Properties of Compatibilized Polylactide Blend Films with Gelatinized Corn and Tapioca Starches

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ABSTRACT: Blend films containing two types of starch, various amounts of methylenediphenyl diisocyanate (MDI), and polylactide were prepared. The effects of MDI level and starch type on the tensile, thermal, and morphological properties of these films were investigated. The MDI amount was varied from 0 to 10 wt % on the basis of gelatinized starch (GS) content, whereas two types of starch (corn and tapioca) were added as fillers. In this study, the blend films were hot-mixed at 180°C by an internal batch mixer and then compression-molded to form test specimens. The results show that the addition of MDI as a compatibilizer led to an increase in the tensile properties compared with the uncompatibilized films. Furthermore, the thermal properties indicated some improving interfacial adhesion between the two phases, as evidenced by the morphological results. These behaviors were observed in the blends with both gelatinized tapioca starch and gelatinized corn starch. The different types of starch had no effect on the glass-transition and melting-temperature shifts, including water absorption of the blend films. On the other hand, the mechanical properties of the blends with gelatinized corn starch were higher than those of the others. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2305–2311, 2010

Key words: biodegradable; blends; compatibility; films

INTRODUCTION

The evergrowing production and development of plastics have resulted in not only profitable usages but also serious problems. Thousands of tons of plastic waste are discarded every year. They cannot be degraded when they are exposed to the environment because, generally, they are inherently inert to microorganisms and some chemicals in nature. Disposal of these wastes is expensive and leads to environmental problems, such as air, water, and soil contamination.[1,2] Moreover, alternative disposal methods, such as recycling, reuse, and the burying of plastic trash, are uneconomical and troublesome. For these reasons, there has been increased interest in the production and utilization of fully biodegradable polymers to replace nonbiodegradable plastics, especially those used in packaging applications.

Generally, polymers from renewable resources can be classified into three groups: (1) natural polymers, such as starch, protein, and cellulose; (2) synthetic polymers from natural monomers, such as polylactide (PLA); and (3) polymers from microbial fermentation, such as polyhydroxybutyrate.[3] Like most petroleum-based polymers, many properties of polymers from renewable resources can also be improved through blending and composite formation. Hence, the development of synthetic polymers with monomers from natural resources together with blending technology is one alternative direction for the expansion of various implementations of biodegradable polymers.

One of the most promising polymers in this regard is PLA because it is readily biodegradable and several properties of PLA are comparable to commercial polymers. PLA, a linear aliphatic polyester, is commercially interesting, not only because of its biodegradability but also because of its good strength, film transparency, biocompatibility, and availability from renewable resources; however, PLA is brittle and still more expensive than conventional plastics.[4–9] To modify various properties or to lower its costly price, studies on PLA blends with other polymers have been carried out.[10–16] The blending of PLA with starch and an appropriate plasticizer is one of several methods for improving these drawbacks because starch is readily available and is one of the most economical biopolymers.[17–21]

Tapioca and corn are the main economic crops in Thailand. They are inexpensive and abundant; therefore, it would be a great opportunity for Thailand to exploit them as raw materials for the preparation of

biodegradable plastics. Moreover, the incorporation of these low-cost biodegradable raw materials into PLA is another promising route for increasing their added value. Although incompatibility and poor interfacial adhesion due to differences in the polarity and hydrophilicity of these two phases, PLA and starch, leads to poor mechanical properties, these problems can be overcome with an efficient compatibilizer that can react with both matrix and filler. Methylenediphenyl diisocyanate (MDI), which is highly reactive with both hydroxyl and carboxyl groups to form urethane linkages, could be a good compatibilizer between starch and PLA.[22,23]

Therefore, in this research, we focused on the preparation of biodegradable polymer blends of gelatinized corn starch (GCS) and gelatinized tapioca starch (GTS) with PLA (40 : 60 w/w). The effects of MDI level and starch type on the mechanical, thermal, and morphological properties, including the water absorption, of the blend films were investigated. Glycerol and poly(ethylene glycol) 400 (PEG400) were used as plasticizers, whereas MDI was used as a compatibilizer to improve the interfacial interaction and compatibilization of the blends.

