Development of Novel Wax-enabled Thermoplastic Starch Blends and Their Morphological, Thermal and Environmental Properties

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Abstract Novel thermoplastic starch (TPS) melt-blends were prepared while using glycerol as plasticizer. To impart hydrophobicity, beeswax (BW) and paraffin wax (PW) polymers were introduced in combination with commonly available interfacial coupling agent, maleic anhydride (MA). Representative melt-blends of TPS containing different concentration of BW, PW and MA were prepared through *in-situ* reactive extrusion in a custom designed twin screw extruder. The modified TPS was comprehensively evaluated for morphology, thermal stability and moisture resistance properties, while keeping both the temperature profile of extruder and glycerol concentration at constant level. The results showed that the plasticization becomes problematic at wax levels more than 10% at required extrusion temperatures due to lower melting points of these compounds, however FTIR studies exhibited an effective grafting of MAH compounds on wax polymers. Although phase separation was observed during morphological studies for BW-enabled TPS blends, but MA treated PW and their TPS blends showed homogenous structure of extruded samples. It was further observed that PW-enabled TPS blends had better thermal stability and enhanced hydrophobicity compared to BW-enabled formulations due to unique chemical structure of paraffin wax.

Keywords Corn starch, Biopolymers, Thermoplastic starch, Biodegradable, Extrusion, Hydrophobic, Water absorption, Melt-blending of starch, Renewable resources

1. Introduction

The development of biomaterials from renewable sources have gained considerable momentum in recent times due to unprecedented environmental and global climate change issues linked to mass-scale exploitation of petroleum-based feedstock [1-4]. Starch–based biopolymers from various plant sources present a viable alternative to develop biodegradable plastics for a variety of applications [5-7]. The main motivation to use starch as a suitable material for the production of biodegradable plastics is due to its low cost and abundant availability [8, 9]. Starch, produced naturally during photosynthesis in plantslike potatoes, corn, and rice, functions as the principal polysaccharide reserve material deposited in the form of granules [10-12].

The transformation of starch into bioplastic for any application needs disruption of granules through heating in the presence of plasticizers, usually glycerol and water, under specific conditions; the biopolymer thus produced is known as thermoplastic starch (TPS) [13-16].

Plasticized starch or thermoplastic starch (TPS) is prepared under specific extrusion conditions and in the presence of plasticizers, such as glycerol and water [14-16]. Although being compostable bioplastic, the mass-scale application of untreated TPS has been hindered largely due to its moisture absorbing ability at ambient environment [5, 8]. Sain et al. have reported a novel biodegradable modified TPS manufactured from a native starch using a polysaccharide produced by the fungus species Ophiostomaulmi. This modified TPS exhibits low water absorbency and high tensile strength and may be used to manufacture films or molding products by casting, extrusion, injection, or compression techniques [17]. In other works, researchers have tried to enhance the water resistance of TPS by melt-blending starch with hydrophobic polymers, such as poly(e-caprolactone) [18], cellulose acetate [19], poly (butylene adipate-co-terephthalate) [20], polylactides [21] and processing amylose-free corn starch with poly butylene succinate (PBS) [22]. However, the commercial application

of these hydrophobic polymers have been restricted due to their high cost and poor functionality compared to commodity plastics. For the first time, this current work has investigated the potential of two common and low cost waxes, paraffin wax and beeswax, to be melt-blended with TPS in order to improve its water resistance.

Waxes are hydrophobic organic compounds often used for waterproofing purposes in applications such as wax paper and wood composites [23]. Beeswax is a natural, hydrophobic, and biodegradable wax produced in the beehive by honey bees. The chemical nature of beeswax is basically lipoid, with the major components being 14% hydrocarbons, 35% monoesters, 3% diesters, and 12% free acids [24]. Previous studies on melt-blending esters with TPS have found that the mixtures are immiscible; however, they form compatible blends as a result of the hydrogen bonding interaction between the ester carbonyl group and the OH groups on starch [25], thereby, beeswax may show similar behaviour in the absence of any compatibilizer.
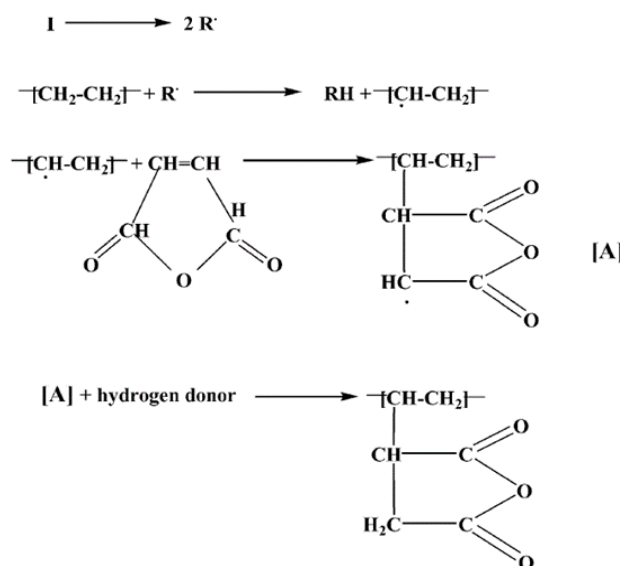
Figure 1. Reaction scheme for grafting maleic anhydride onto paraffin wax [27]

Paraffin wax, a petroleum derived polymer, is composed of a mixture of alkanes ranging from 20 to 40 carbon chain-length. In order to improve the compatibility between starch and paraffin wax, a compatibilizer such as MAH, in the presence of dicumyl peroxide (DCP) as initiator, must be used when they are melt-blended [26]. The maleation reaction of paraffin wax, Figure 1, has been studied in the literature [27] and is believed that maleated paraffin wax will react with starch in a similar fashion to maleated polyethylene [28].

