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Preparation of Polylactide/Modified Clay Bio-composites Employing Quaternized Chitosan-Modified Montmorillonite Clays for Use as Packaging Films

Tu Phuong Pham Le, Pakorn Opaprakasit*

School of Bio-Chemical Engineering and Technology, Sirindhorn International Institute of Technology (SIIT), Thammasat University, Pathum Thani 12121, Thailand
pakorn@siit.tu.ac.th

Composite materials of polylactide (PLA) have been a popular environmentally-friendly and low-cost bio-composite that is used for packaging applications. Clay has been used as fillers to improve the mechanical properties of PLA and enhance the gas permeation properties of the composites. However, adding unmodified clay to PLA leads to a reduction in its tensile strength and elongation at break, due to its incompatibility with PLA. In this study, Montmorillonite clay was modified with highly-positive charged quaternized chitosan (QC) by a solution mixing process. The modification efficiency was evaluated through the change in d-spacing values of the clays by X-ray diffraction spectroscopy. Fourier transform infrared (FTIR) spectroscopy was used to study the changes in the structures of the clays. QC with 50 % DQ at 10 % concentration, 2.5 % solid content, 1,000 rpm of stirring speed, and by ultra-sonication (70 % amplitude in 15 min) were observed as the optimum conditions to modify Montmorillonite. The d-spacing value increased from 12.4 Å to 20.3 Å, after the modification, which is comparable to the 18.2 Å of commercial Cloisite 30B. The modified clays were then mixed with PLA to generate bio-composite materials. The results show that adding the modified clays (at up to 5 wt%) leads to a slight reduction in tensile strength and modulus, but a modest increase in the elongation at break of the material, compared to neat PLA. Tensile strength, strain, modulus, and elongation at break of the bio-composite are 41.60 ± 2.06 (MPa), 2.97 ± 0.15 (%), 1,740 ± 140 (MPa), and 3.00 ± 0.16 (%), in comparison with 46.20 ± 4.04 (MPa), 2.67 ± 0.26 (%), 2,015 ± 301 (MPa), and 2.79 ± 1.28 (%) for neat PLA. Moreover, the bio-composite shows an impact strength improvement of about 20 %, compared to neat PLA. Hence, QC can be applied as a promising agent to modify Montmorillonite clay for preparing bio-composites. These composites can maintain high mechanical properties and degradability with an improvement in impact strength are suitable for packaging applications.

1. Introduction

The replacement of petroleum-based polymers by degradable polymers in commercial use has been a major research focus, due to serious environmental issues. Poly(lactic acid) (PLA) is a thermoplastic polyester produced from polycondensation of lactic acid or ring-opening polymerization of lactide dimer, which has attracted vast attention. This is due to its impressive degradability, good mechanical properties, and proficient processing. Nevertheless, low flexibility, brittleness, poor thermal stability, and a low oxygen barrier have been significant disadvantages of PLA, which limit its use in packaging applications (Lv et al., 2018). Remarkable enhancements of mechanical, gas barrier, and optical properties of polymers can be achieved with an addition of a small amount of nano-scaled fillers into the polymer matrix (1 wt% or lower of nano-fillers), compared to conventional micro-composites (more than 30 w% of micro-fillers), due to stronger interactions and better compatibility with the organic polymer matrix. Clay minerals, such as montmorillonite, hectorite, saponite, and their derivatives have been commonly employed as either micro- or nano-scaled fillers. Among these, montmorillonite is a preferred choice as a cationic clay, for producing polymer/nano-composites. Small positive- charged species between the silicate layers of clays can be replaced by more hydrophobic ammonium cation groups with long alkyl chains, by clay modification processes. Upon mixing these modified

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clays with the polymer matrix, intercalation and exfoliation affect the morphologies of the resulting nanocomposites. These morphologies depend on the distribution/dispersion of these silicate platelets in the polymer matrix (Roy et al., 2019).