EXPERIMENTAL

Materials

PLA resin (PLA 4042D) was purchased from Nature-Works LLC (Cargill-Dow, Minneapolis, MN). The PLA pellets were transparent with a glass transition temperature (T_g) of 58–60°C and a density of 1.24 g/cm^3, as reported by the manufacturer. The weight-average molecular weight of PLA was 130,000 Da (polydispersity index = 1.46), as determined by gel permeation chromatography in tetrahydrofuran. Glycerol (99.5% pure), PEG400, and MDI were obtained from Siam Chemical Industry Co., Ltd., Bangkok, Thailand. The tapioca and corn starches, containing amyloses of approximately 30 and 32 wt %, respectively, were used as biodegradable additives. The percentages of amylose were determined by a rapid method for the estimation of amylose in maize starches.[24]

PLA plasticization

The PLA pellets were dried in a vented oven at 60°C overnight before processing. Then, they were mixed together with 10 wt % PEG400 with an internal batch mixer (PL2000, Brabender Plasticorder, South Hackensack, NJ) at 180°C and 60 rpm for 20 min. After that, the plasticized PLA was pulverized by means of a crusher. Finally, the plasticized PLA powder was dried in a vented oven at 60°C and stored in a desiccator.

Gelatinization

The corn and tapioca starches were premixed with water and glycerol at 10 and 25 wt %, respectively, with a high-speed mixer and then mixed in a two-roll mill (Scientific, Labtech Engineering, Samutprakarn, Thailand) at a rolling speed of 10 rpm at 130°C for 10 min until GS was homogeneously formed. Then, they was pulverized by means of a crusher and dried in an air oven at 60°C for 24 h.

Film preparation

The gelatinized starches (GSs) and PLA (40 : 60 w/w) were blended in an internal batch mixer at 180°C for 4 min. The operating screw speed of the internal batch mixer was 90 rpm. Five different amounts of MDI (0.62, 1.25, 2.50, 5.0, and 10 wt %), on the basis of GS content, were added as compatibilizers. An uncompatibilized blend was also taken in the same way for use as a reference material. After that, each blend specimen was pulverized by means of a crusher and was then compression-molded. The optimum holding pressure, temperature, and time were 1500 psi, 170°C, and 15 min, respectively.

Morphological studies

Scanning electron microscopy (SEM; JSM 6480, JEOL, Tokyo, Japan) was used to characterize the surface of the blend films. For SEM analysis, the surface and fractured surface of the blend films were coated with a thin layer of gold before scanning. SEM was done at 15 kV to image the films.

Thermal properties

The thermal properties of the GS/plasticized PLA (40/60 w/w) blend films were evaluated with a differential scanning calorimeter (DSC7, PerkinElmer, Waltham, MA). Samples with an average weight of 12 mg encapsulated in a hermetically sealed aluminum pan were prepared for each test. The thermal histories of all of the samples were removed first by heat scanning from 25 to 200°C, followed by sample quenching to −30°C, and finally by heating again to 200°C at heating and cooling rates of 10 and 20°C/min, respectively. T_g, the melting temperature (T_m), and the heat of fusion of the samples were recorded. The degree of crystallinity for the PLA phase was calculated with the following equation:

$$\% \, \text{Crystallinity} = \frac{\Delta H_f^*}{\Delta H_f^0} \times 100 \qquad (1)$$

where ΔH_f^* is the heat of fusion for the semicrystalline PLA blend and ΔH_f^0 is the heat of fusion for the 100% crystalline PLA, which was equal to 93.6 J/g.[23]

Tensile testing

Tensile testing of rectangular film specimens with 15 mm wide, 150 mm long, and about 250 μm thick was conducted with a universal testing machine (LR100K, Lloyd, Fareham, UK) at a crosshead speed of 10 mm/min and a gauge length of 100 mm, according to ASTM D 882-02. A 100-N load cell was used to measure the tensile properties of the blend films. At least five specimens of each film were tested, and the results were averaged to obtain a mean value.

