Current Applied Science and Technology Vol. 23 No. 4 (July-August 2023)

Research article

Effects of Hydroxypropyl Methylcellulose Fiber Amounts and Aspect Ratios on Properties of Biodegradable Composites Prepared from Thermoplastic Starch

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Received: 28 September 2022, Revised: 2 November 2022, Accepted: 14 December 2022

DOI: 10.55003/cast.2022.04.23.003

Abstract

Keywords	Because of the low tensile properties and high hydrophilicity of thermoplastic starch (TPS), this research was focused on improving
biodegradable polymer; composite; fiber:	its characteristics through the addition of the natural cellulose fiber, hydroxypropyl methylcellulose (HPMC). Different TPS composites reinforced with HPMC fibers were compounded using an internal mixer and were shaped using a compression molding machine. The
thermoplastic starch	effects of HPMC fiber content and aspect ratios were examined. It was found from infrared spectra that the wavenumbers of the O-H stretching of TPS polymer clearly shifted to lower wavenumber with the incorporation of HPMC fibers, which indicated new hydrogen
	and elastic modulus of TPS/ HPMC fiber composites was detected. A clear drop in moisture uptake was also found when HPMC fibers were added into the TPS polymer matrix. In addition, scanning electron microscopy and thermogravimetric analysis were used to
	characterize several TPS composites. Biodegradability for various composites was also determined.

1. Introduction

Recently, biodegradable products based on agricultural materials have attracted interest because they are potentially more environmentally friendly than other currently used substances. Biopolymers that are starch-based have become popular due to their natural abundance, wide.

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availability and biodegradability. Starch is a biomacromolecule mainly composed of α -D-glucose units, and is composed of both amylose and amylopectin [1]

Commonly, starch is in a granule form containing approximately 15-45% crystallinity. With the application of high shear force and high temperature, plasticized starch can be transformed into thermoplastic starch (TPS) [2]. TPS can be molded with conventional processing machines that are used for common thermoplastics via compression molding and injection molding. However, its high hydrophilicity and low tensile properties remain problematic. An interesting way to solve the drawbacks of TPS is to incorporate with natural cellulose fibers as reinforcement since the chemical structures of polysaccharide starch and cellulose are similar. Cellulose fibers are mainly collected from different plants, for example, luffa, coir, cotton, jute or kapok fibers, with different cellulose contents. It was mentioned in previous research that the tensile strength and modulus of TPS polymers increased considerably after cellulose fiber reinforcement [2-7]. In addition, an improvement of water absorption and thermal resistance were observed due to the high crystallinity and hydrophobic properties of the cellulose fibers [2-7].

One remarkable polymer that can reinforce TPS polymer is hydroxypropyl methyl cellulose (HPMC). HPMC is in the group of cellulose ethers, all of which have hydroxyl groups that have been replaced by one or more of the hydroxypropyl and methoxy groups present in cellulose rings [8]. HPMC is a hydrophilic, biodegradable and biocompatible polymer that can be applied in many applications including drug delivery, cosmetics, coatings, and textiles [9]. It is commonly used for edible and biodegradable films with good processing and tensile strength, tasteless, oil-resistant and transparent [9].

Casted HPMC films have been blended with many substances including nanocellulose, alginate, starch, beewax, collagen, and xanthan gum [10]. It was mentioned that silver particles added into HPMC films could extend papaya shelf-life [11] and the antibacterial activity of HPMC could be improved by the incorporation of chitosan [12]. Casted film from xanthan gum was prepared, and it was found that the film's tensile properties and water vapor transmission rate were improved by the addition of HPMC [10]. Moreover, HPMC films modified by treatment with curcumin via antisolvent precipitation presented better distribution and barrier properties than films not treated with curcumin [13]. It was also reported that the incorporation of HPMC-grafted succinic acid (HPMCS) into HPMCS-crosslinked chitosan resulted in enhanced tensile properties in both dry and swollen states [14].