In this work, melt blending and reactive extrusion, have been used to explore the efficacy of Beeswax and paraffin wax as compatible biopolymers to reduce moisture sensitivity of novel TPS formulations. Beeswax was melt-blended with starch by extrusion, whereas, paraffin wax was melt-blended as well as reactive extruded with starch facilitated by MAH and dicumyl peroxide (DCP).

2. Experimental

2.1. Materials

Industrial grade cornstarch (11% moisture) was obtained from Casco Inc. (Cardinal, ON., Canada). Glycerol was purchased from ACP Chemicals Inc. (Montreal, QC, Canada). Beeswax (BW), paraffin wax (PW, T_m = 80-90°C), maleic anhydride (MAH), and dicumyl peroxide (DCP) were purchased from Sigma-Aldrich (Oakville, ON, Canada).

2.2. Plasticization

Starch and glycerol were mixed with a high speed kitchen mixer for 30min. BW or PW or PW, MAH, and DCP were added and mixed for an additional 10min. The compositions of ten samples prepared are listed in Table 1.

The plasticization was done through A twin screw extruder, ONYX TEC 25/40, available at Center for Biocomposites and Biomaterials Processing (CBBP), University of Toronto, Canada, was used for plasticization with a temperature profile along the extruder barrel (from feed zone to die) as given in Table 2.

Table 1. Sample labels and their compositions

Sample	Weight Proportion						
	Starch	Glycerol	Water	BW	PW	MAH	DCP
TPS	100	45	30	0	0	0	0
5BW	100	45	30	5	0	0	0
10BW	100	45	30	10	0	0	0
20BW	100	45	30	20	0	0	0
5PW	100	45	30	0	5	0	0
10PW	100	45	30	0	10	0	0
20PW	100	45	30	0	20	0	0
5MPW	100	45	30	0	5	0.05	0.005
10MPW	100	45	30	0	10	0.1	0.01
20MPW	100	45	30	0	20	0.2	0.02

Table 2.   Temperature profile across the screw barrel used for plasticization

Zone	1	2	3	4	5	6	7	8	9	10
Temperature (ºC)	155	155	155	160	160	160	160	165	170	180

2.3. FTIR

The functional groups of PW and MPW were identified through use of a Bruker Tensor-27 spectrometer. All spectra were captured over a range of 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} with 200 scans. To determine the grafting of maleic anhydride, paraffin wax was extruded separately at the same processing conditions and in the presence of MAH and DCP. The extrudate was purified to remove any unreacted MA by dissolution of PW in boiling water for 10min, followed by vacuum filtration.

2.4. SEM

The exposed surfaces of specimens, fractured through a sharp-edge knife, were coated with gold and observed with a JEOL JSM-840 scanning electron microscope (Tokyo, Japan). The electron gun voltage was set at 15 kV. The micrographs were arranged at 200x magnifications to observe surface morphology.

2.5. TGA

The thermal behaviour of TPS blends was studied with a TGA Q500 type thermal analyzer (TA Instruments - New Castle, DE, USA). Samples, weighting from 1 – 5 mg, were heated on a platinum pan from ambient temperature to 600°C at a rate of 15°C/min. Derivatives of TGA were obtained using TA Instruments Universal Analysis software.

2.6. Water Absorption

Water absorption (WA) of TPS blend-extrudates was determined by preparing 2x2square inch thin film specimens using hydraulic press, ARG-450-Dieffenbacher N.A. Inc. Windsor - Canada, followed by hot pressing for 4min at 160℃ and 500kPa, cut into square specimens, and dried overnight in a desiccator. Dried specimens were placed in a desiccator containing distilled water at room temperature (23℃, 100% RH) and weighed every 24h. WA of each specimen was calculated by the following equation:

$$WA = \frac{W_a - W_i}{W_i} \qquad (1)$$

where W_a is the weight of the specimen at a specific time interval and W_i is the initial dry weight of the specimen. Equilibrium moisture was assumed when the difference between successive WA values was less than 1%.

3. Results and Discussion

3.1. FTIR

The different methods of grafting of maleic anhydride and its isostructural analogues on natural and synthetic polymers have been discussed in detail in literature [26,29]. Reactive extruder systems and in-situ compatibilazation for grafting of MAH onto various thermoplastic polymers, especially polyolefins, to prepare high performance engineering materials have been significantly developed [30]. For the maleated wax, the characteristic FTIR absorption band has been reported at 1790 cm^{-1}, corresponding to C=O of five-membered cyclic anhydride. [31]. The unreacted MAH, if any, is usually represented by the peak at 698cm^{-1}, attributed to the C=C bond in MAH [32].