Water absorption

The blend films (25.4 mm × 76.6 mm × 250 μm) were used for a water absorption test. These specimens were dried at 50°C for 24 h and cooled to room temperature. The dried films were immersed in distilled water at 25°C for specific intervals according to ASTM D 570-98. The specimens were removed from the water, blotted with tissue paper to remove excess surface water, and then weighed. Three replicates were tested for each treatment. The water absorption was calculated on a dry basis.

Figure 1 Tensile properties of GS and plasticized PLA blend films (40 : 60) with various MDI contents: (a) tensile strength and (b) elongation at break. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Mechanical properties

The tensile strength and elongation at break of the GS/plasticized PLA (40/60 w/w) blend films with different MDI contents are illustrated in Figure 1(a,b), respectively. Poor adhesion between the plasticized PLA and GS was evidenced by weak tensile strengths [i.e., 8 and 12 MPa for blend films without MDI of GTS and GCS, respectively] because the GS in the plasticized PLA matrix without MDI acted as a stress concentrator. Obviously, at lower MDI contents (0.62 and 1.25 wt %), both the tensile strength and elongation at break increased compared to those in the blend films without MDI. However, with further increasing MDI concentration (i.e., >1.25 wt %), the tensile properties of the blend films gradually decreased and were even lower than those with 0.62 wt % MDI or without MDI. These results can be described as follows: in the blending system without MDI, the interfacial bonding was poor, and the particles of the dispersed starch phase acted as stress concentrators, which resulted in a low strength and elongation at break. As MDI was added, chemical bonding likely occurred between the starch and plasticized PLA phases; this implied that the interfacial bonding between the two phases was improved, and consequently, the tensile strength and elongation increased.
