Polymer Communication

Ductile PLA modified with methacryloyloxyalkyl isocyanate improves mechanical properties

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ABSTRACT

The majority of the biodegradable polymers in clinical use are composed of stiff materials that exhibit limited extendibility with unsuitably high Young's modulus and low elongation at break values that make them non-optimal for various biomedical applications. Polylactide (PLA) is often used as a biomedical material because it is biodegradable, but the physical and mechanical properties of PLA need to be improved for biomedical applications. In order to improve the flexibility and strength of biodegradable PLA, various reaction conditions were studied. Urethane structure polymer materials were prepared; PLA was reacted with a small amount of methacryloyloxyethyl isocyanate (MOI) to obtain a ductile PLA with markedly improved mechanical properties. Elongation at break increased by 20 times when compared to neat PLA. Impact resistance (notched) improved 1.6 times. Thus, this modified PLA biodegradable polymer may have greater application as a biomedical material with increased mechanical properties.

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1. Introduction

Biodegradable polymers are used in traditional biomedical applications, such as surgical sutures and matrices for drug delivery [1,2]. In recent years, they have also been utilized in the field of tissue engineering as temporary scaffolds for cell growth and tissue regeneration [3–5]. Mechanical parameters play a crucial role in determining the *in vivo* performance of biomedical systems [6,7]. Though polylactide (PLA) is biodegradable and has been useful in various biomedical applications, its physical and mechanical properties must be improved to allow for more applications [8]. Since the majority of the biodegradable polymers in clinical use are rather stiff materials exhibiting limited extendibility with low elongation at break values, they are unsuitable for use in numerous applications. Implants must be tailored so that their mechanical behavior mimics that of the host tissue, since the stress field induced by the implant largely affects the healing and remodeling potential of the natural tissue surrounding it [9]. To expand the clinical applicability of biodegradable polymers, materials with better mechanical properties should be engineered.

In recent years, many researchers have copolymerized PLA with other organic compounds, such as polyethylene oxide (PEO), polypropylene oxide (PPO), 4,4-methylene diphenyl diisocyanate (MDI) or ε-caprolactone, to improve the physical, chemical and mechanical properties of PLA [10–13]. Cohn synthesized poly (caprolactone)/poly(ethylene oxide) (PCL/PEO) block copolymers [10]. Xiong et al. grafted PLA to both ends of Pluronic F87 block copolymer (PEO–PPO–PEO) to obtain amphiphilic P(LA-b-EO-b-PO-b-EO-b-LA) block copolymers, and used these temperature-sensitive copolymers in drug release studies [11]. Cohn prepared a series of multiblock PEO/PLA thermoplastic elastomers [9]. The first step of synthesis consisted of ring-opening polymerization of L-lactide, followed by the chain extension of these PLA–PEO–PLA triblocks using hexamethylene diisocyanate (HDI). The synthesized multiblock copolymers exhibited superior mechanical properties, with ultimate tensile strength values around 30 MPa, Young's moduli as low as 14 MPa and high elongation at break values. To further the applicability of biodegradable polymers, many researchers have worked to improve the toughness of PLA by adding plasticizers. Choi and Park studied the effects of several plasticizers including soybean oil, epoxidized soybean oil, dibutyl phthalate (DBP) and triethyl citrate (TEC) on the thermal and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxy valerate) (PHBV) [14]. They found that adding TEC and DBP resulted in increased toughness and improved performance. McCarthy and Song investigated the effect of biodegradable plasticizer on PLA

properties [15]. Martin and Averous plasticized PLA with several biocompatible plasticizers such as polyethylene glycol (PEG) and oligomeric lactic acid, which have shown significant decrease in glass transition temperature (T_g) and rise in elongation at break [16]. In addition, PLA has been melt-blended with thermoplastic starch (TPS). Microscopic observations revealed non-uniformly dispersed PLA inclusions in the TPS matrix, demonstrating that phase separation occurred [16]. Ljungberg and Wesslen blended PLA with tributyl citrate (TBC) and its oligomers, which decreased T_g of PLA. The PLA matrix became saturated with these plasticizers at certain concentrations and phase separation occurred [17]. Ouchi et al. synthesized branched PLAs with various lengths of graft chain by ring-opening polymerization of L- or D-lactide. The branched PLLA or PDLA film exhibited a lower T_g, melting temperature (T_m), crystallinity, Young's modulus and a higher strain at break point compared to the corresponding linear PLLA or PDLA film [18]. Recently, Oyama demonstrated a dramatic improvement in the mechanical characteristics of PLA by reactive blending with poly (ethylene-glycidyl methacrylate) [19].