Various types of cationic polymers have been developed and employed in the preparation of modified clays. Chitosan, the second most abundant natural polysaccharide after cellulose, is promising candidates. Chitosan has been modified by grafting with glycidyl trimethyl ammonium chloride (GTMAC) and carboxymethylation. The modified chitosan has been used as intercalating agents for modifying clays and further generating nano-composites for antimicrobial and biomedical applications (Liu et al., 2013). Self-assembled quaternized chitosan nanoparticles have been used to expand interlayers of clays to form an inorganic-organic nanohybrid of clay-chitosan, and used as reactive reinforcing agents for toughened epoxy nanocomposites (Zabihi et al., 2017).

Insights into the effects of the preparation conditions on the properties and performance of the modified clays and resulting nano-composites are essential in further improvements of the materials for specific applications. However, these have not been investigated in detail. In this study, the clay-modification parameter effects, i.e., positive charge density of QCs, concentration of QCs, solid content, stirring speed, and ultra-sonication power, on the degree of intercalation are examined. Mechanical properties of the resulting PLA/modified montmorillonite bio-composites are also studied.

2. Materials

Chitosan (MW= 232.48 KDal, average deacetylation degree of 82.6 %) and glycidyltrimethylammonium chloride (GTMAC) (90 % purification and 75-80 % in water) were purchased from Sigma Aldrich (USA). Montmorillonite, naturally occurring mineral mined and crushed to 200 mesh powder without any chemical processing, was supplied by Alfa Aesar (USA). Polylactide (PLA) LX175 was provided by Corbion Purac (Netherlands) with density of 1.24 g/cm^3 and melt flow index (at 190 °C) of 3 g/10 min . Acetic acid, acetone, and ethanol were of analytical grade, and were used without further purification.

3. Experimental

3.1 Synthesis and characterization of quaternized chitosan (QC)

Quaternized chitosan (QC) was prepared by grafting GTMAC onto the chitosan structure, utilizing the reactions of -OH or -NH$_2$ groups and epoxy groups (Loubaki et al., 1991). Chitosan (2.5 %) was partially dissolved in 80 mL of water for 24 h. GTMAC was then added to the dispersion, followed by heating to 60 °C for 24 h. The solid product was collected by precipitation in cold acetone, washed several times with ethanol in an ultra-sonication bath, and dried at 60 °C. The chemical structures of the obtained QC products were characterized by Fourier transform infrared (FTIR) spectroscopy (Thermo Nicolet. 6,700, USA) and nuclear magnetic resonance (NMR) spectroscopy (Bruker 300 MHz NMR spectrometer, USA). The water solubility of the products was tested by dissolving in distilled water at room temperature for 24 h, and separated by centrifugation at 5,000 rpm for 15 min.

3.2 Modification and characterization of Montmorillonite clay

Chitosan and QC samples were dissolved in water containing 100 µL of 1 M acetic acid. Montmorillonite clay was incubated in water at 37 °C for 24 h. Solutions of different chitosan samples were then added to the clay dispersion under strong mechanical stirring and kept stirring at the same speed for 2 h, followed by drying in an oven at 60 °C for 24 h. The clay samples before and after modification were characterized by X-ray diffraction spectroscopy (XRD PANalytical X'Pert PRO) to assess the intercalated extent of the clays by chitosan derivatives. FTIR spectra of the samples were measured on a Thermo Nicolet-6,700 spectrometer to observe the presence and effects of chitosan derivatives on the clay structure.

3.3 Fabrication and characterization of bio-composite films

The modified and original Montmorillonite clays were blended with PLA in an internal mixer (Chareon Tut, Thailand) at 170 °C for 10 min, using a stirring speed of 50 rpm. The resulting PLA/clay composites and neat PLA were then pressed into a film form by a compression molding machine (Chareon Tut, Thailand) at 170 °C, using 2,000 psi pressure for 5 min. The specimens for tensile testing were prepared in a rectangular shape, 15 mm width and 100 mm of gauge length, following the ASTM D882 standard procedure. The tensile tests were performed at least 5 times for each sample on a Universal testing machine (H5TK, Tinius Olsen, UK). For Izod Impact (Notched) tests, the specimens were prepared in a similar procedure, with dimensions of 64×12.7×3.2 (mm) according to the ASTM D256, followed by making notches using a milling machine (ComeTech testing machine, Taiwan). The measurements were conducted at least 5 times for each sample on an impact tester (ComeTech testing machine, Taiwan).