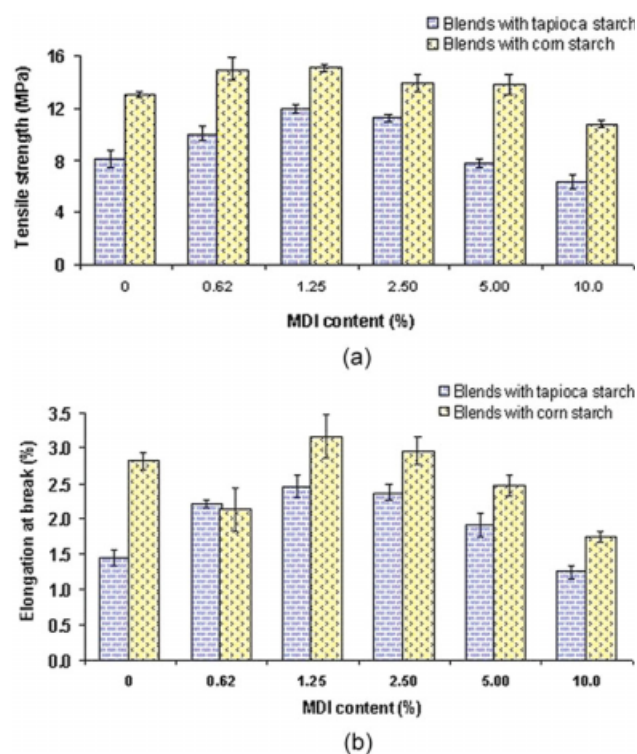
From these results, the addition of 1.25% MDI in the blend films was the optimum amount to compatibilize the GS and plasticized PLA phases and strengthen the interfacial adhesion. This was because strong adhesion existed between the starch and PLA matrix when an appropriate amount of MDI was present, so the mechanical properties of the blends improved greatly with 1.25% MDI. With MDI, a covalent linkage was likely formed at the PLA and GS interface so that the interfacial adhesion was enhanced, and consequently, the tensile strength improved. On the other hand, the addition of too much MDI (>1.25 wt %) generated more defects in the blend films, which resulted in a decrease in the mechanical properties. It may have been that because MDI could react between GS and GS molecules, some agglomeration of GS molecules occurred, which eventually caused defects and cracks in the blend films. These behaviors were observed in both of the blends with GTS and GCS. However, comparatively, the overall tensile properties of the blends with GCS were higher than those of the others. This result was supported by the morphological properties because the mechanical properties of the blend films were closely related to their morphology (Fig. 2).
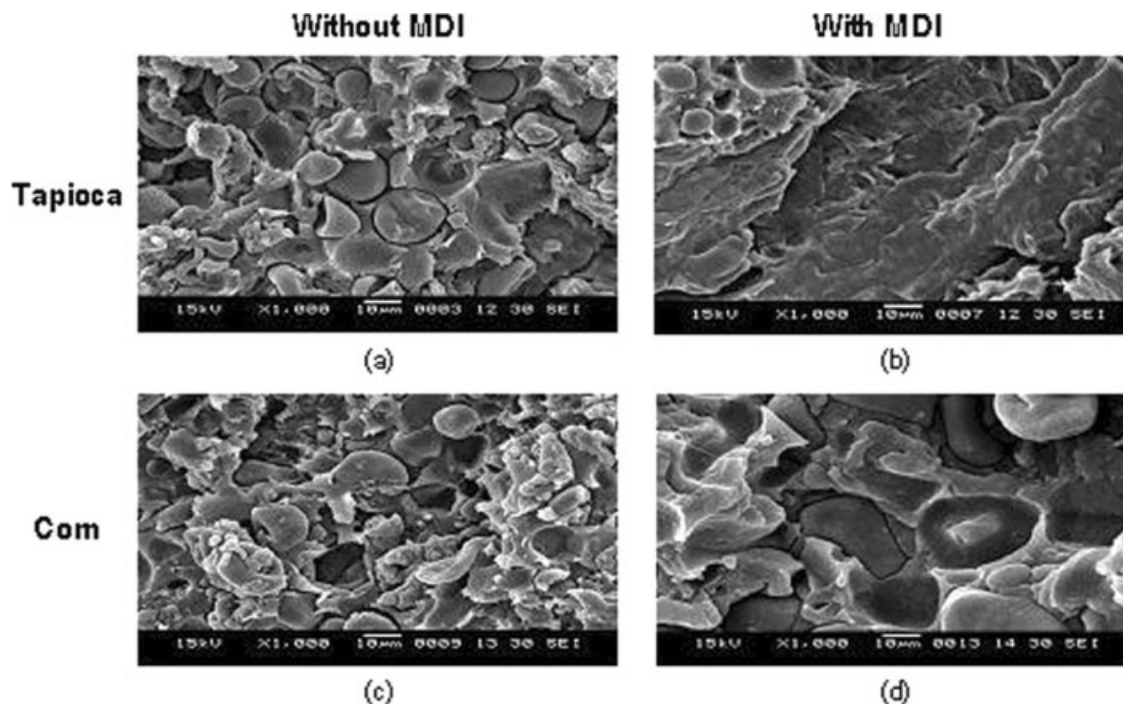
Figure 2 SEM micrographs of the fractured surface of GTS (a) without and (b) with 1.25% MDI and GCS (c) without and (d) with 1.25% MDI/plasticized PLA blend films (40/60 weight ratio).