However, casted HPMC films still showed limited barrier properties. It was also mentioned that the addition of HPMC into corn starch film barely affected water barrier properties but increased oxygen permeability [15]. Besides, nanocomposite film from cellulose whickers showed better water barrier and tensile properties than HPMC films [16]. In addition, HPMC/bovine collagen and HPMC/nano TiO₂ were prepared and the introduction of bovine collagen and nano TiO₂ produced improvements in tensile, barrier and thermal properties [17].

Cassava starch (CS) is one of the largest sources of global [1]. However, to the best of our knowledge, the use of HPMC fibers for the reinforcement of thermoplastic starch (TPS) prepared from CS has never been reported. The objective of this study was to improve the hydrophilicity and tensile properties of TPS. In this research, we therefore focused on the properties of TPS reinforced with HPMC fibers at the different aspect ratios of 3.61 and 6.04. A compression molding technique was used. Various TPS/HPMC composites were characterized by FTIR and SEM techniques. The tensile properties, moisture uptake, thermal stability and biodegradability of the composites were also investigated.

2. Materials and Methods

2.1 Materials

CS with approximately 11.5%-13.0% moisture was received from Thaitam (Chonburi, Thailand). It was composed of about 15.9-22.4% wt amylose and 61.8-83.0% wt amylopectin. Glycerol (used as the plasticizer) was purchased from Lab System Co. Ltd. (Thailand). HPMC with 29.1% methoxy groups and 6.0% hydroxypropyl groups (food grade) was obtained from Ruam Chemie 1986, Co. Ltd. (Bangkok, Thailand). HPMC fibers of length to diameter (L/D) ratios of 3.61 and 6.04 were selected for the study.

2.2 Sample preparation

Firstly, starch, glycerol and HPMC fibers were mixed in a plastic bag manually and left overnight. The CS to glycerol weight ratio was preserved at 65:35. Compounding was performed using an internal mixer (Brabender, PL 2000/PL 2001) at a rotor speed of 40 rpm at 150°C for 5 min. After that, the compounded sample was hot-pressed using a compression molding machine (LabTech Engineering, Thailand) with 2 mm thick mold at 150°C. The property modification of TPS composites was established using HPMC fibers. Different amounts of HPMC fibers, 0%, 10%, 20% and 30% were included into the TPS matrix. The modification of TPS matrix was also achieved by the reinforcement with HPMC fibers at a fixed weight of 30% by TPS weight, with 2 different aspect ratios of 3.61 and 6.04.

2.3 Functional group analysis

FTIR spectra of a sample were performed on a Spectrum 2000 GX spectrometer (Perkin Elmer, USA) using the KBr disk method for sample preparation. A spectral range of 4000-600 cm⁻¹ with 4 cm⁻¹ resolution was carried out and repeated for 16 scans.

2.4 Morphology

Scanning electron microscope (FEI Quanta 250, USA) was employed to study a composite morphology. A thin gold layer was sputter- coated onto the samples and the samples were cryogenically cracked before the observation.

2.5 Tensile properties

Tensile tests were conducted after conditioning at the temperature of 23 ± 1 °C and relative humidity of $60\pm5\%$ (ASTM D-638). Tensile measurement of the composites was performed on a Universal Testing Machine (Lloyd, LR 5K, West Sussex, UK) equipped with a 100 N load cell and operated at 40 mm/min. The tensile data of the composites were averaged from ten samples.

2.6 Moisture uptake

A composite was first dried at 105°C for 3 h and then conditioned at $99\pm1\%$ relative humidity and $30\pm2°$ C before the test. Approximately 100% relative humidity was created using distilled water in a closed container. The absorbed water amount was examined when the constant weight of the sample was reached. The percentage of moisture uptake was determined as follows:

Moisture uptake =
$$(W_2 - W_1)/W_1 \times 100$$
 (1)

where W₂ and W₁ were the wet and dried weights of a sample, accordingly.

2.7 Biodegradability

Biodegradability of a composite was performed by soil burial test. A dog-boned sample was buried in soil for 3 days. The soil water content was approximately 5-10% and the tensile test of a soil-buried sample was then carried out.