Figure 2 shows the spectra for unreacted paraffin wax and maleated paraffin wax. The spectrum for the unreacted wax, as anticipated, shows no peaks at 1790cm^{-1} and 698cm^{-1}, eliminating the chance of any succinic anhydride or maleic anhydride presence in the sample. On the other hand, a prominent characteristic peak at 1790cm^{-1} is visible in the spectrum of maleatedwax (MPW), confirming the grafting of MAH onto the wax in the form of succinic anhydride. Further, absence of any peak at 698 cm-1 in same spectrum rules out possibility of any unreacted MAH in maleated wax sample.

3.2. Morphology Study

Previous works have reported that the morphology structure of TPS depends to a great extent on the starchtype and plasticizer amount used [33, 34]. Micrographs of the fragile fracture surface obtained by SEM of BW-enabled TPS samples are shown in Figure 3. Some unplasticized starch particles were removed from the surface of the blends during the fracture of the specimen, leaving some pits in the fractured surface, as visible in Figure 3a. The mechanism of anti-plasticization effect of plasticizer on TPS has not been fully understood, but some efforts have been made to explain its mechanism [35]. Zhang & Han (2010) [36] observed that starch retrogradation results in antiplasticization phenomenon. At temperatures above glass transition, retrogradation process in TPS is pronounced with the evolution of the crystallinity and rearrangements of plasticizer molecules into the material, thus, reaction kinetics depending largely on the macromolecules mobility, on the plasticizer type and content [37].

It seems BW may have interfered with starch plasticization as well and there also appears a phase separation between TPS and BW, especially at higher BW content as shown in Figure 3b. Unfortunately, to the best of authors' knowledge, no effort has been made so far to develop beeswax-enabled melt-blends of TPS, although use of beeswax as an auxiliary water-repelling film on TPS has been reported with encouraging results [38].
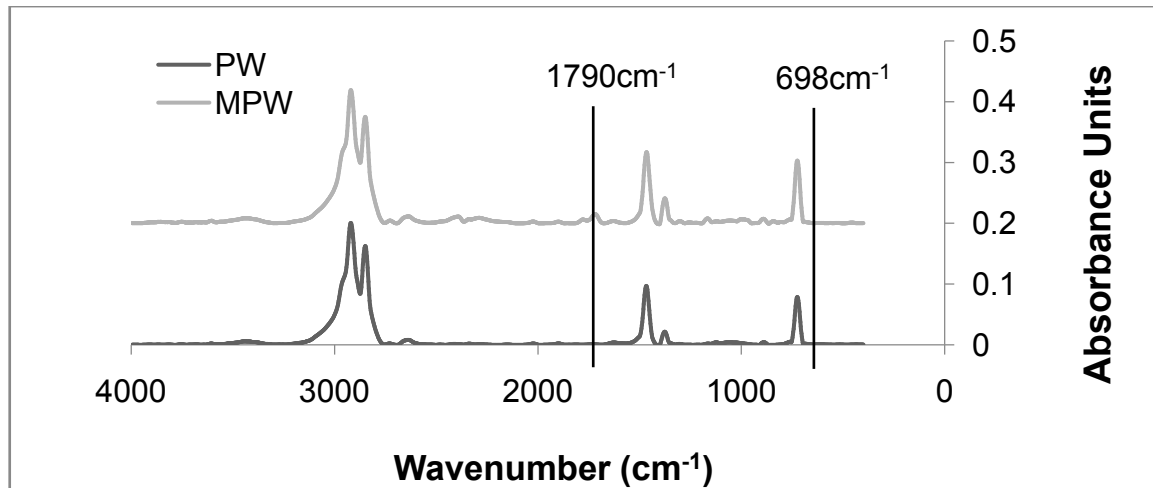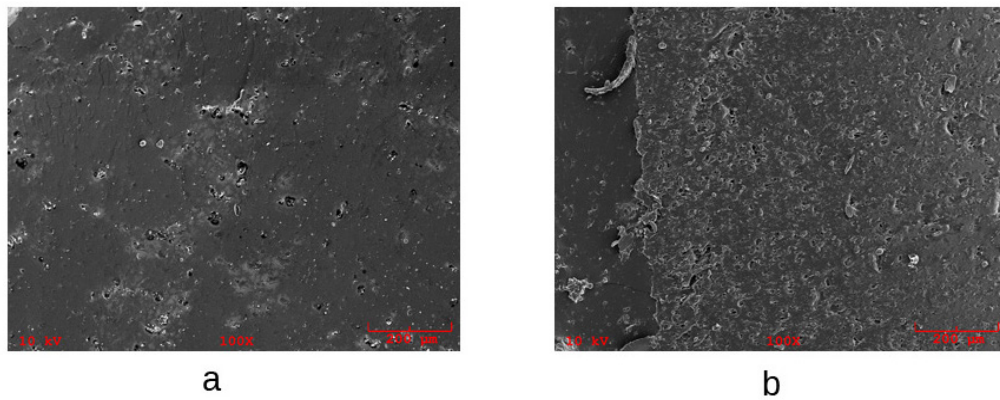
Figure 2. FTIR spectrum for PW and MPW