4. Results and discussion

4.1 Structures and properties of QC

The quaternizing efficiency of chitosan is monitored by the changes in the intensity and pattern of bands in the 3,200-3,500 cm^{-1} region. Sharp splitting bands of the N-H stretching mode of primary amine disappear in this region, resulting in a broad smooth band of the O-H stretching modes of the remaining hydroxyl groups. There is also a reduction in the intensity of the 1,590 cm^{-1} band of the N-H bending mode of primary amine. These bands indicate a decrease in the content of the primary amine groups. In contrast, an appearance of a sharp strong band at 1,480 cm^{-1} of the C-H bending mode and an increase in the intensity of a band at 1,607 cm^{-1} of the C-N-C bending mode of trimethyl ammonium groups are observed in QC, as shown in Figure 1a. This implies a successful introduction of GTMAC into the chitosan structure. If excess GTMAC (relative to the amount of primary amine groups) is used (Figures 1a-iv and 1a-v), the grafting reaction occurs at both the primary amine and primary alcohol positions, resulting in an increase in the intensity of the C-O-C bending at 1,050-1,150 cm^{-1} (Santos et al., 2016).

^{1}H NMR spectra of the chitosan samples before and after modifications, measured in D_2O/CD_3COOD and D_2O solvents, are compared in Figure 1b. For the samples prepared from GTMAC: NH_2 molar ratios of 1:3 and 1:1, QC(13) and QC(11), the proton signal H^{-2} at 2.85 ppm decreases, while a new peak at about 3 ppm (assigned to protons in $N^{+}(CH_3)_3$) emerges. Other signals in the region of 3.4-3.7 ppm are relatively unchanged after the quaternization. However, in samples with excess GTMAC, QC(31) and QC(51), the signal at 3.5 ppm of H^{-6} also decreases along with a sharp reduction of the H^{-2} signal. This implies that grafting also occurs on the primary alcohol group at the C-6 position (Song et al., 2018). The degree of quaternization (DQ %) is calculated, based on the integral of the $N^{+}(CH_3)_3$ signal at 3.0 ppm and that of H^{-1} signal at about 4.05-4.35 ppm (Luan et al., 2018). The calculated-DQ (%) values for QC(13), QC(11), QC(31), and QC(51) are 19, 32, 56, and 90 %, respectively . In terms of water solubility, QC(31) with 56 % DQ and QC(51) with 90 % DQ are almost completely dissolved in water. The QC with 19 % DQ and 32 % DQ show only about 15 % solubility, which are in a good agreement with those previously reported (Loubaki et al., 1991).

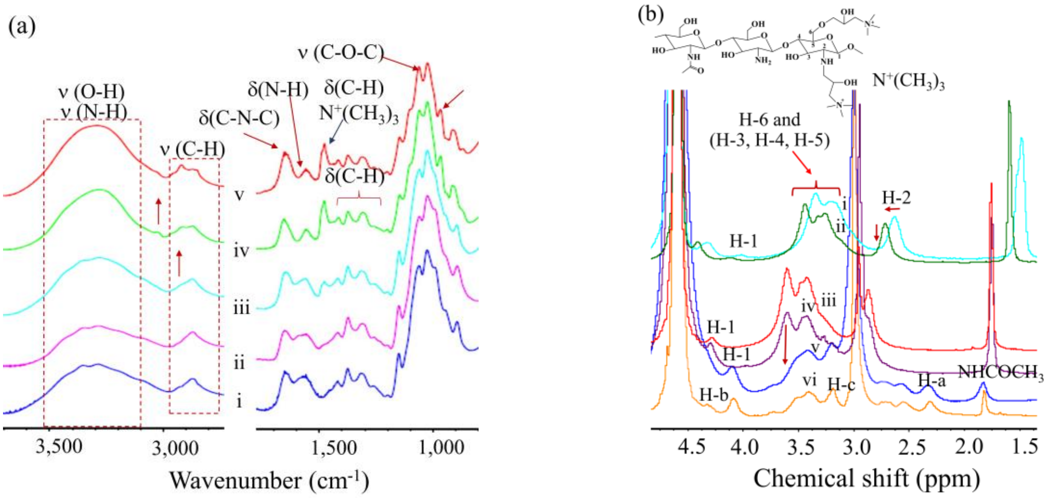

Figure 1: (a) FTIR spectra of (i) native chitosan, (ii) QC(13), (iii) QC(11), (iv) QC(31) and (v) QC(51); and (b) ^{1}H NMR spectra of (i, ii) native chitosan, (iii) QC(13), (iv) QC(11), (v) QC(31) and (vi) QC(51)