2.8 Thermal properties

Thermograms of a composite were determined by a thermogravimetric analyzer (Perkin Elmer, Pyris 1, Massachusetts, USA). Each sample was analyzed under nitrogen atmosphere at 50-600°C and 10°C/min heating rate. Thermal decomposition temperature (T_d) and weight loss (%) were reported as the highest degradation rate and weight loss, respectively.

3. Results and Discussion

3.1 Functional group analysis

The FTIR technique is very valuable for the functional group characterization of many materials. It was expected that starch polysaccharide containing hydroxyl groups would be phase compatible with HPMC fibers, which are based on cellulose chemical structures with some substitution of methoxy and hydroxypropyl groups. New hydrogen bond formation can be formed in the TPS matrix reinforced with HPMC fibers as shown in Figure 1. The FTIR spectra of various TPS/HPMC composites are presented in Figure 2. It can be seen that TPS sample showed its main IR peak positions at 3409 cm⁻¹ (O-H stretching), 2933 cm⁻¹ (C-H stretching) 1646 cm⁻¹ (bounded water) and 1414 cm⁻¹ (O-H bending). In addition, the wavenumbers at 1261 cm⁻¹, 1154 cm⁻¹ and 1024 cm⁻¹ were assigned for C- O stretching, C- O stretching and C- O- H bending, respectively. The wavenumbers at the positions of 926 cm⁻¹ and 856 cm⁻¹ were designated as C-H bending [18].

It was observed that no new IR peak positions were detected when the HPMC fibers were added into the TPS matrix (Figures 2(a)-2(b)). However, the insertion of HPMC fibers into the TPS matrix at various HPMC content levels and aspect ratios led to the O-H stretching and O-H bending peak positions being shifted to lower wavenumbers because of new hydrogen bond formation. Phase compatibility between two polymers causes changes (such as band shifts or band broadening) in IR spectra [19]. Similar observations were mentioned for TPS reinforced by luffa fibers [3], cotton fibers [5], jute or kapok fibers [6]. The wavenumber shift suggests the increase of intermolecular hydrogen bond in TPS/HPMC composites occurs because of their phase compatibility.

3.2 Morphology

Phase morphology from fractured samples of different TPS/HPMC composites was examined by SEM technique at the magnifications of 300X and 1500X. The TPS sample exhibited smooth fractured morphology under the processing condition, as presented in Figures 3(a)-3(b). The incorporation of HPMC fibers into the TPS matrix (Figures 3(c), 3(e) and 3(g)) with the 300X

magnification clearly produced good HPMC fiber distribution within the matrix because of good phase compatibility, and this was consistent with the IR peak shift data (Figure 2). The increase of HPMC fiber content resulted in an increase in the HPMC fibers distributed in the TPS matrix (Figures 3(c), 3(e) and 3(g)). When different aspect ratios of HPMC fibers were considered, different phase morphologies of the TPS/HPMC samples were observed, as presented in Figures 3(f)-3(h). Longer HPMC fibers were evident for HPMC fibers at the 6.04 aspect ratio. It should be noted that fiber surface wetting was clearly detected, and this was probably due to the good phase compatibility between the TPS and HPMC polymers.



Figure 1. Possible chemical interactions between TPS matrix and HPMC reinforcement



Figure 2. FT-IR spectra of different TPS/HPMC composites determined for different HPMC (a) contents and (b) aspect ratios



Figure 3. SEM micrographs of several TPS/HPMC composites (a)-(b) TPS polymer (c)-(d) TPS/10HPMC3.61 (e)-(f) TPS/30HPMC3.61 and (g)-(h) TPS/30HPMC6.04

3.3 Moisture uptake

Moisture uptake is one of the concerned properties when using TPS in various applications due to its high hydrophilicity. The moisture uptake was performed at $99\pm1\%$ and 30 ± 2 °C. It can be seen in Figure 4(a) that the insertion of HPMC fibers into the TPS matrix brought about a significant reduction in the moisture uptake because HPMC fibers contained lower numbers of free hydroxyl groups than the starch matrix due to the methoxy and hydroxypropyl group substitution. In addition, the new hydrogen bond formation (IR section) caused the reduction of free hydrogen bonds that could interact with hydrogen bonds of water molecules.