a

b

Figure 3. SEM images of extruded samples: (a) 5BW (b) 10BW
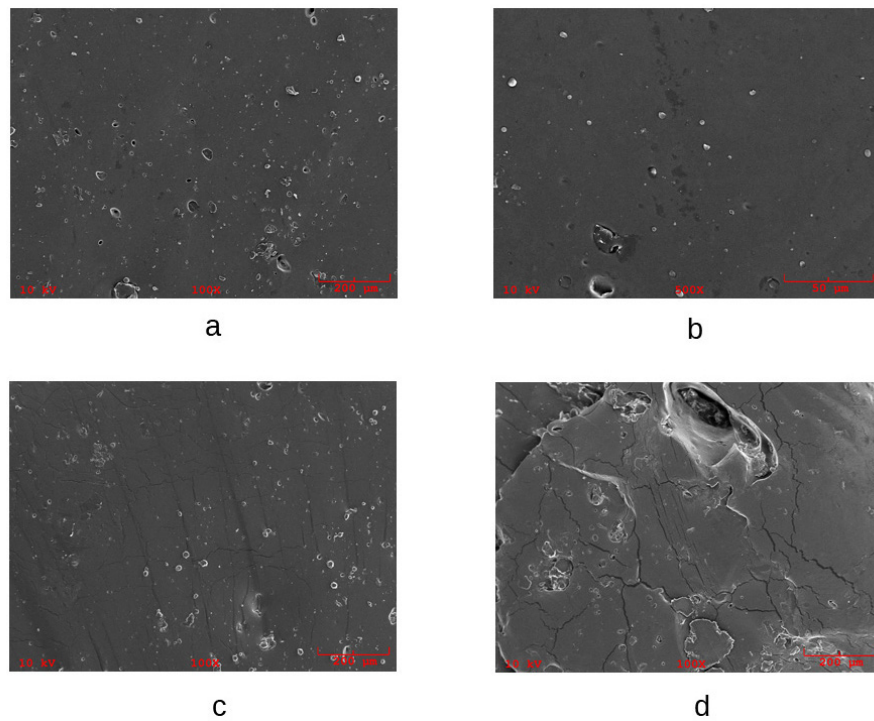

a

b

c

d

Figure 4. SEM images of extruded samples: (a) 5PW (b) 10PW (c) 5MPW (d) 10MPW

The morphology of PW and MPW-enabled TPS samples is demonstrated in Figure 4; as with BW-TPS blends, some unplasticized starch particles are visible in the images as explained earlier. Also, cracks caused by retrogradation or damage by the electron beam are visible in all samples. It appears that TPS and wax combined in a continuous phase with no interface visible in both the PW and MPW-enabled TPS samples, largely due to compatibility among paraffin wax and starch. Although no reactive extrusion example of PW-TPS melt blends is available, however, dip-coating of paraffin wax on Cassava starch to prepare hydrophobic films has been reported [39].

3.3. Thermal Analyses

TGA curves for all wax/TPS samples are shown below in Figure 5 (a,b,c) with wax and TPS as references. In the case of all BW, PW, and MPW samples, there were two well defined shifts in the TGA curve. First, at around 100℃, water evaporation caused the initial weight loss. Weight loss continued gradually as water continued to evaporate along with glycerol (starting at 150℃), and then wax (at 150-200℃). A second major shift occurred from 300℃ to 350℃ where the thermal degradation of starch occurred.
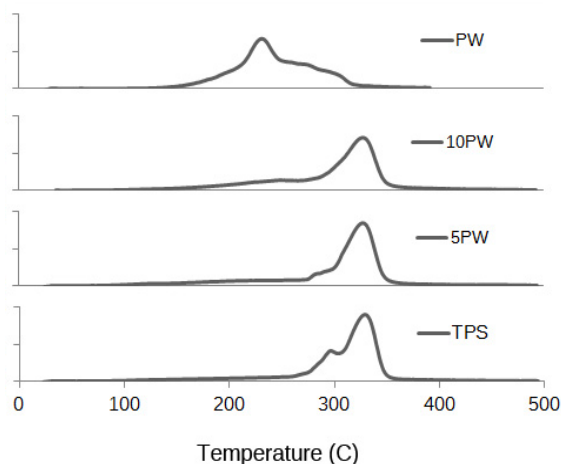

(a)

(b)

