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CHARACTERIZATION OF POLYLACTIC ACID/MICROCRYSTALLINE CELLULOSE/MONTMORILLONITE HYBRID COMPOSITES

(Pencirian Komposit Polilaktik asid/Selulosa Mikrohablur/ Hibrid Montmorilonit)

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Abstract

The objective of this study is to investigate the effect of montmorillonite (MMT)/microcrystalline cellulose (MCC) hybrid fillers on mechanical properties and morphological characteristics of polylactic acid (PLA) composites. PLA/MMT nanocomposites and PLA/MMT/MCC hybrid composites were prepared by solution casting method. Morphology and tensile properties of PLA composites were investigated using Field emission scanning electron microscopy and Instron tensile testing machine. The maximum tensile strength of PLA/MMT nanocomposites was obtained with 5 phr contents of MMT, which corresponding to 30.75 MPa. Based on optimized formulation of PLA/MMT nanocomposites (5 phr MMT contents), various amounts of MCC (0 to 7 phr) were added into optimum formulation of PLA/MMT in order to produce PLA/MMT/MCC hybrid composites. Fourier transform infrared spectroscopy revealed some level of interaction between PLA and both MMT and MCC in the hybrid composites. However, the percent elongation at break of the hybrid composites was generally higher than PLA/MMT nanocomposites. Additionally, Young's modulus of the PLA/MMT/MCC hybrid composites increased gradually with increasing of MCC contents and was higher than PLA/MMT at all compositions. The present results are the first among a series of experiments that have been designed in order to probe the effect of MMT and MCC in the PLA.

Keywords: Hybrid composites, microcrystalline cellulose, polylactic acid, montmorillonite, solution casting

Abstrak

Objektif kajian ini adalah untuk mengkaji kesan pengisi hibrid montmorilonit (MMT)/selulosa mikrohablur (MCC) ke atas sifat mekanikal dan ciri-ciri morfologi komposit polilaktik asid (PLA). Nanokomposit PLA/MMT dan komposit hibrid PLA/MMT/MCC telah di sediakan menggunakan kaedah larutan beracun. Morfologi dan sifat regangan komposit PLA telah dikaji menggunakan mikroskop pengimbas electron kawasan terpancar (FESEM) dan mesin ujian regangan Instron. Kekuatan regangan maksimum nanokomposit PLA/MMT telah diperolehi dengan 5 bsg kandungan MMT, yang bersamaan dengan 30.75 MPa. Berdasarkan formulasi optimum nanokomposit PLA/MMT (5 bsg kandungan MMT), pelbagai jumlah MCC (0-7 bsg) telah ditambah ke dalam formulasi optimum PLA/MMT untuk menghasilkan komposit hibrid PLA/MMT/MCC. Spektroskopi inframerah transformasi fourier (FTIR) mendedahkan beberapa tahap interaksi di antara PLA dan kedua-dua MMT dan MCC dalam komposit hibrid. Walaubagaimanapun, peratusan terikan pada takat putus bagi komposit hibrid adalah lebih tinggi daripada nanokomposit PLA/MMT. Selain itu, modulus Young bagi komposit hibrid PLA/MMT/MCC meningkat secara beransur-ansur dengan peningkatan kandungan MCC dan ia adalah lebih tinggi daripada PLA/MMT pada semua komposisi. Keputusan ini adalah yang pertama dalam kalangan satu siri eksperimen yang telah direka untuk mengkaji kesan MMT dan MCC di dalam PLA.

Kata kunci: komposit hibrid, selulosa mikrohablur, polilaktik asid, montmorilonit, larutan beracun

Introduction

In recent decades, the use of biopolymers materials has been attracting more interest in the public research due to the increasing in environmental concerns and diminishing petrochemical resources. One of the most promising biopolymers is polylactic acid (PLA). PLA is a linear aliphatic thermoplastic polyester which synthesized by ring-opening polymerization of the cyclic lactide dimer. PLA is a widely studied biodegradable polymers because of its high mechanical properties and the easy production from its monomer (i.e. lactic acid) [1]. The majority of lactic acid used for PLA production is produced by fermentation of agricultural products (e.g. corn). The high biocompatibility and biodegradability of PLA make it a good candidate to be used in biomedical and packaging applications. In spite of all these advantages, its range of application is still limited by its high production cost, its brittleness and its low thermal stability. PLA nanocomposites containing high aspect ratio fillers have been developed to further enhance the strength, stiffness and thermal stability while lowering the production cost [2, 3].