Morphological properties

The SEM micrographs of the fractured surface of the GS/plasticized PLA (40/60 w/w) blend films with and without MDI are compared in Figure 2. For the GS and plasticized PLA blend film without MDI [Fig. 2(a,c)], the dispersion of GS was observed, where some starch granules detached from the plasticized PLA matrix and then showed hollow cavities. In addition, some aggregated GS was observed by the naked eye, and the GS at the fractured surface was embedded somewhat loosely in the plasticized PLA matrix. Large voids were visible in the surface where GS was pulled away during tensile testing; this indicated that the fracture occurred at the interface between the two phases. This resulted from phase separation between the GS and plasticized PLA. These results show poor interfacial adhesion between the two phases. The fracture of the blend films without MDI occurred predominately at the interface between the GS and plasticized PLA rather than through the matrix phase; this indicated that the GS were not well wetted by the plasticized PLA matrix.

On the contrary, a uniform dispersion of starch granules in the plasticized PLA matrix and some pullouts were observed for the GS/plasticized PLA (40/60 w/w) blend films with MDI [Fig. 2(b,d)]. As MDI was added to the GS and plasticized PLA system, the apparent surface tension of GS was possibly reduced because of the molecular interaction between MDI and GS. Therefore, GS made intimate contact with plasticized PLA during mixing. Also, covalent bonding could have been generated between the GS and plasticized PLA through MDI during mixing. These SEM results of the blends with MDI exhibit few gaps and holes between the two phases; this indicates that GS phase was well enveloped by the plasticized PLA phase. Furthermore, fractures occurred through the plasticized PLA matrix; this suggested that some interaction between the GS and plasticized PLA increased. According to the mechanical properties, as previously described, the addition of MDI led to an increase in the tensile properties compared with the film without MDI.

Thermal properties

The thermal properties of the blend films with various MDI contents are reported in terms of differential scanning calorimetry (DSC) thermograms. These results were used to consider compatibility between the two phases of the blend films. It was one of the several applications of DSC characterization in which T_g shifts were analyzed. The DSC thermograms of these blend films are displayed in Figures 3 and 4. From Figure 3(a,b), the blend films showed two midpoints of heat-capacity changes (T_g) of the plasticized PLA (ca. 35–45°C) and GS (ca. −20 to −15°C); this indicated immiscibility between the two phases. The T_g of GS was not clearly seen because the step changes of GS (T_g) had a very small scale compared to the large scale of the exothermic and
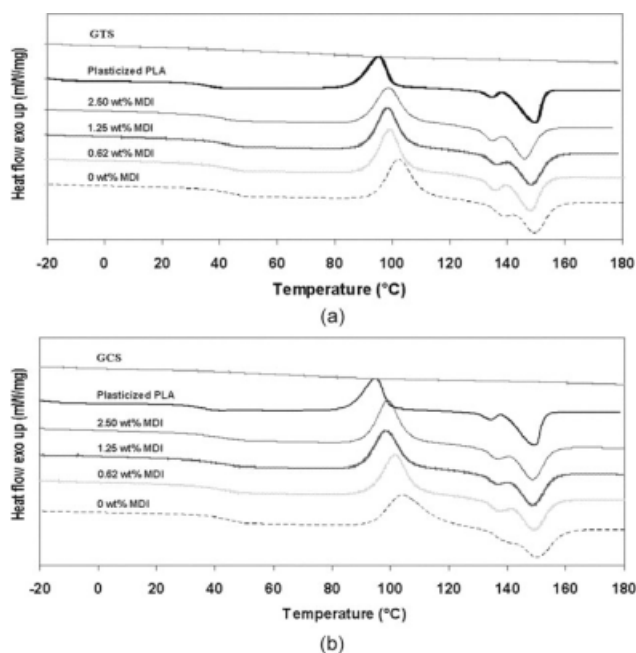
Figure 3 DSC thermograms of GS/PLA (40/60 w/w) blend films with various MDI contents: (a) GTS and (b) GCS.

endothermic peaks of T_c (cold crystallization temperature) and T_m, respectively. Thus, DSC thermograms with an extended scale in the range of subambient temperature of the GS/plasticized PLA (40/60 w/w) blend films are shown in Figure 4(a,b). These results indicate that with increasing MDI content, the T_g of the plasticized PLA phase decreased gradually, whereas the T_g of GS phase increased. In other words, the T_g of each phase shifted toward each other (Table I). These behaviors were similar in blends containing both GTS and GCS. These T_g shifts implied that the blending of GS and plasticized PLA films with the presence of MDI showed some improvement in the interfacial adhesion between the two phases; this supported the morphological study, as discussed earlier (Fig. 2).

Water absorption

Figure 5(a,b) illustrates the water absorption isotherms as a function of time for the neat PLA and GS/plasticized PLA (40/60 w/w) blend films at various MDI contents. The neat PLA film reached its equilibrium water absorption value at about 1%. The GS/plasticized PLA (40/60 w/w) blend films absorbed more water. These results could be explained by the fact that GS was more hydrophilic than plasticized PLA and could also enhance the interaction of hydrogen bonding between the hydroxyl groups in GS and water.[15] Hence, the water uptake of the blends was higher than that of the plasticized PLA film. The water absorption of all

blends increased rapidly during the first 5 days and then leveled off.