(c)
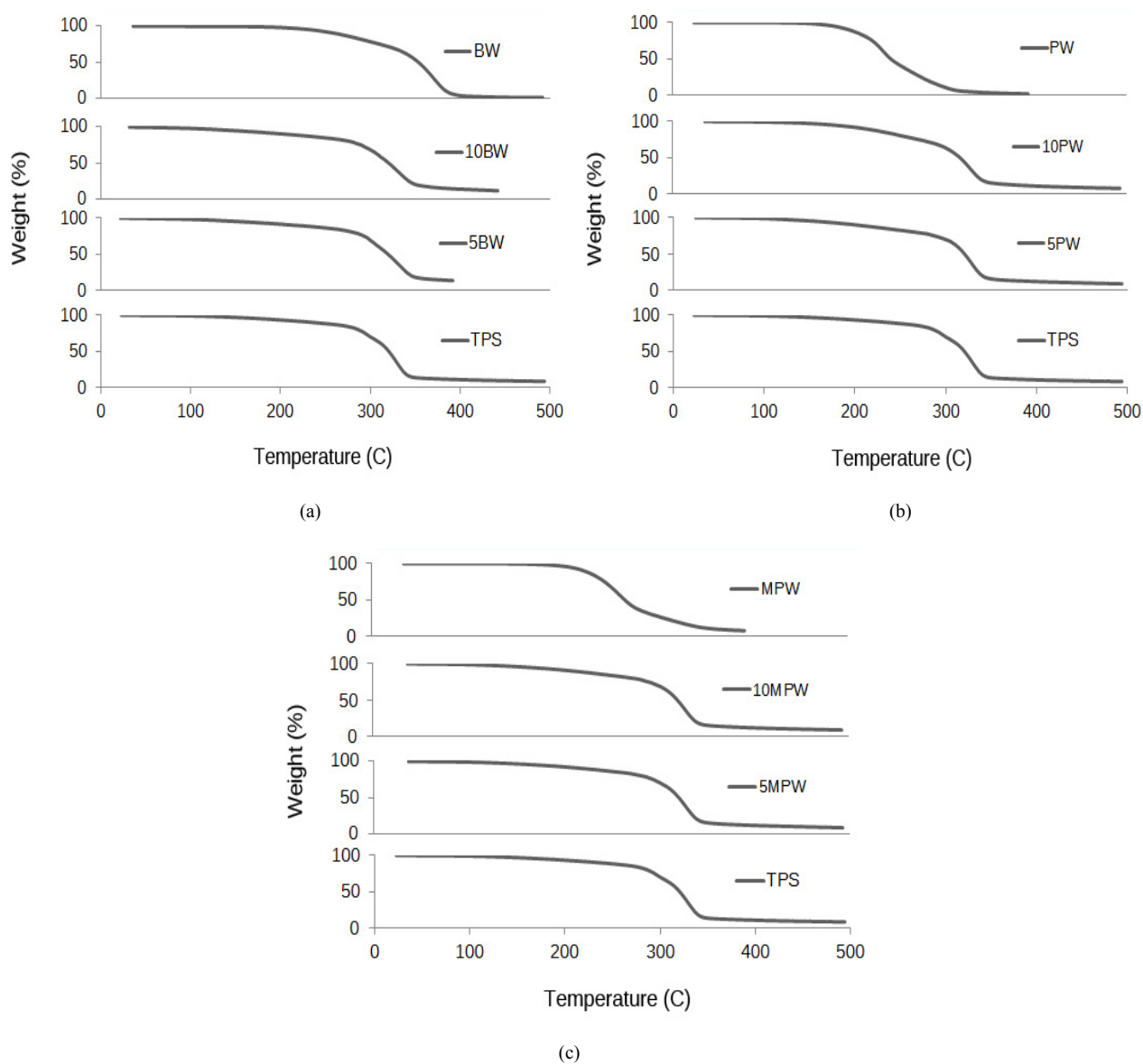
Figure 5. TGA curves for pure BW, TPS and blends of TPS/BW (a), pure PW, TPS and blends of TPS/PW (b), MPW, TPS and blends of TPS/MPW (c)
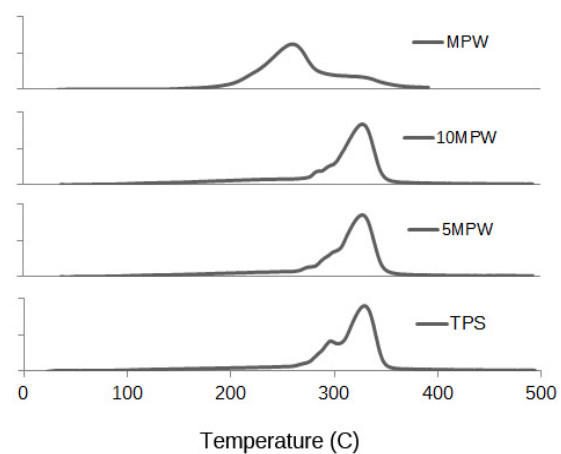
Derivative TGA curves for all wax/TPS samples are shown in Figure 6 with wax and TPS as references.
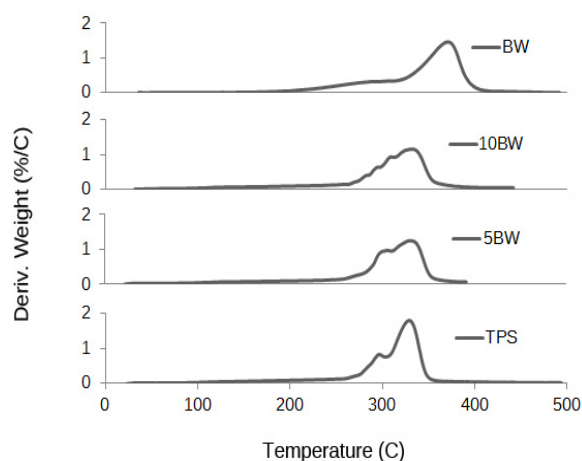
(a)