Montmorillonite (MMT) is the most familiar clay among the commonly used fillers. It consists of two fused silica tetrahedral sheets sandwiching an edge shared octahedral sheet of either magnesium or aluminum hydroxide [4]. MMT with nano-sized layered structure has a large surface area providing sufficient interfacial regions in polymer nanocomposites that offer tremendous improvement in wide range of physical and engineering properties for polymers. [3, 5]. Montmorillonite (MMT) is a suitable filler for PLA nanocomposites because it has the ability to fine-tune its surface chemistry through ion exchange reactions with organic and inorganic cations [3]. PLA/MMT nanocomposites have been most well studied [2, 6]. Despite the all benefits of MMT, ductility is detrimentally affected by the addition of MMT. The replacement of MMT with other renewable and biodegradable fillers like as cellulose could minimize the production costs of the polymer nanocomposites, enhance the biodegradability, mechanical and thermal behaviors of PLA [1, 7].

One of the most fascinating natural fillers is cellulose. Microcrystalline cellulose (MCC) is a kind of cellulose fillers, which used as a reinforcement in a polymer matrix [8, 9]. MCC is produced by combining mechanical (e.g., pressure homogenizing) and chemical (e.g., acid hydrolysis) processes of natural celluloses such as plant and wood. MCC possesses a relatively high specific surface area compared with other fillers such as natural fiber, glass fiber, talc, and mica [10, 11]. As a result, MCC have a great potential to be used as reinforcing agent in composites. Few studies have been done on PLA/MCC composites and it is shown that the stiffness of PLA/MCC composites improved with the addition of MCC [12]. However, the ductility and tensile strength decreased with the addition of MCC [13].

It would be interesting to study the combined effect of MCC and MMT on stiffness, strength and ductility of PLA. Therefore, the objective of this study is to compare the mechanical and morphological properties of PLA/MMT nanocomposites and PLA/MMT/MCC hybrid composites. To the best of our knowledge, no study has been reported on using of MMT/MCC hybrid filler in order to enhance the mechanical properties of PLA composites using solution casting method.

Materials and Methods

Materials

Polylactic acid (NatureWorkTM PLA 300ID) in pellet form was obtained from NatureWork® LLC, Minnetonka, MN USA. It has a density of 1.24 g cm^{-3} and melt flow index (MFI) around 15 g/10 min (190 °C/2.16 kg). MCC was supplied by Sigma-Aldrich (Avicel; type PH-101). It was obtained from a cotton linter and had an average particle size of 50 μm. Organo-modified montmorillonite, Nanomer 1.30TC was obtained from Nanocor Inc. (Arlington Heights IL, USA) Nanomer 1.30TC is organically modified with around 30 wt.% of octadecylamine with mean dry particle size of 16–22 mm. The reagent used was chloroform secured from Merck, Malaysia.

Preparation of PLA and PLA/MMT nanocomposites

10 g pellets of PLA were fully dissolved in 64 ml of chloroform and stirred in water bath for 2 hours at 60 °C [14]. The PLA solution was immediately casted on a clean glass plates and left to allow the solvent to evaporate at room temperature for 48 hours. The thickness of the casted film was approximately 100 μm.

The PLA/MMT nanocomposites were prepared by mixing the 10 g of PLA pellets with different MMT contents (1, 3, 5, and 7 phr) at 60 °C. The various mixtures were placed in 64 ml of chloroform and stirred with strong agitation for 2 hours at 60 °C until PLA pellets were dissolved. The suspension was then sonicated for 5 minutes and immediately casted on a clean glass plate to obtain the composite of ~100 µm thickness. The composites were designated as P/MT1, P/MT3, P/MT5, and P/MT7 are shown in Table 1.

