

Novel Biodegradable Form Stable Phase Change Materials: Blends of Poly(ethylene oxide) and Gelatinized Potato Starch

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ABSTRACT: Novel biodegradable form stable phase change materials were obtained in a process involving potato starch gelatinization in water/poly(ethylene oxide) (PEO) solution. DSC and microscopic investigations revealed that the presence of the starch considerably changes PEO phase transition behavior—in the blends solid–solid phase transition for PEO/starch 1 : 3 and 1 : 1 w/w has been observed; for PEO/starch blend 3 : 1 w/w solid–solid phase transition with a partial melting of PEO unbounded through hydrogen bonds with starch has been

detected. The heat of phase transition depends on the strength of hydrogen bonds between PEO and starch. The intermolecular interactions were evidenced by FTIR analysis, which showed considerably shift of the stretching vibration bands of both the O–H group (proton-donor group) from starch and PEO. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1725–1731, 2010

Key words: poly(ethylene oxide); phase change materials; polysaccharides; phase behavior; thermal properties

INTRODUCTION

Latent heat thermal energy storage with phase change material (PCM) is one of the most preferred forms of energy storage, because of its high storage density and small temperature variation from storage to retrieval.

Phase change materials include solid–liquid phase change materials and solid–solid phase change materials. Solid–liquid phase change materials such as paraffin, fatty acids, or some polymers are traditional phase change materials used in the field of thermal storage. However, they must be loaded in the containers if they are used because of leakage. To avoid this phenomenon, shape-stabilized or solid–solid phase-change materials are preferred.^{1–3} They are characterized by small change in volume, lack of leakage and no phase separation.

Among solid PCMs, starch, one of the most inexpensive and most readily available of all natural polymers, is getting an increased attention. Starch is composed of repeating 1,4- α -D-glucopyranosyl units, and is generally a mixture of linear (amylose) and

branched (amylopectin) components. The linear component, amylose, is the minor component, typically ranging from 20 to 30%, which has a molecular weight of several hundred thousand.⁴ Owing to its complete biodegradability, low cost, and renewability, starch is considered as a promising candidate for developing sustainable materials that does not require a costly recycling procedure after its life time. Starch is totally biodegradable in a wide variety of environments - it can be hydrolyzed into glucose by microorganism or enzymes, and then metabolized into carbon dioxide and water.⁵

It is believed that short branches of amylopectin are arranged in clusters that form into double helical structures. The double helices are further arranged, to some extent, into two types of crystallites or polymorphs.⁶ Imberty and Perez⁷ proposed a crystal model, which has left handed double helices packed in a monoclinic space group B2 having eight water molecules per unit cell, called A-type. The other model suggested is a double helix packed in a hexagonal unit cell with the P61 space group, with 36 water molecules in the unit cell, called B-type. A-type crystals are formed in the dry and warm conditions during biosynthesis normally obtained for cereal starches. B-type crystals are present in native potato and high amylose starches. By heating potato starch in a proper moisture at 100–120°C the B-type is converted to the A-type.⁸

The crystalline or semicrystalline properties of native starch are attributed to the short-chain fraction of amylopectin arranged as double helices and packed in crystallites. Like in other polymers, the

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crystallites have a lamellar structure. However, the lamellae (9 nm) found in the native starch exhibit some novel features. Their appearance has more in common with a side-chain liquid-crystalline polymer, double helices arranged side by side in a smectic or nematic type structure, than with spherulitic structures with chain-folded lamellae as in synthetic polymers.⁹ The differences in the physical properties between the different kind of starch were clearly influenced by the amylose/amylopectin ratio.¹⁰

Hydrogen bonding has long been postulated as playing a critical role in the gelatinization of starch. In this process whole starch granules are swollen and eventually ruptured by heating in the presence of excess water to form a gel structure.¹¹ In an early starch gelatinization was explained by hydrogen bonding of the starch hydroxyl groups through water molecules.