While the above copolymerization or modifications were synthesized to improve the mechanical properties of PLA, they involved tedious processes, lacked toughness, or had phase separation. Thus, to improve the physical and mechanical properties of PLA for biomedical applications, we investigated the synthesis of a family of toughening biodegradable polymers with PLA [20]. PLA was reacted with 2-methacryloyloxyethyl isocyanate (MOI) and platicizers (TEC, DBP, acetylated monoglyceride, acetyl TBC). In this study, poly(ester-urethane) structured polymer materials were prepared. The synthesized polymers were characterized by FT-IR and NMR to identify the chemical structures. Their mechanical and thermal properties are presented and discussed. We found that the addition of MOI significantly improved the ductility of PLA and provided superior mechanical properties with much higher elongation and impact strength compared to PLA alone.

2. Experimental

2.1. Materials

Polylactide (PLA) (product NCP0003) was purchased from NatureWorks. 2-methacryloyloxyethyl isocyanate was obtained from Showa Denko. High purity toluene (HPLC grade) was
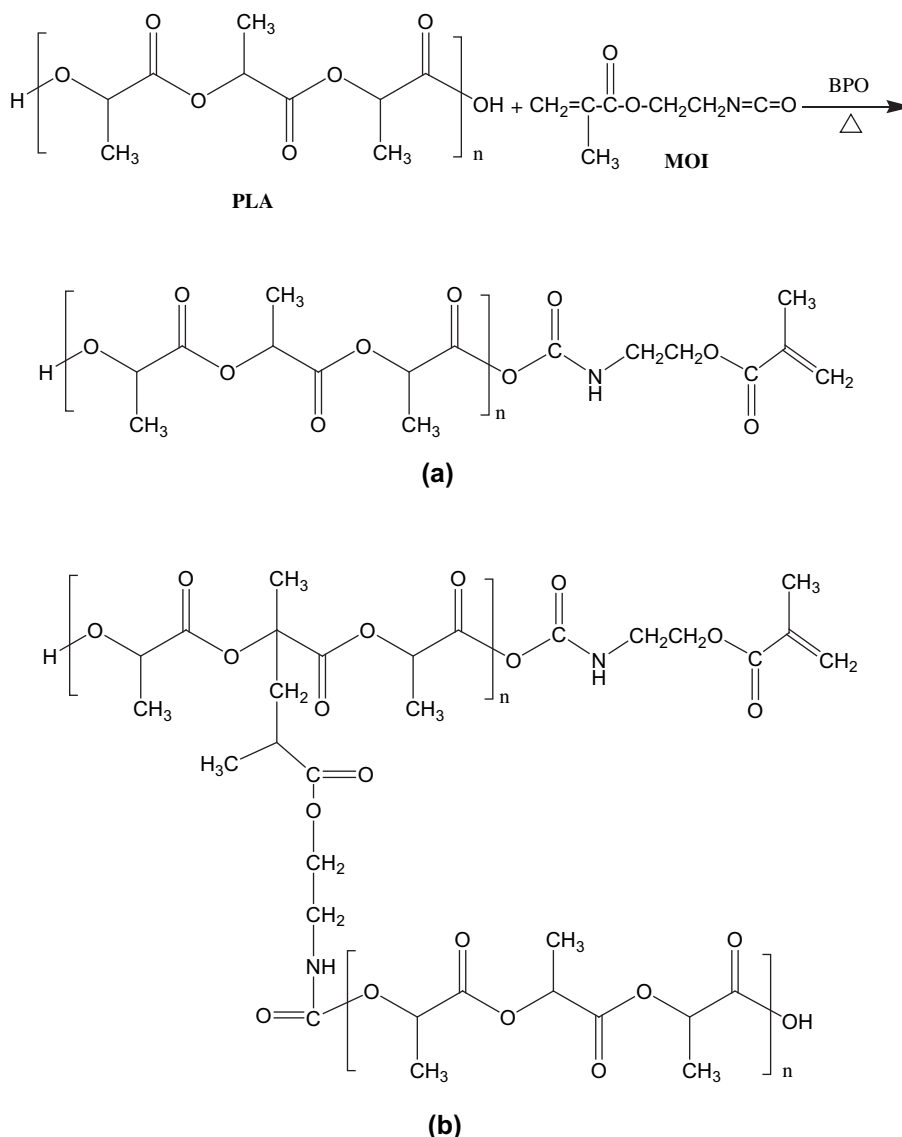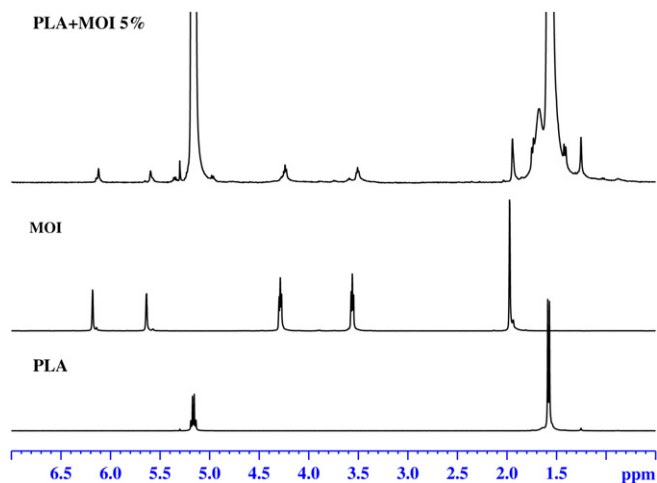