Preparation of PLA/MMT/MCC hybrid composites

The PLA/MMT/MCC hybrid composites were prepared by mixing 10 g of PLA pellets with 5 phr of MMT and different MCC contents (1, 3, 5, and 7 phr) at 60 °C. The various mixtures were placed in 64 ml of chloroform and stirred with strong agitation for 2 hours at 60 °C until all the PLA pellets dissolved. The suspension were then sonicated for 5 minutes and were immediately casted on a clean glass plate to obtain the composite of ~100 µm. The hybrid composites were designated as P/MT5/MC1, P/MT5/MC3, P/MT5/MC5, and P/MT5/MC7 are summarized in Table 1.

Table 1. Polylactic acid composites formulation

Designation	PLA (wt. %)	MMT (phr)	MCC (phr)
PLA	100	0	0
P/MT1	100	1	0
P/MT3	100	3	0
P/MT5	100	5	0
P/MT7	100	7	0
P/MT5/MC1	100	5	1
P/MT5/MC3	100	5	3
P/MT5/MC5	100	5	5
P/MT5/MC7	100	5	7

phr = parts per hundred parts of polymer (PLA)

Characterization

Fourier transform infrared

Fourier transform infrared (FT-IR) analysis was performed on a Perkin Elmer 1600 Infrared spectrometer. FT-IR spectra of the samples were recorded by using Nicolet's AVATAR 360 at 32 scans with a resolution of 4 cm^{-1} and within the wave number range of 4000 to 370 cm^{-1}.

Mechanical testing

Mechanical test was done using the Instron 4400 Universal Tester to measure the tensile strength at the point of breakage for each sample and Young's modulus. Tensile tests were carried out at room temperature, according to the ASTM D882 type V. A fixed crosshead rate of 10 mm/min was utilized in all cases and the results were taken as an average of 10 tests.

Morphology analysis

The morphology of samples was characterized by using Field emission scanning electron microscopy (FESEM). FESEM was conducted using a Carls Zeiss (Germany) Supra 35 VP and an extra high tension (EHT) of 8–10 kV. The samples were sputter-coated with gold prior to observation.

Results and Discussion

FT-IR spectroscopy analysis

FT-IR spectroscopy was used to observe the interfacial interaction between PLA matrix and both MMT and MCC. FT-IR spectra of pure PLA, a P/MT5 nanocomposite and a P/MT5/MC1 hybrid composite are shown in Figure 1a-c, respectively. As can be seen from Figure 1a, the peak at 3508 cm^{-1} was assigned to the -OH stretching vibration [15, 16]. The 2997 and 2948 cm^{-1} absorption peaks attributed to the asymmetric stretching vibration of -CH [15, 17]. Stretching vibration of carbonyl groups (C=O) appeared at 1764 cm^{-1} and the peak at 1089 cm^{-1} indicate the stretching vibration of C-O. Similar results were reported by other studies [15-17]. The peaks at 1457 and 1049 cm^{-1} are ascribed to the $–CH_3$ bending and –OH bending, respectively and stretching vibration of C-C single bond was situated at 868 and 920 cm^{-1} [15-18].

Figure 1b and c revealed the character peaks of a P/MT5 nanocomposite and a P/MT5/MC1 hybrid composite, respectively. As shown in Figure 1b, the presence of new peaks at 465 and 520 cm^{-1} for nanocomposites spectra were attributed to the absorption peak of SiO_2 and Si-O vibration, respectively [19]. As can be clearly observed from Figure 1b, the O-H (3508 cm^{-1}), C=O (1764 cm^{-1}) and C-O (1089 cm^{-1}) stretching peaks were shifted to lower wave numbers of 3502 cm^{-1}, 1760 cm^{-1} and 1084 cm^{-1}, respectively. This was attributed to the strong polar interaction between the PLA and the MMT platelet surfaces and the hydroxyl groups of the ammonium surfactant in the organically modified clay [19]. Figure 1c illustrates that no new peak was created when MMT/MCC hybrid fillers were added into PLA matrix, because lower amount of fillers used to produce the hybrid composites and only physical interaction occurred between PLA and MMT/MCC hybrid fillers, instead of chemical interaction [13, 17]. On the other hand, the peak at 3502 cm^{-1} for P/MT5/MC1 hybrid composite (Figure 1c) becomes broader as compared to P/MT5 nanocomposite (Figure 1b) when MCC filler was added. The broadness of the peak in the P/MT5/MC1 hybrid composite indicates the existence of good interaction between PLA and both MMT and MCC [20].