A significant difference in the water absorption between the blends with and without MDI was obvious. The blends without MDI had a higher percentage of water uptake than those with MDI. These results indicate that MDI content significantly affected the water absorption of the plasticized PLA and starch blends. The water absorption isotherm of the blends decreased when the MDI content increased. This was because in the blending system without MDI, the interfacial adhesion between the GS and plasticized PLA was poor; this resulted in gaps between the two phases. Thus, water was easily absorbed into the GS/plasticized PLA blend films without MDI. As MDI was added, the interfacial bonding between the two phases improved. Furthermore, the gaps were also enveloped, which led to lower water absorption. This was a reason why the blend film compatibilized with 1.25% MDI had the lowest water absorption. However, at 2.50% MDI, the water uptake of the film was higher than the other compatibilized blend films, as also shown clearly in Figure 6(a,b). This was probably due to the separated phases and large voids of the blend films, which was attributed to some agglomeration of GS molecules. These results are in agreement with the tensile properties and morphological studies.
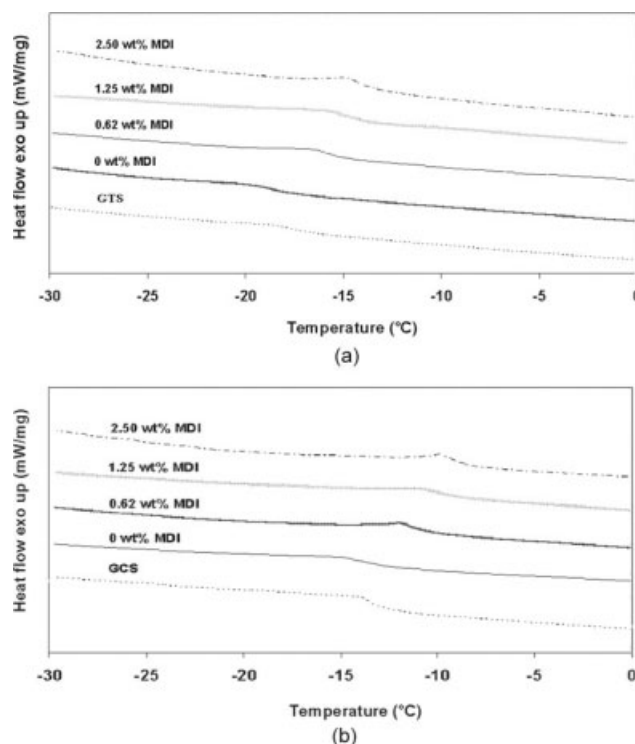

Figure 4 DSC thermograms in the range of subambient temperature of GS/PLA (40/60 w/w) blend films with various MDI contents: (a) GTS and (b) GCS.

TABLE I
Thermal Properties of Plasticized PLA, GSs, and GS/Plasticized PLA Blends

Formulation name	T_g (°C)	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)
Plasticized PLA	35.5	95.4	135.1	150.1
GTS	−17.2	—	—	—
GCS	−13.7	—	—	—
GTS/plasticized PLA				
0% MDI	−18.4	44.6	103.1	139.0	150.3
0.62% MDI	−15.6	43.0	99.8	136.4	148.7
1.25% MDI	−14.9	42.2	99.2	136.6	148.8
2.50% MDI	−14.4	40.4	99.4	135.3	146.6
GCS/plasticized PLA blend				
0% MDI	−14.1	45.7	104.9	140.1	150.8
0.62% MDI	−11.5	43.4	102.3	137.9	149.8
1.25% MDI	−10.1	42.6	99.2	137.3	149.3
2.50% MDI	−9.3	43.0	99.5	137.0	149.2

T_{m1}, low-melting temperature and T_{m2}, higher-melting temperature.