It should be noted that higher HPMC content led to slightly lower moisture uptake in the composites, as shown in Figure 4(a). This could be due to the higher hydrophobicity of HPMC reinforcement, compared to the TPS matrix. When different HPMC aspect ratios were considered, it was observed that the lower aspect ratio of 3.61 of HPMC fibers caused higher moisture uptake than that of 6.04 because of the higher surface area of the lower aspect ratio of HPMC fibers. The decrease of moisture uptake result was consistent with previous reports for TPS reinforced with luffa, coir, cotton, jute, kapok fibers, and neem wood sawdust [3-7]. The effect of the fiber aspect ratio on moisture uptake was different from reports in other literature, which concluded that the cotton fiber aspect ratio had no effect on the absorption of water by TPS [5]. The difference in polarity between HPMC and cotton fibers may have contributed to this result; since cotton fibers show more hydrophilicity than HPMC fibers, the HPMC fiber surface area, therefore, affects the moisture uptake. In this study, the lowest moisture uptake was observed for the TPS/30HPMC6.04 composite.

3.4 Tensile properties

Tensile properties are one of the important considerations for many applications of polymers. Maximum stress, elastic modulus and maximum strain were examined for various TPS/HPMC composites, and the results are presented in Figure 5. It is obvious that the inclusion of HPMC fibers into the TPS matrix brought about a significant rise of the maximum stress and elastic modulus but caused a drop in the maximum strain. This was clearly because of HPMC fiber reinforcement, as confirmed by the new hydrogen bond formation (Figure 2), and also the good phase compatibility between HPMC fibers and the TPS matrix (Figure 3).



Figure 4. Moisture uptake of different TPS/HPMC composites determined for different HPMC (a) contents and (b) aspect ratios



Figure 5. Tensile properties of TPS/HPMC particle composites determined for various contents and aspect ratios

Comparison of the addition of 10, 20 and 30% of HPMC fibers revealed that the TPS/30HPMC3.61 showed the highest maximum stress and elastic modulus. Additionally, the use of longer HPMC fibers caused slightly higher maximum stress and elastic modulus than those of shorter HPMC fibers. This was because longer HPMC fibers produced good phase compatibility with the TPS matrix without voids at the interface boundary (Figure 3), resulting in many good stress transfer points to the TPS matrix. Generally, longer fiber length or higher fiber aspect ratio causes greater stress transfer; as a consequence, a composite of high tensile strength was obtained [20]. Evidence of an increase in stress and modulus was reported for several TPS/ cellulose composites such as cotton [5], jute, and kapok fibers [6]. The highest maximum stress and elastic modulus was found in the TPS/30HPMC6.04 composite.

3.5 Biodegradability

The soil burial test was selected to determine the biodegradability of various TPS/ HPMC composites. The change in tensile properties at day 0 and day 3 was examined. It can be seen in Table 1 that the maximum stress and elastic modulus of TPS and all composites obviously dropped after burial in soil. This was because of the moisture that existed in soil leading to biodegradation by starch hydrolysis. The results also related to the moisture uptake results in Figure 4. After the soil burial test, the TPS/HPMC composites showed more extensibility which may be due to less hydrophilicity of HPMC fibers than that of the TPS sample. However, the reduction in the maximum strain of TPS sample after the test was possibly due to starch hydrolysis that could cause starch chain cleavage; therefore, the maximum strain of TPS sample was clearly reduced. It should be noted that the HPMC fiber content and aspect ratios did not have significant impact on the tensile properties of different TPS/HPMC composites after soil burial test.