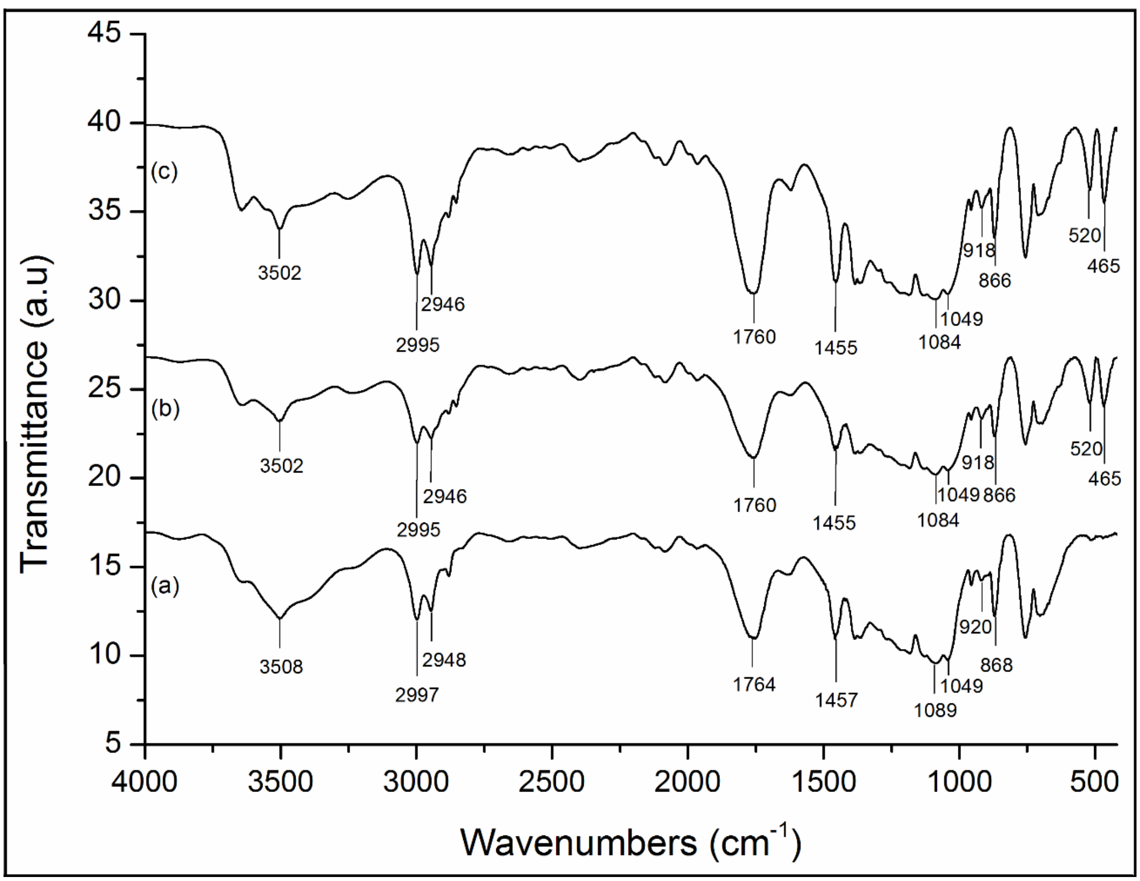

Figure 1. Typical FT-IR spectroscopy of (a) Pure PLA, (b) a P/MT5 nanocomposite and (c) a P/MT5/MC1 hybrid composite.