(b)

(c)

Figure 6. Derivative TGA curves for pure BW, TPS and blends of TPS/BW (a), pure PW, TPS and blends of TPS/PW (b), MPW, TPS and blends of TPS/MPW (c)

Table 3 demonstrates the data extracted from the derivative TGA curves for all pure polymers and TPS blends tested.

Table 3. Data from derivative TGA curves

Sample	$T_{5\%}$ (°C)	Starch T_{max} (°C)	Wax T_{max} (°C)
TPS	182	329	N/A
BW	235	N/A	372
PW	179	N/A	232
MPW	209	N/A	260
5BW	157	332	N/A
10BW	151	332	N/A
5PW	159	328	N/A
10PW	179	328	N/A
5MPW	176	328	N/A
10MPW	167	328	N/A

$T_{5\%}$, the temperature corresponding to 5% weight loss of the sample was greater for the PW and MPW blends than the BW blends, despite the values for pure PW and MPW being lower than that of BW; indicating that these samples were more stable than the BW, forming more compatible blends with TPS, as shown in the SEM images. There was no trend evident in the starch T_{max} values for the blended samples, which all have a T_{max} value close to that of TPS. Therefore, it does not appear that any significant starch degradation occurred in the BW, PW, or MPW samples. It was not possible to analyze wax T_{max} values because of degradation overlapping with TPS.

3.4. Water Absorption

Figure 7 shows the water absorption results for all TPS/wax blended samples with TPS as a reference. The tested value for TPS water absorption (66%) is comparable to the literature value (62%) for glycerol plasticized (50wt%) TPS [40].

In case of TPS and beeswax blends, the average water absorption values decrease when beeswax is added to TPS and continue to decrease as the concentration of beeswax increases from 5 to 10%. The classical theory in literature supports this result which predicts that water absorption of the polymer blend is dependent on the weight fraction of TPS, weight fraction of hydrophobic polymer, the thermodynamic interaction energy between TPS and the hydrophobic polymer, and their respective diffusion coefficients [41]. However, the reduction in water absorption is not statistically significant for either the 5BW or 10BW sample. This may be a result of the sample preparation method used. When the samples were pressed at high temperature, some of the wax migrated out of the samples because of its low viscosity. Therefore, the water absorption of the extruded blends may be lower than the values reported here for the hot pressed samples.
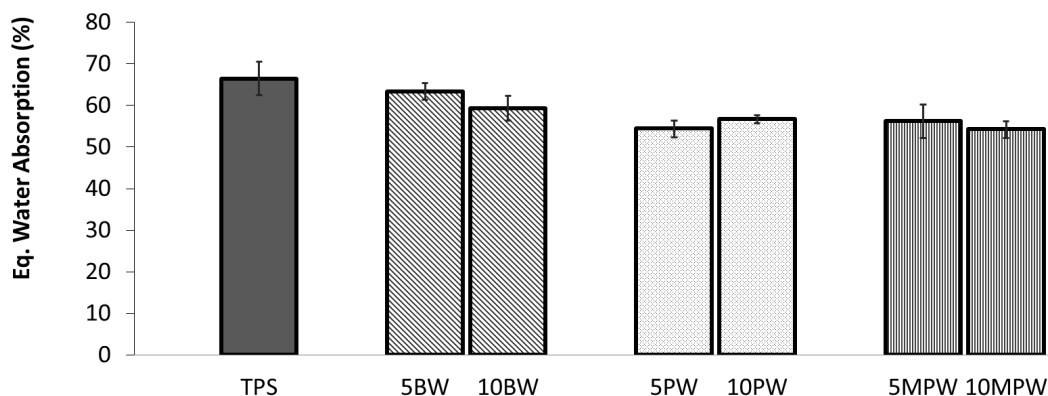
Figure 7.   Water absorption at equilibrium for TPS and TPS/Wax formulations

The water absorption results for TPS blended with paraffin wax and paraffin wax with MAH also exhibit same trend, however, contrary to the BW samples, the reduction in water absorption is statistically significant for both the PW and MPW samples. This observation confirms the fact that paraffin wax more effectively reduces water absorption in TPS, the main reason being the advantageous chemical structure of paraffin wax containing only hydrocarbon chains, whereas beeswax contains water attracting groups such as esters as well. Interestingly, the water absorption values for all PW and MPW samples were statistically equal with 95% confidence, therefore, using MAH as a compatibilizer had no significant effect on reducing the hydrophobicity of TPS blends.