Composites	Maximum stress (MPa)		Elastic modulus (MPa)		Maximum Strain (%)	
	Day 0	Day 3	Day 0	Day 3	Day 0	Day 3
TPS	1.19±0.30	1.11±1.45	8.37±2.23	0.26±0.12	228.06±9.88	44.95±24.73
TPS/10HPMC3.61	1.17 ± 0.08	0.26±013	24.81±6.59	0.93±0.38	63.41±8.27	73.11±28.51
TPS/20HPMC3.61	2.61±0.29	0.44 ± 0.07	59.21±9.28	1.77±0.43	8.65±1.83	44.53±5.17
TPS/30HPMC3.61	3.93±0.51	0.50 ± 0.06	106.89±10.79	4.13±0.51	6.89±1.01	30.62±2.85
TPS/30HPMC6.04	4.16±0.56	0.31±0.06	113.34±13.25	5.49±6.42	5.50±1.02	34.71±18.39

Table 1. Tensile properties of different TPS/HPMC composites before and after soil burial test

3.6 Thermal properties

The thermal behavior of various TPS/HPMC composites was determined by a thermogravimetric analyzer. It can be seen from Figure 6 and Table 2 that TPS showed 2 different thermal decomposition temperatures; at 184.9°C and 313.8°C, which corresponded to the decomposition of glycerol plasticizer and starch, respectively [6]. For TPS/HPMC composites, another degradation step was observed, at approximately 340°C, which was probably attributed to the decomposition of HPMC component [21].



Figure 6. Thermal behavior of several TPS/HPMC composites determined by thermogravimetric analyzer for different HPMC (a) contents and (b) aspect ratios

Table 2. Thermal decomposition temperatures and percentage weight losses of various TPS/HPMC
composites with different contents and aspect ratios

	Thermal dec	Weight loss		
Composites	1 st Step (Glycerol)	2 nd Step (Starch)	3 rd Step (HPMC)	(%)
TPS	184.9	313.8	-	79.9
TPS/10HPMC3.61	187.3	307.7	349.2	50.8
TPS/20HPMC3.61	197.5	311.6	341.3	44.2
TPS/30HPMC3.61	194.2	312.0	347.8	32.2
TPS/30HPMC6.04	187.3	312.6	340.7	34.4

It can also be seen in Figure 6 that the addition of HPMC into the TPS matrix led to the decrease of the starch thermal degradation temperature. A similar finding was claimed for TPS/kapok fiber composites [6]. However, the increase of HPMC contents tended to cause a rise in the thermal decomposition temperature of various TPS/HPMC fiber composites. This could be because of the formation of new hydrogen bonds and phase compatibility between HPMC reinforcement and the TPS matrix, which was described in Figures 2 and 3. However, the thermal decomposition temperatures of various TPS/HPMC composites were similar, regardless of the different aspect ratios of HPMC fibers. It should be noted that percentage weight loss significantly decreased after the addition of HPMC fibers into the TPS matrix, and the results suggested that higher thermal stability of TPS/HPMC composites was caused by the reinforcement with HPMC fibers.

4. Conclusions

Various TPS/HPMC composites were successfully prepared by compression molding technique. The incorporation of HPMC into TPS caused an IR peak shift, probably due to new hydrogen bond formation. Good phase compatibility and surface wetting were also observed for the different TPS/HPMC composites. A significant decrease of the moisture uptake and ane obvious increase of the tensile properties were detected for the TPS/HPMC composites. The HPMC aspect ratios clearly affected the moisture uptake and tensile properties; meanwhile, the HPMC contents significantly affected moisture uptake, tensile properties and thermal properties of the TPS/HPMC composites. All the composites showed biodegradability in the soil burial test, regardless of HPMC content or aspect ratio. In this study, TPS/30HPMC6.04 presented the best overall properties. It showed the highest tensile properties, the lowest moisture uptake, and the highest thermal degradation temperature.

5. Acknowledgements

The authors sincerely thank the KMITL research fund (KREF 046108) for the financial support and the Department of Chemistry, School of Science, KMITL for facility assistance.

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