Tensile properties

Figure 2a demonstrates the effect of MMT contents on tensile strength and Young's modulus of PLA and PLA/MMT nanocomposites. The results revealed that the addition of MMT gradually increased the tensile strength and Young's modulus of the nanocomposites. The PLA/MMT nanocomposites exhibited approximately 63 % (at 5 phr MMT contents) increase in the tensile strength as compared to pure PLA. As the MMT contents further increased, the tensile strength decreased, which is attributed to the aggregation of MMT particles. Previous studies also reported that higher contents of MMT (>5 wt.%) in polymer can result in its agglomeration resulting in deprived mechanical performance compared to lower contents [21, 22]. The Young's modulus values of PLA/MMT nanocomposites increased steadily with increasing MMT contents. The PLA/MMT nanocomposites exhibited approximately 18 % increase in modulus as compared to the pure PLA. The improvement in modulus of PLA nanocomposites is due to the high rigidity exerted by the MMT as it does not deform and therefore the PLA's chain movement was suppressed by MMT particles [23]. This improvement in modulus may also be ascribed to the dispersion and alignment of MMT platelets within PLA and enhancement of the silicate interlayers incorporated into the polymer matrix. [2, 23].

Figure 2b displays the effect of MCC contents on the tensile strength and Young's modulus of PLA/MMT nanocomposites. It can be seen that, the addition of MCC give negative impact on the tensile strength. It is interesting to note that the Young's modulus of PLA/MMT/MCC hybrid composites increase gradually with increase in MCC contents and higher than PLA/MMT nanocomposites in all compositions (from 4.8 GPa to 5.25 GPa). This improvement in modulus of PLA/MMT/MCC hybrid composites is due to the increase in stiffening effect of the MCC [13, 24]. The tensile strength values of PLA/MMT/MCC hybrid composites however, decreased due to the presence of MCC. This could may be attributed to agglomeration of MCC due to Van der Waal's forces or there is practically no interfacial bonding between the reinforcing fillers and the polymer matrix [17, 20].

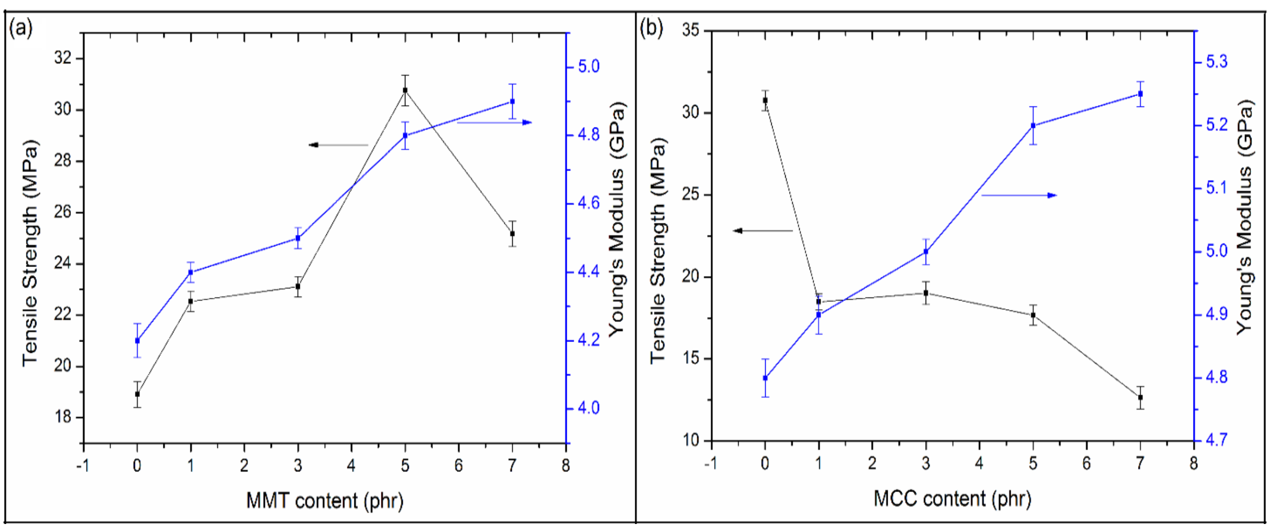

Figure 2. Tensile strength and Young's modulus of (a) PLA/MMT nanocomposites (b) and PLA/MMT/MCC hybrid composites.