3.5. Conclusions

TPS formulations with beeswax and paraffin wax were developed through melt blending and reactive extrusion facilitated by MAH and DCP. The effect of different weight fractions of BW and PW were studied for physico-chemical properties while keeping glycerol level at constant levels. Also studied was effect of maleated PW over a range of concentrations and, subsequently, comprehensive morphological, thermal and hygroscopic analyses demonstrated some predicted and also novel results.

- Morphological studies through SEM micrographs consistently showed some unplasticized areasowing to single-feeder system and retrogradation phenomenon, a common drawback involving rearrangements of plasticizer molecules into the starch material.
- Phase separation was observed in BW-enabled TPS extruded samples, whereas, PW-enabled TPS blended systems' morphology showed much better and homogenous interfacial phase even in the absence of compatibilizer, MAH. The main reason for this could be attributed to different chemical structures of both waxes; BW being rich in esters while PW containing mostly homologous series of hydrocarbon chains.

- The grafting of MAH as succinic anhydride on PW was confirmed through FTIR spectra as supported by literature examples; although MPW-enabled TPS blends did not exhibit any better surface morphology compared to PW-enabled blends, but their thermal performance improved compared to other formulations.
- Thermal analysis during derivative TGA curves validated the enhanced stability of PW and MPW blends of TPS compared to BW blends; a phenomenon substantiated through SEMs as well by showing no phase separation of said formulations.
- Although some reduction in moisture absorption was observed for TPS/BW blends during hygroscopic studies, but it was not significant compared to neat TPS; main reasons being loss of some uncontrolled amount of BW during sample preparation and presence of water-attracting esters in its chemical structure.
- A significant reduction of 20% in moisture uptake was observed for PW blended TPS extrudates due to favorable chemical structure of paraffin wax. The differences in surface chemistry and physical structure of the waxes appear to be critical for the improvement of hydrophobicity of TPS blends.
- The results of this study could be served as benchmark in developing moisture resistant bioplastics from renewable resources.

REFERENCES

[1] Pervaiz, M., Sain, M., 2003. Carbon storage potential in natural fiber composites. Resources, Conservation and Recycling, 39,325–40.

[2] Faruk, O., Bledzki, A.K., Fink, H.P., Sain, M., 2014. Progress report on natural fiber reinforced composites. Macromol. Mater. Eng. 299, 9–26. DOI: 10.1002/mame.201300008.

[3] Pervaiz, M., Sain, M., 2012. High-yield protein recovery from secondary sludge of paper mill effluent and its characterization. BioResources 7(3), 2933-2947.

[4] Thakur, V.K., Thakur, M.K., Raghavan, P., Kessler, M.R., 2014. Progress in green polymer composites from lignin formultifunctional applications: A review. ACS Sustainable Chem. Eng. 2, 1072−1092. dx.doi.org/10.1021/sc500087z.

[5] Humairah, A.R.N., A. Zuraida, S. Norshahida and Z.S. Naqiahet, 2014. Characterizations of thermoplastic starch and starch reinforced montmorillonite clay nanocomposite. Advances in Environmental Biology, 8(3): 792-796.

[6] Liu, H., Xie, F., Yu, L., Chen, L., Li, L., 2009. Thermal processing of starch-based polymers. Prog. Polym. Sci. 9, 34,1348–1368.

[7] Yu, L., Dean, K., Li, L., 2006. Polymer blends and composites from renewable resources. Prog. Polym. Sci., 31, 576–602.

[8] Dubois P., Narayan R., 2003. Biodegradable compositions by reactive processing of aliphatic polyester/polysaccharide blends. Macromolecular Symposium, 198, 233-243 (2003).

[9] KalamburS., Rivzi S., 2006. An overview of starch-based plastic blends from reactive extrusion. Journal of Plastic Film and Sheeting, 22(39), 39-58.

[10] Chandra R., Rustgi R., 1998.Biodegradable Polymers. Progress in Polymer Science, 23: 1273-1335.

[11] Cornell H., 2003. Starch in food; structure, function, and applications. Woodhead Publishing Limited, CRC Press, 211-240.

[12] Donald A. M., 2003. Starch in food; structure, function, and applications. Woodhead Publishing Limited, CRC Press, 156-184.

[13] Luo, X., Li, J., Lin, X., 2012. Effect of gelatinization and additives on morphology and thermal behavior of corn starch/PVA blend films. Carbohydr. Polym. 90: 1595–1600.

[14] Forssell P., Mikkilä J., Suortti T., Seppäl J., Poutanen K., 1996. Plasticization of barley starch with glycerol and water. Journal of Macromolecular Science, Part A. 33(5): 703-715.

[15] Shogren R.L., Fanta G.F., Doane W.M., 1993. Development of starch based plastics – a re-examination of selected polymer systems in historical perspective. Starch, 45(8): 276-280.

[16] Stepto R.F.T., 2003. The processing of starch as a thermoplastic. Macromolecular Symposium, 20: 203-212.

[17] Sain, M., Robert, J., Martin, H., 2011. Modified thermoplastic starch from Ophiostomaulmi polysaccharide conversion. US Patent: 7943349, WO 2008154729 A1.