Scheme 1. Reaction scheme of MOI modified PLA.

Fig. 1. ^{1}H NMR spectra of PLA, MOI and modified polymer.

purchased from Tedia and used as received. 98% benzoyl peroxide (BPO) was obtained from Yuh Tzong Enterprise.

2.2. Synthesis of MOI modified PLA polymer

15 g of PLA was dissolved in 105 g of toluene while stirring at 85 °C in a 500 mL round-bottom flask purged with nitrogen. Various amounts of MOI (0.45, 0.75, or 1.5 g) and BPO (0.045 g) were added. The mixture was stirred for 8–12 h and the temperature was maintained at 105 °C.

The final mixture was spread onto glass plates to obtain modified PLA films. The films were vacuum dried at 60 °C for 2 h to remove solvent in a pre-heated forced air oven. The films (with a thickness of 50–60 μm) were cooled and stripped from the plates. To measure impact strength, these films were hot pressed to make Izod-type test specimen according to ASTM D256.

IR: 699 (N–H), 816 (C=CH$_2$), 1,094 (vs, C–O–C), 1,188 (vs,C–N, (CO)–O), 1,359 (CH), 1,449 (CH$_3$), 1,643 (C=C), 1,758 cm^{-1} (vs, C=O).

2.3. Characterization

^{1}H and ^{13}C NMR spectra were performed on a Bruker AMX-500 spectrometer with CDCl$_3$ as the solvent. Fourier transfer infrared (FT-IR) spectra were recorded on a Bio-Rad Digilab FTS-40 spectrometer. An Instron universal tester model 3369 was used to study the stress–strain behavior. The load cell used was 5 kg and the crosshead rate was 5 mm/min. Measurements were performed with film specimens (1.35 cm wide, 6 cm long and 50–60 μm thick). Impact strength was measured by an Izod impact tester according to ASTM D256. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer Pyris 1 TGA at a heating rate of 20 °C/min in N$_2$. Differential scanning calorimetry (DSC) data were obtained from a Perkin–Elmer Pyris Diamond DSC. Samples were scanned at a heating rate of 10 °C/min under N$_2$. The T_g values were measured as the change of the specific heat in the heat flow curves. Molecular weight was determined by gel permeation chromatography (GPC) with polystyrene calibration using a Perkin–Elmer series 200 HPLC system equipped with a Jordi Gel DVB column at 40 °C. Since the modified material is insoluble in THF, we dissolved the material in chloroform first and then mixed it with THF, prior to filtration and injection into GPC. The melt index was measured by a melt flow indexer GT-7100-MIB manufactured by GOTECH. Test procedure followed ASTM D1238 and the load was 2.16 kg. X-ray diffractograms (XRD) were obtained at room temperature on a Rigaku RINT 2000 instrument, using Ni-filtered Cu Kα radiation (40 kV, 100 mA). The morphologies of the polymer materials were observed with a JEOL JSM-6700 scanning electron microscope with an accelerating voltage of 3–5 kV.