The effect of MMT and MCC contents on the elongation at break of PLA/MMT nanocomposites and PLA/MMT/MCC hybrid composites was shown in Table 2 and Table 3, respectively. It can be clearly seen that, the elongation at break values of PLA/MMT/MCC hybrid composites (Table 3) increased with the presence of MCC in hybrid composites as compared to PLA/MMT nanocomposites (Table 2). The elongation at break values of the

PLA/MMT/MCC hybrid composites increased from ~10 to ~60 % in the presence of MCC. As the MCC contents further increased, the elongation at break decreased, which is ascribed to the aggregation of MCC particles. The initial increment in elongation at break with the presence of the MCC in PLA/MMT/MCC hybrid composites may be attributed to the interaction between reinforcements and matrix, which enhanced the interfacial bonds of MMT/MCC hybrid fillers and PLA matrix [2]. This results corroborates the observation made in the FT-IR analysis.

Table 2. Elongation at break of PLA/MMT nanocomposites

Designation	**Elongation at break (%)**
PLA	124.8±0.5
P/MT1	55.0±0.3
P/MT3	29.5±0.5
P/MT5	10.6±0.4
P/MT7	6.4±0.5

Table 3. Elongation at break of PLA/MMT/MCC hybrid composites

Designation	**Elongation at break (%)**
P/MT5/MC1	60.0±0.5
P/MT5/MC3	35.5±0.3
P/MT5/MC5	11.0±0.4
P/MT5/MC7	8.1±0.5

Field emission scanning electron microscopy

Figure 3 shows the field emission scanning electron microscopy (FESEM) images of fractured cross-sectional surfaces of pure PLA, a P/MT5 nanocomposites and a P/MT5/MC1 hybrid composites. Due to the lack of large scale plastic deformation, pure PLA showed a fairly smooth fracture surface (Figure 3a) [6]. It can be clearly seen from Figure 3b, MMT was dispersed uniformly throughout PLA matrix due to its finer particle size and the MMT was embedded within PLA matrix, as indicated by arrows. Figure 3c indicates the presence of MMT and MCC in the PLA matrix. However, adding the MCC has been resulting in agglomeration of MCC in the PLA matrix (as indicated by circle), and decreased the tensile strength of hybrid composites compared to the PLA/MMT nanocomposites. Due to the stiffening action of fillers in general, Young’s modulus increased as compared to PLA/MMT nanocomposites.