[18] Averous L., Moro L., Dole P., Fringant C., 2000. Properties of thermoplastic blends: starch–polycaprolactone. Polymer, 41: 4157-4167.

[19] Shogren R.L., 1996. Preparation, thermal properties, and extrusion of high-amylose starch acetates. Carbohydrate Polymers, 29(1); 57-62.

[20] Nabar Y., Raquez J.M., Dubois P., Narayan R., 2005. Production of starch foams by twin-screw extrusion: effect of maleatedpoly (butylene adipate-co-terephthalate) as a compatibilizer. Biomacromolecules, 6: 807-817.

[21] Dubois P., Narayan R., 2003. Biodegradable compositions by reactive processing of aliphatic polyester/polysaccharide blends. Macromolecular Symposium, 198: 233-243.

[22] Li, J., Luo, X., Lin, X. and Zhou, Y., 2013. Comparative study on the blends of PBS/thermoplastic starch prepared from waxy and normal corn starches. Starch/Stärke, 65: 831–839. doi: 10.1002/star.201200260.

[23] Kamke F.A, Miller T.R., 2006. Enhancing composite durability using resins and waxes – a review. Wood Protection Conference, New Orleans, LA.

[24] Jiminez J.J., Bernal J.L., Aumente S., NozalMa.J del., Martín Ma.T., Bernal J, 2004. Quality assurance of commercial beeswax. Part I. Gas chromatography – electron impact ionization mass spectrometry of hydrocarbons and monoesters. Journal of Chromatography A, 1024:147-154.

[25] Shin B.Y., Lee S., Shin Y.S., Balakrishnan S., Narayan R., 2004. Rheological, mechanical and biodegradation studies on blends of thermoplastic starch and polycaprolactone. Polymer Engineering and Science, 44(8): 1429-1438.

[26] Rzayev Z.O., 2011. Graft Copolymers of Maleic Anhydride and Its Isostructural Analogues: High Performance Engineering Materials. International Review of Chemical Engineering, 3(2): 153-215.

[27] Krump H., Alexy P., Luyt A.S., 2005. Preparation of a maleatedfischer-tropsch paraffin wax and ftir analysis of grafted maleic anhydride. Polymer Testing, 24: 129-135.

[28] Kalambur S., Rivzi S., 2006. An overview of starch-based plastic blends from reactive extrusion. Journal of Plastic Film and Sheeting, 22(39): 39-58.

[29] Uzdoğan A., Rzaev, Z.O., Okay G., 2007. Bioengineering functional copolymers: Synthesis and characterization of (N-isopropylacrylamide-co-3,4-2H-dihydropyran)s, J. Polym. Res. 32: 534-595.

[30] Fenouillot F, Cassagnau P, Bounor-Legaré V., 2007. Reactive processing of thermoplastic polymers: A review of thefundamental aspects, Int. Polym. Processing, 3: 218-258.

[31] Novak I., Krupa I., Luyt A.S., 2004. Modification of a Fischer-Tropsch wax by grafting with maleic anhydride, J. Appl. Polym. Sci. 93: 662-668.

[32] Shujun W., Jiugao Y., Jinglin Y.: Preparation and characterization of compatible thermoplastic starch/ polyethylene blends. Polymer Degradation and Stability, 87, 395-401(2005).

[33] Zullo R., Iannace, S., 2009. The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: correlation among process, elongational properties and macromolecular structure. Carbohydr. Polym. 77:

376–383.

[34] Xie, F., Halley, P. J., Averous, L., 2012. Rheology to understand and optimize processibility, structures and properties of starch polymeric materials. Prog. Polym. Sci. 37: 595–623.

[35] Zhang Y., Rempel C., 2012. Retrogradation and Antiplasticization of thermoplastic Starch, Thermoplastic Elastomers, Prof. Adel El-Sonbati (Ed.), ISBN: 978-953-51-0346-2, InTech, Available from: http://www.intechopen.com /books/thermoplastic-elastomers/retrogradation-and-antiplast icization-ofthermoplastic-starch.

[36] Zhang, Y., Han, J.H., 2010. Crystallization of high-amylose starch by the addition of plasticizers at low and intermediate concentrations. *Journal of Food Science*, 75: 8-16.

[37] Van Soest, J. J. G.; Knooren N., 1997. Influence of glycerol and water content on the structure and properties of extruded starch plastic sheets during aging. J. Appl. Polym. Sci. 64: 1411-1422.

[38] Yang L., Paulson A. T., 2000. Effects of lipids on mechanical and moisture barrier properties of edible gellan film. Food Research International, 33 (7): 571-578. ISSN: 0963-9969.

[39] Auras R., Arroyo B., Selke S., 2009. Production and Properties of Spin-Coated Cassava-Starch-Glycerol-Beeswax Films. Starch – Stärke, 61(8): 463–471.

[40] Mathew A.P., Dufresne A., 2002. Plasticized waxy maize starch: effect of polyols and relative humidity on material properties. Biomacromolecules, 3: 1101-1108.

[41] Paul D.R., 1984. Gas transport in homogenous multicomponent polymers. Journal of Membrane Science. 18: 75-86.