Fig. 2. ^{13}C and DEPT 135 NMR spectrum of MOI modified PLA.
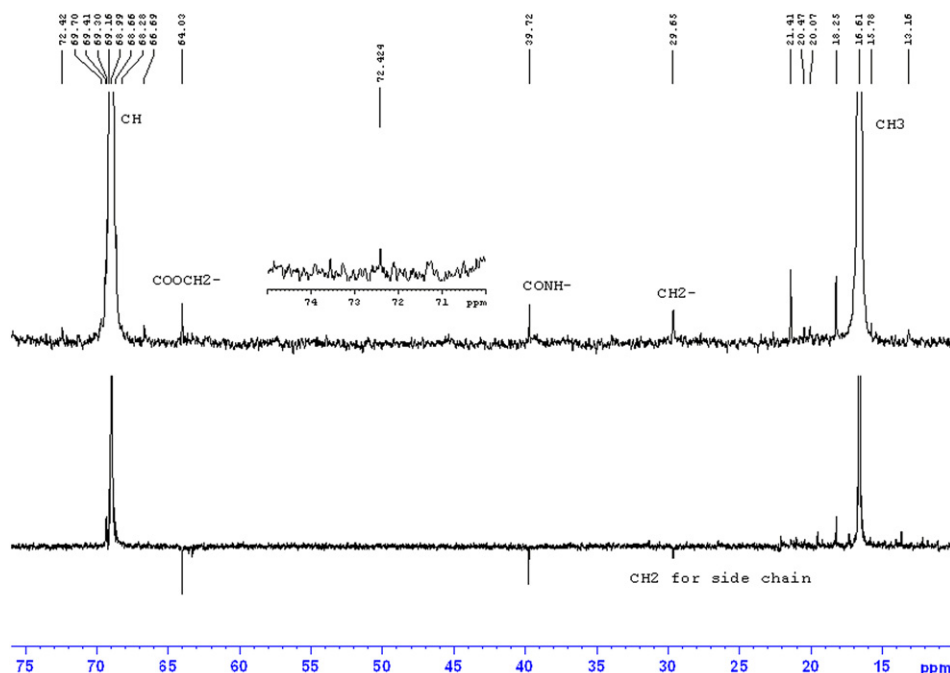
3. Results and discussion

3.1. Structure and NMR characterization

Based on the chemical structures of PLA and MOI, a reaction scheme was shown in Scheme 1a. Fig. 1 shows the ^{1}H NMR spectra of PLA, MOI and the modified polymer. Upon synthesis, MOI [$\delta = 1.97$ (CH$_3$), 3.56 (m, CH$_2$–NCO), 4.28 (m, CH$_2$–O(C=O)R), 5.63, 6.18 (CH$_2$=)] reacted with PLA [$\delta = 1.58$ (m, CH$_3$), 5.17 (m, CH)] and formed a modified PLA. However, after further investigation, we found that there was a small degree of crosslinking; ^{13}C and DEPT 135 NMR spectra revealed that $\delta 72.4$ is the position for a quaternary carbon atom (Fig. 2). Also, from heteronuclear multiple bond coherence (HMBC) spectrum (Fig. 3), we demonstrate that this compound has ^2J correlation between $\delta 72.4$ and CH$_2$ ($\delta 1.67$). An alternate reaction scheme was proposed, as shown in Scheme 1b. All of the spectroscopic data obtained were in agreement with the proposed structure.

3.2. Mechanical properties improvement

PLA materials are stiff, brittle and exhibit limited extendibility. The MOI modified PLA substantially improved the mechanical properties. Various mechanical properties of the prepared materials are summarized in Table 1. The prepared new ductile materials have a very high elongation at break (increases by ∼20 times when compared to neat PLA), but with lower tensile strength around 30 MPa (Fig. 4). The ultimate strain in all modified samples increased with the addition of MOI. Young's modulus of these samples decreased with the addition of MOI. All have observed yield points in the modified materials. For the PLA modified with 5% MOI and 8 h reaction time, elongation at break increased from 2.5% to 51%, tensile stress was decreased from 49 MPa to 26 MPa, Young's modulus was decreased from 3.29 GPa to 1.64 GPa, and impact resistance (notched) improved 1.6 times from 44.3 J/m to 71.2 J/m.

