydrogen bonding among chitosan and MCC, the distance between the molecules decreases alternative increases the molecular attraction caused high $T_m$ [45]. A higher percentage, more than 5% caused low $T_m$ may be due to the increase of the amorphous region caused by MCC or intermolecular bond formation between consecutive cellulose units.
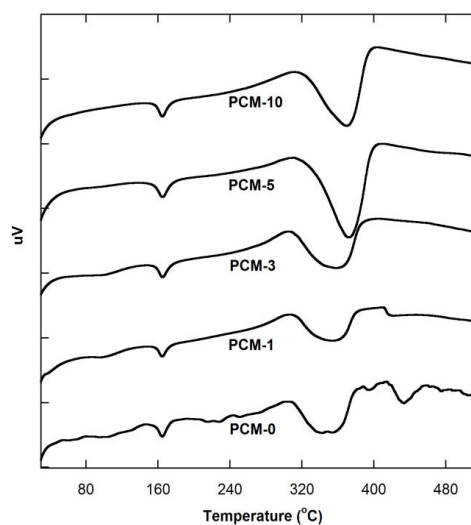


**Fig. 6. Comparison between DTA curves of different blends**

## 4. CONCLUSIONS

In this work we prepared and characterized PLLA/Chitosan/MCC tri-blend. PLLA, Chitosan, and MCC have better compatibility in blends via intermolecular hydrogen bonding. After decreasing the crystallinity with the initial addition of MCC, it increased with the addition of the MCC up to 5% and showed maximum crystallinity among blends. Also, MCC increased the thermal stability of the blends and consistent with WAXD results.

## ACKNOWLEDGEMENTS

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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