CONCLUSIONS

MDI level affected the mechanical, thermal, physical, and morphological properties of the GS and plasticized PLA blend films. The DSC thermograms displayed T_g shifts between the plasticized PLA and GS; this implied that the blending of the two phases with the presence of MDI improved the interfacial adhesion some, as also evidenced by SEM analysis. Both the tensile strength and elongation at break of the blends with lower MDI contents (0.62 and 1.25 wt %) were greater than those of the blend films without MDI. Nevertheless, when the MDI concentration was greater than 1.25 wt %, the tensile properties of the blend films were gradually decreased.
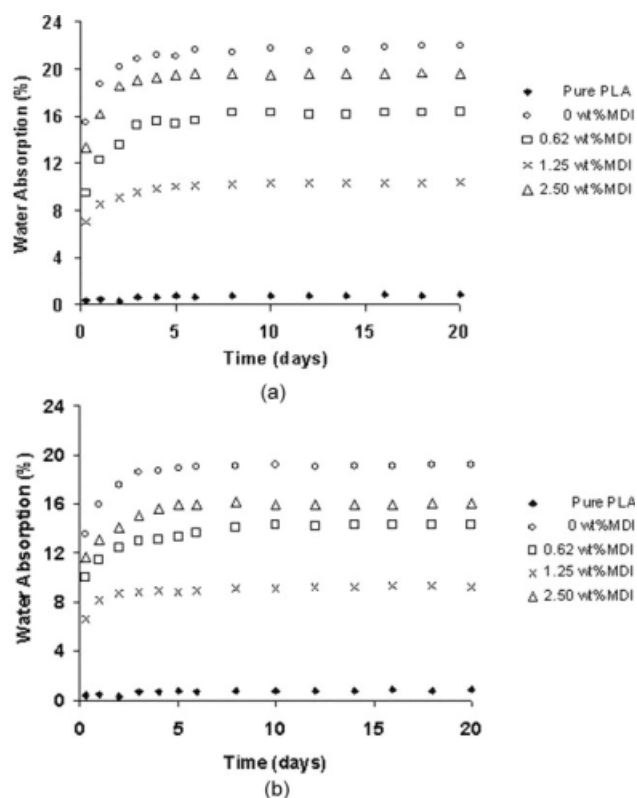

Figure 5 Water absorption isotherms of GS and PLA blend films (40 : 60) at various MDI content compared with pure PLA: (a) GTS and (b) GCS.
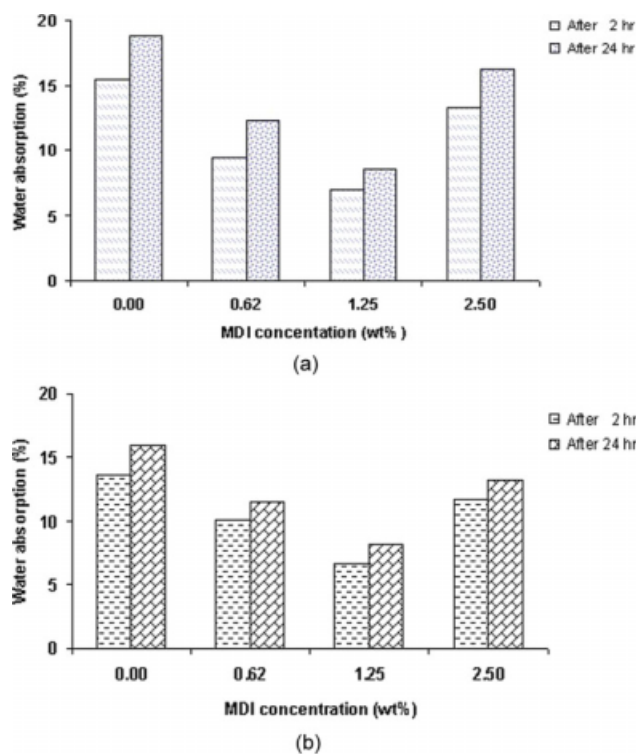

Figure 6 Effect of MDI content on the water absorption of GS and PLA blend films (40 : 60) after 2 and 24 h: (a) GTS and (b) GCS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thus, the optimum amount of MDI to compatibilize the GS and plasticized PLA phases and strengthen the interfacial adhesion was 1.25 wt %. Both types of GS exhibited the same behavior but with different magnitudes. Comparatively, the overall tensile properties of the blends with GCS were higher than the blends containing GTS. The water absorption values of the GS/plasticized PLA blend films (40 : 60) decreased when the MDI content increased; this resulted from the enveloped gaps and improved interfacial adhesion between the two phases. Unlike the tensile properties, the water uptake was not affected by the different types of starch in the blend films.

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