4.2 Optimum conditions for modifying Montmorillonite clays by QC

The resulting QCs were employed in the modification of Montmorillonite clays. Effects of modification parameters on inter-lamellar structures of the clays are investigated by observing their maximum basal spacing (d-spacing) from XRD spectra. The inter-layer distance (d_{001}) is observed at 2θ= 7.1° (12.4 Å) for neat montmorillonite. In addition, diffraction peaks at 19.8° (4.5 Å), 29° (3.0 Å), and 35° (2.6 Å) also contribute to the clay's sheet structure. In contrast, characteristic signals of quartz are observed at 20.8° (4.3 Å) and 26.6°

(3.3 Å), and illite is at 27.6° (3.2 Å) (Maina et al., 2016). Upon treatment at a stirring speed of 1,000 rpm, in combination with ultra-sonication (70 % amplitude for 15 min), QC (50 % DQ) at 10 % concentration in 2.5 % solid content, the basal spacing has been shifted from 12.4 Å to 20.3 Å. This is comparable to the 18.2 Å for commercial Cloisite 30B (Figure 2a). The shift of the basal spacing to a lower angle at 2θ= 3-5° implies the penetration of QC molecules into the interlayers of clay, resulting in the expansion between interlayers. This confirms the formation of an intercalated nano-structure (Hong et al., 2011). When the clay was treated by only sonication without chemical modifiers, the basal spacing signal at 7.1 ° is broad, while the 27.6° signal is split into two signals at 27.4° and 28.1°. This reveals a loss in well-ordered coherence between the clay layers in the structure (Tiwari et al., 2008). This is in good agreement with those observed in FTIR spectra, in which the tetrahedral Si-O band at 1,050 cm^{-1} shifted to the Si-O of amorphous silica at 1,095 cm^{-1}. This indicates the presence of a higher content of amorphous silica in the structure after modification, originating from the partial collapse of the tetrahedral sheets (Krupskaya et al., 2017) (Figure 2b).

The position and curve-resolved areas of the interlayer spacing signal located in the 4-10° region were employed to examine the degree of the clay's interaction/exfoliation, as summarized in Table 1. Under ultrasonication, modified montmorillonite achieves three major peaks at 11.6 Å, 14.3 Å, and 16.8 Å with an area integration for α-Cristobalite of 25, 22, and 13, respectively, compared to 37 for the major peak at 12.4 Å of neat Montmorillonite. A portion of the structure has a basal spacing of 11.64 Å, as a result of the aggregation of silicate layers, which is the tactoid structure of clays (Hong et al., 2011). Hence, ultra-sonication without QC could not effectively intercalate montmorillonite. Under mechanical stirring with QC as the modifier, a new peak at 19.7 Å appears with an area peak integration of 14. The peak integration at 12.4 Å reduces from 37 to 33. Under assisted ultrasonication, QC shows better penetration into inter-layers Montmorillonite with a lower area for the peak integration at 12.4 Å of 29 and a higher area the peak integration at 14.1 Å, 17.2 Å, and 20.3 Å of 28, 50, and 25, respectively. Moreover, the appearance of different major peaks shows that the modified montmorillonite has different basal spacings.