An 8 h reaction time was chosen because modified PLA exhibited better mechanical properties at that reaction time than at 6 or 10 h. The molecular weight measurements (by GPC) also demonstrated that the M_w and M_n of modified PLA increased with a reaction time up to 8 h. M_w increased from 15.4×10^4 (PLA) to more than 17×10^4, and then gradually decreased after 8 h.

Our results clearly show that reacting MOI with PLA is very effective for overcoming the brittleness of PLA and results in significant improvement in mechanical properties.

3.3. Thermal properties of modified PLA

Fig. 5 shows the DSC traces for the original PLA sample and MOI modified materials following heating to 200 °C and subsequent quenching. It is to be noted that all samples were characterized by a glass transition temperature (T_g), and melting peak (T_m), typical of semi-crystalline polymers. The values for these transitions are recorded in Table 2. Also listed in this table are estimates of the degree of crystallinity of these samples (χ_c%) calculated using a value of 87 J/g for the heat of fusion of the pure PLLA crystal [21]. The data shows that T_m of modified PLA materials decreases slightly with the addition of various amount of MOI. This trend is also reflected in the crystallinity. For the thermal decomposition of PLA materials, the 10% thermal decomposition temperature ($T_{d,10\%}$) reduced slightly from 357 °C (PLA) to 342 °C for PLA modified with 10% MOI (Table 2). $T_{d,10\%}$ also decreased with increased reaction time, which can be attributed to the thermal degradation of PLA at longer reaction times due to its thermal instability. The heat deformation temperature (HDT) for these PLA materials reduced slightly from 71 °C of PLA to 69 °C of 10% MOI modified material. These results indicate that the improvements in mechanical properties of PLA were achieved without sacrificing the thermal properties.

Table 1
Mechanical properties of PLA and modified polymer materials[a].

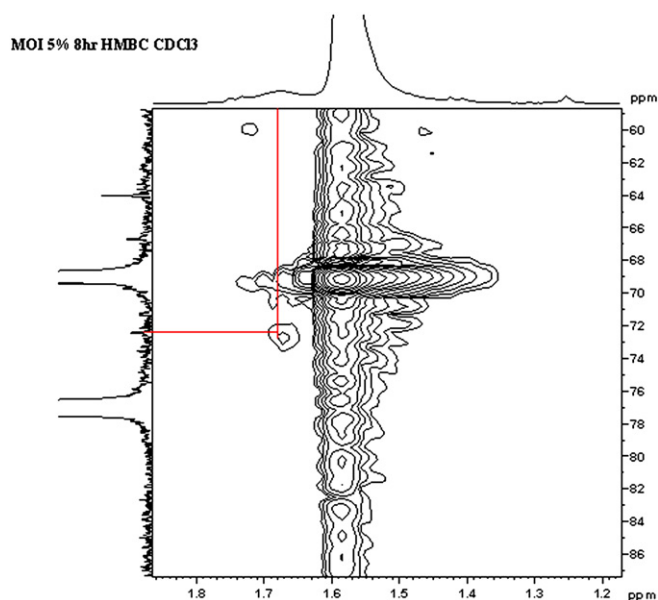| Material	Tensile strength MPa	Elongation at break %	Young modulus GPa	Impact resistance J/m
PLA	49.2	2.46	3.29	44.34
PLA + MOI(3%)	30.2	17.97	2.15	46.72
PLA + MOI(5%)	25.8	51.50	1.64	71.23
PLA + MOI(10%)	29.0	45.87	1.88	70.96

[a] Reaction time 8 h.