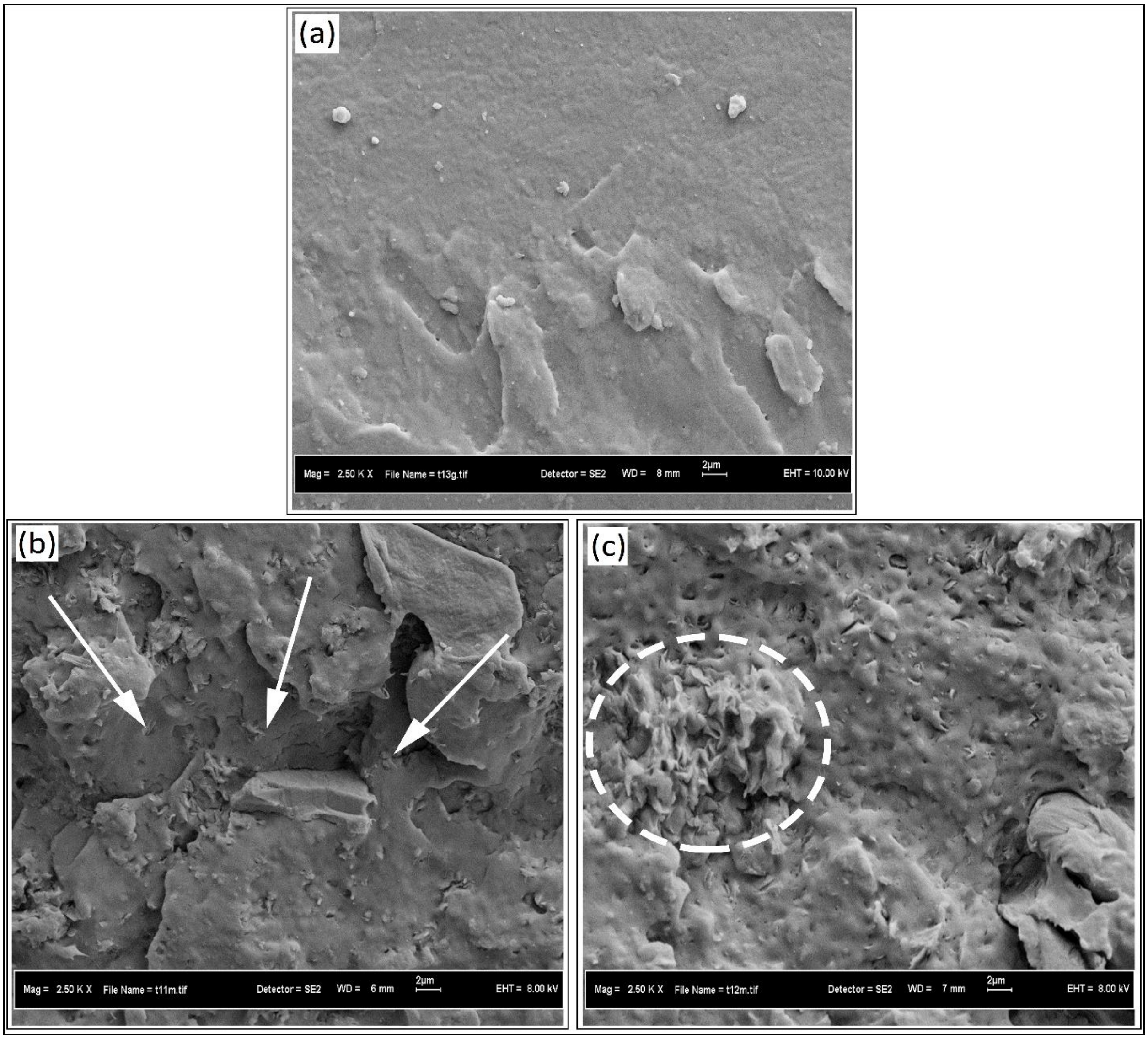

Figure 3. Field emission scanning electron micrographs of fractured cross-sections of (a) Pure PLA, (b) a P/MT5 nanocomposite and (c) a P/MT5/MC1 hybrid composite.

Conclusion

PLA/MMT nancomposites and PLA/MMT/MCC hybrid composites were successfully prepared by solution casting technique. The FT-IR results indicated that good interaction between PLA and MMT occurred due to presence of new peaks. Only physical interaction in recorded between PLA and MMT/MCC hybrid fillers, due to absence of new peaks. Tensile properties of the PLA/MMT nanocomposites showed an increased in tensile strength up to 5 phr of MMT contents and increased Young's modulus with increasing MMT content due to the adequate dispersion and alignment of MMT platelets within PLA. However, Young's modulus and elongation at break of PLA/MMT/MCC hybrid composites increased due to the increased in stiffening effect of the MCC and interaction between MMT/MCC hybrid fillers and PLA polymer, respectively. The morphological observations using FESEM showed the uniformly dispersed MMT in PLA matrix and agglomeration of MCC by adding MCC in the hybrid composites.

The development of PLA/MMT/MCC hybrid composites is expected to play an important role in membrane technology and packaging.

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