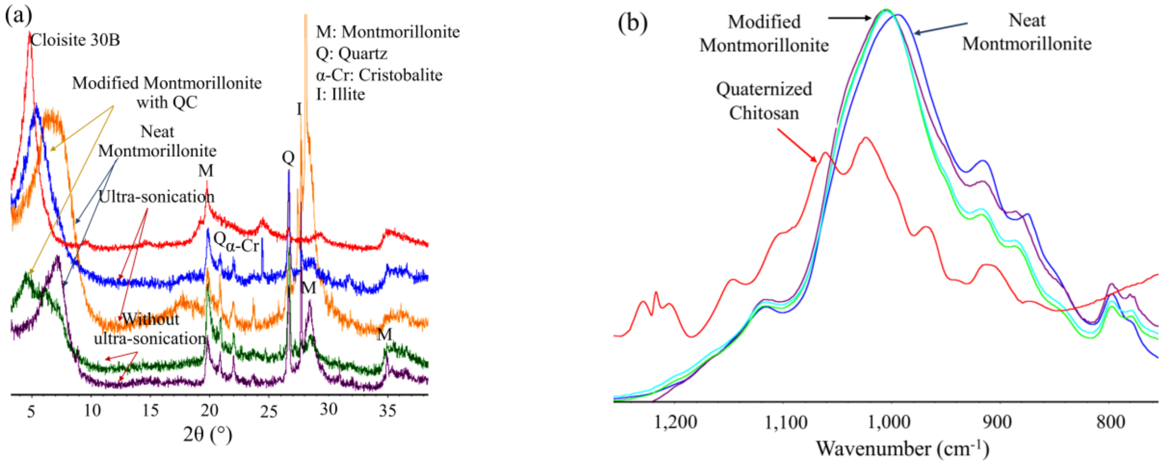

Figure 2: (a) XRD results and (b) FTIR spectra of neat Montmorillonite and modified Montmorillonite

Table 1: Summary of modification efficiency, based on the change in the area ratio A/A', in which A' is the area of the peak for α-Cristobalite

Sample	d-spacing (Å)	Peak Area (A)	A/A' ratio
Neat Montmorillonite	12.4	1222	37
Montmorillonite with QC(31)	19.7	350	14
	12.4	831	33
Montmorillonite_ultra-sonication	16.8	465	13
	14.3	775	22
	11.6	882	25
Montmorillonite_QC(31) and ultra-sonication	20.3	406	25
	17.2	793	50
	14.1	455	28
	12.4	461	29

4.3 Characterization and mechanical properties of PLA/modified clay bio-composites

The chemical structure and properties of the resulting bio-composites are examined. FTIR spectra of the composites (not shown) show an increase in the intensity of the O-H stretching band, reflecting a slight degradation of PLA chains after the mixing process at 170 °C. Similarly, the degradation with Cloisite 30B at high temperature (175 °C) in an internal mixer was evaluated via intrinsic viscosity. PLA with 3 wt% of Cloisite 30B shows a significant reduction in intrinsic viscosity, compared to neat PLA. The thermal degradation of composites can be accelerated by modified clays due to the association between the organic modifier on the silicate layers and the PLA matrix (Meng et al., 2012). In terms of mechanical properties (Figure 3), the bio-composites of PLA/modified montmorillonite with QC (50 % DQ) show a slight decrease in tensile strength and modulus, compared to neat PLA, for up to 5 wt%. Similar results are also observed in PLA/Cloisite 30B composite and PLA/modified silica composite. However, with 10 % of the clays, the tensile strength experiences a significant drop. This is likely because of the poor interface between the fillers and the polymer matrix as a result of a broad distribution of clay interlamellar structures that are observed by XRD. Mohamad et al. (2018) similarly found that tensile strength of PLA/natural rubber/graphene nano-composite is remarkably dependent on good dispersion of graphene in the matrix of PLA/natural rubber and graphene with lower amount can be well dispersed in the polymer matrix leading to the enhancement of interfacial banding between filler and polymer matrix (Mohamad et al., 2018). At a mixing ratio of 1.25 wt%, the bio-composite shows an improvement in elongation at break of about 20 %, and impact strength of 25 %. Increasing amount of modified montmorillonite in bio-composite from 1.25 wt% to 5 wt% cause a slightly decrease in elongation at break and impact strength which also happened in the case of adding graphene into PLA/epoxidized natural rubber (ENR) matrix. The impact strength of PLA/ENR/graphene composite increases almost twice with 1 phr of graphene but remarkably decreases with 2 phr of graphene. The reduction of load transfer efficiency from polymer matrix to nano-filler is a result of agglomeration and stacking of the nano-filler in the polymer matrix at high loading amount (Abdullah et al., 2019).