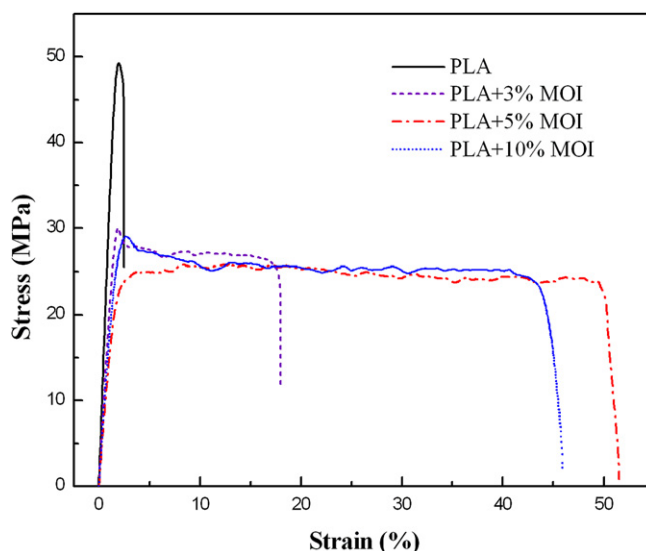Fig. 3. HMBC spectrum of 5% MOI modified PLA.

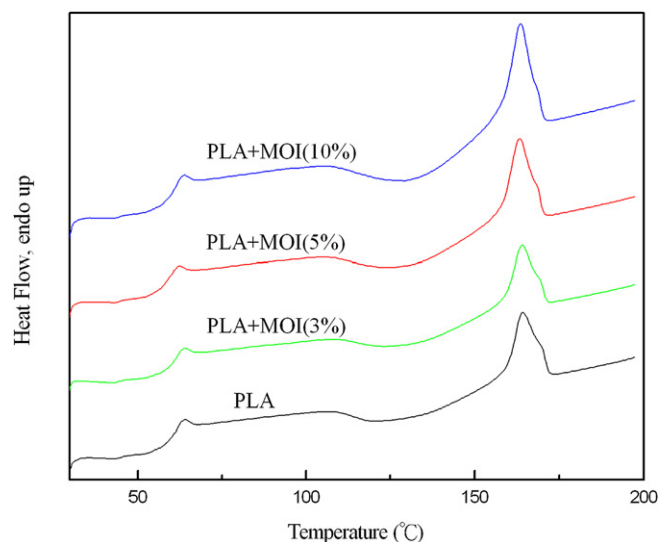Fig. 4. Stress–strain relationship for various amounts of MOI modified PLA materials.

Fig. 5. DSC scan of various amounts of MOI modified PLA materials.

Fig. 6. Melt index of PLA and 5% MOI modified material at various temperatures.

The melt index (MI) of modified PLA showed significant improvement as depicted in Fig. 6. At 240 °C, which is the operating temperature for melt-spun PLA, the MI for PLA modified with 5% MOI was 106.5 versus 68 for PLA alone. This indicates that the modified PLA material is suitable for textile processing to make biomedical materials.

Based on the mechanical and thermal properties data, we found that the effect of a small degree of crosslinking in the modified PLA was too little to have significant impact on the properties of these ductile materials. As for the amount of MOI, the optimum addition is around 5%.

3.4. Morphology of ductile PLA

The morphology of the ductile PLA materials was examined by XRD and SEM. XRD showed the strongest diffraction peak at $2\theta = 16.78°$, corresponding to the (200,110) reflection of the α-form crystals. As the data in Table 2 shows, the crystallinity of modified PLA decreases slightly with the addition of various amount of MOI. This trend was also reflected in the T_m data.

The morphology of the fractured surfaces (from stress−strain test) was elucidated by SEM to investigate the microstructure of modified materials. The SEM in Fig. 7a−b compared the fractured surface of 5% MOI modified film to pristine PLA. In Fig. 7a, pristine PLA showed a smooth and dense morphology. Minor cracks were observed, as a result of cutting brittle PLA. When MOI was reacted with PLA to prepare the modified polymer material, the morphology of the fractured surfaces changed substantially. Instead of a roughened surface, the cut surface of the modified PLA showed no cracks and exhibited a finely interconnected ant nest structure (Fig. 7b). The microstructure of MOI modified PLA material is another indication that reacting MOI with PLA makes ductile PLA materials.

Table 2
Thermal properties of PLA and modified polymer materials.