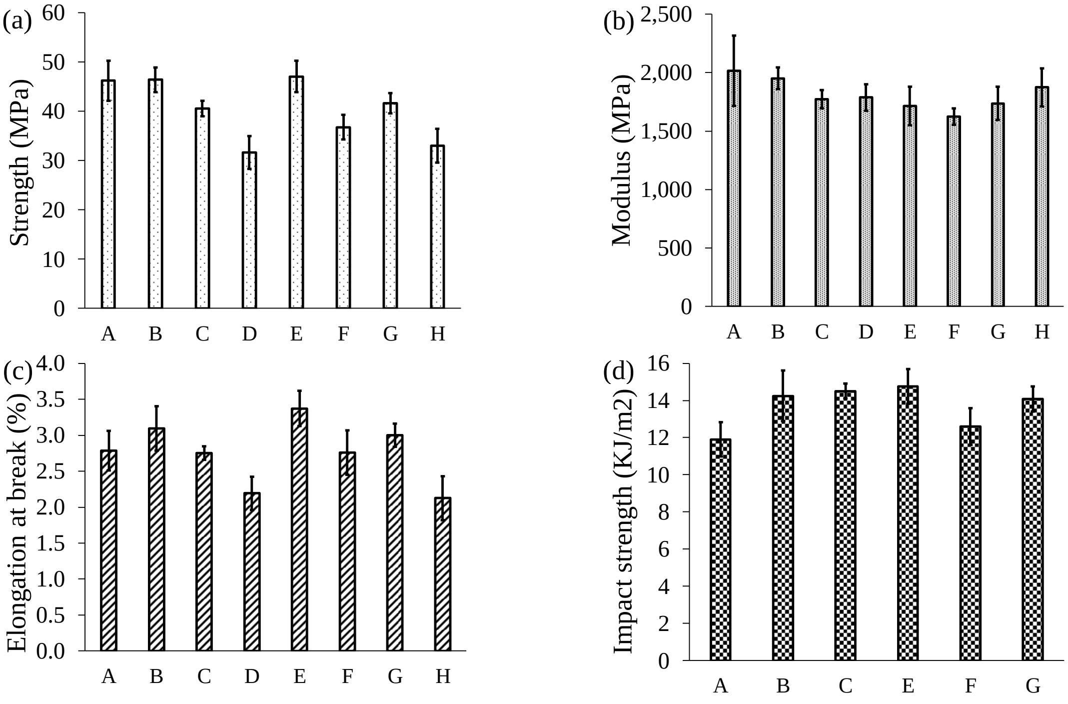

Figure 3: Mechanical properties of (A) Neat PLA, Composite with various unmodified clay percentages: (B) 1.25 %, (C) 5 %, (D) 10 %, and composites with various modified clay percentages: (E) 1.25 %, (F) 2.5 %, (G) 5 %, and (H) 10%

5. Conclusions

Quaternized chitosan has been used as modifiers to intercalate montmorillonite, which is more effective with the application of ultra-sonication. The following treatment conditions are identified as optimized: 10 % concentration of QC (QD= 50 %) in 2.5 % or 5 % of solid content, stirring speed of 1,000 rpm, and ultra-sonication (70 % amplitude) for 15 min. The products are comparable to commercial Cloisite 30B, in terms of interlayer expansion. However, the modified montmorillonite interlamellar structure is not as homogeneous as Cloisite 30B, reflected by a broad basal spacing distribution observed by XRD. The resulting modified clays are then used in the preparation of PLA bio-composites. The addition of this modified Montmorillonite to PLA (up to 10 wt%) leads to significant degradation of PLA chains at high processing temperature in a twin-screw extruder, resulting in a drop in mechanical properties of the composites. However, when lower contents of the modified Montmorillonite are added (up to 5 wt%), only a slight reduction in tensile strength and modulus are observed, but elongation at break and impact strength slightly increase. Hence, this process can modify montmorillonite for further preparation of PLA/modified Montmorillonite bio-composites, for packaging applications.

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