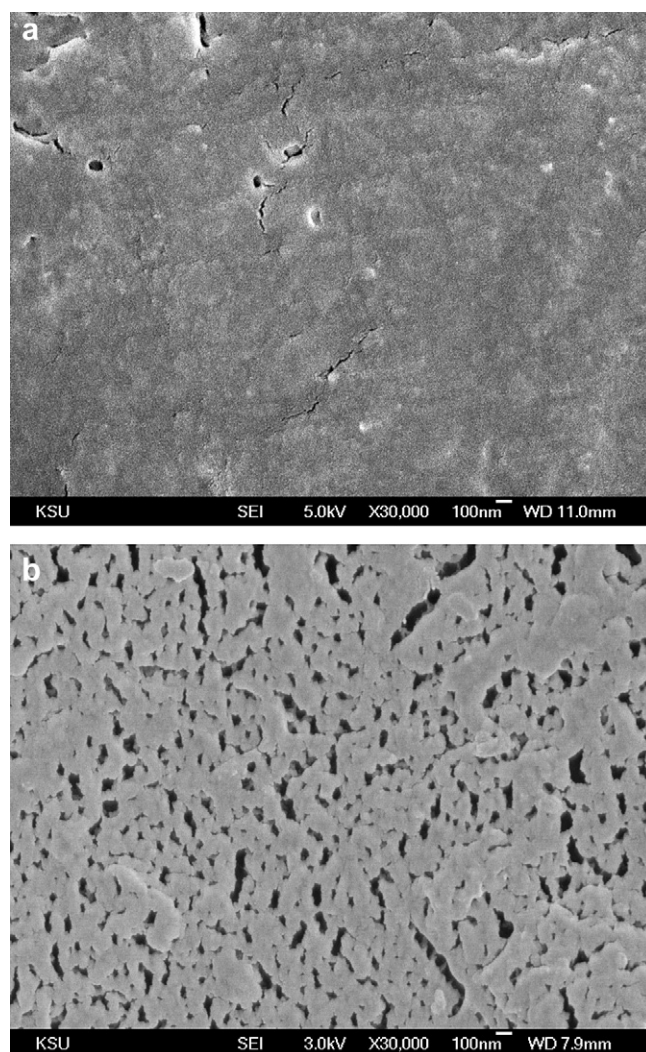| Material	Glass Transition T_g (°C)	Melting Peak T_m (°C)	Crystallinity χ_c(%)	Decomposition Temperature $T_{d,10\%}$ (°C)	Deformation Temperature HDT(°C)
PLA	60.59	164.19	40.76	357	71
PLA + MOI(3%)	60.14	163.37	38.45	347	71
PLA + MOI(5%)	59.23	163.18	37.57	344	70
PLA + MOI(10%)	60.79	163.52	38.29	342	69
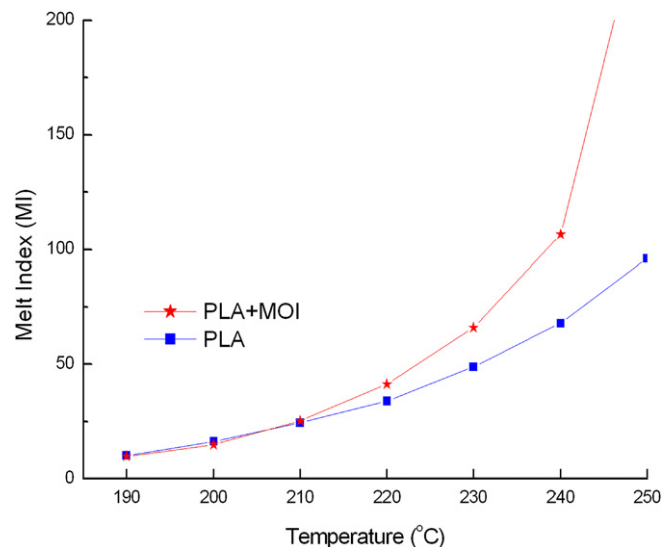
Fig. 7. SEM morphology of (a) pristine PLA and (b) modified with 5% MOI (8 h reaction) material.

4. Conclusions

A novel synthesized MOI modified PLA polymer material demonstrated markedly improved mechanical properties. The prepared ductile PLA material showed elongation at break 20 times higher than that of neat PLA. The PLA + 5% MOI material had impact strengths nearly 2 times higher than that of original PLA. The melting index is higher than 100 at 240 °C. The improvements in mechanical properties were achieved without sacrificing the thermal properties of PLA. Further studies will investigate the biocompatibility of the modified PLA material under physiological conditions to evaluate the ductile polymer material in biomedical applications.

Acknowledgements

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