The role of hydrogen bonding in amylose gelation was investigated by McGrane et al.¹¹ and it was found that in the absence of water, amylose was able to form strong, elastic gels by the addition of various polyols. It was proposed that polyols such as 1,3-propanediol are able to form an intermolecular hydrogen bonded network of amylose molecules, similar to that produced by water.¹¹ A number of studies have looked at the effect of glycerol on the thermal transitions of starch. Soest et al.¹² indicates that the gelatinisation onset temperature T_0 increases linearly with increasing glycerol content for higher moisture content mixtures. However, this linear trend does not hold for moisture contents below 33%. Nashed et al. revealed that glycerol behaves as an "antiplasticiser" as it hinders the gelatinisation process rather than assisting it. A linear increase of T_0 with increasing glycerol content was also observed. Authors postulated that in starch-glycerol mixtures, the hydrophilic nature of glycerol interferes with the moisture uptake of starch, and hence diminishes the effective moisture contents of the starch available to aid gelatinisation.¹³

In our previous papers we studied the application of poly(ethylene oxide)-based materials with different fatty acids, carbon (nano)nuclents and cellulose derivatives as modern PCMs.^{14,15} PEO with —OH end groups is a polymeric diol that should be able to create hydrogen bonds with starch during the gelatinization process. The obtained novel form stable PCMs were investigated by FTIR, (MT)DSC and optical microscopy.

EXPERIMENTAL PART

Materials

Poly(ethylene oxide) (PEO) was produced by Poly-science Co., Warrington, PA. Molecular weight was

determined by GPC performed at 40°C on a Hewlett-Packard 1050 GPC System with a refractometric detector, using Shodex OH-Pac SB803 HQ 8 × 300 mm column from Showa Denko. Average molecular weights were determined as $M_n = 9630$ and $M_w = 13,060$, $M_w/M_n = 1.38$. Degree of crystallinity (X_c) was calculated using DSC data as 0.92. Potato starch was produced by Zakłady Przemysłu Ziemniaczanego, Trzemeszno, Poland.

In the preparation procedure, PEO was dissolved in the distilled water, then the potato starch was added to the solution which was stirred for 5 min. Blends with PEO/starch ratio 3 : 1, 1 : 1, 1 : 3 w/w were obtained, as well as PEO and starch solutions at concentration 2% were prepared for comparison. At the next stage, the dispersions were heated to temperature of starch gelatinization and kept at this temperature for 1 h. The PEO/starch/water gel was put on Petri dishes and dried for 48 h to remove water.

Techniques

(Modulated temperature) differential scanning calorimetry

For the dynamic DSC measurements a Netzsch DSC 200, operating in dynamic mode, was employed. Sample of ca. 5 mg weight was placed in sealed aluminum pan. The heating rate of 10 K/min and cooling rate of 10 K/min were applied; argon was used as an inert gas. Before use the calorimeter was calibrated with an indium and mercury standards; an empty aluminum pan was used as reference. Liquid nitrogen was used as a cooling medium.

modulated temperature differential scanning calorimetry (MTDSC) (Mettler-Toledo 822e) measurement conditions were: amplitude 0.5 K, period 45 s and underlying heating rate 1 K/min. Argon was used as an inert gas.

Infrared spectroscopy (FTIR)

IR spectra of the samples (KBr pellets) were recorded on a Bio-Rad FTS 165 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm⁻¹.

Microscopic investigations

Microscopic investigations were performed by means of polarized light microscope (PLM) with vision track (PZO Warszawa, Poland) equipped with a hot stage.

RESULTS AND DISCUSSION

Temperatures and heat of melting and crystallization for PEO/potato starch blends are collected in Table I.

TABLE I
Temperatures and Heat of Phase Transition for Melting and Crystallization Process of PEO/starch Blends
(DSC, Heating Rate 10 K/min)

Sample	Melting				Crystallization			
	T_{onset} [°C]	T_{end} [°C]	T_{max} [°C]	Heat of melting [J/g]	T_{onset} [°C]	T_{end} [°C]	T_{max} [°C]	Heat of crystallization [J/g]
PEO	58.7	67.6	63.7	177.8	43.1	27.4	29.3 32.8	203.7
PEO/starch 3 : 1 w/w	57.6	74.6	67.3	96.9	38.4	25.3	33.5	94.6
PEO/starch 1 : 1 w/w	51.4	60.8	57.0	46.9	33.1	16.7	20.3 24.1	46.1
PEO/starch 1 : 3 w/w	51.1	59.6	56.4	43.3	32.4	19.2	26.2	41.6
starch	—	—	—	—	—	—	—	—

Results of DSC investigations of PEO/starch blends show that the temperature range and heat of phase transition depend on the composition of the blends – Figure 1.

For blends under consideration, the melting temperature T_{max} of the PEO/starch (3 : 1 w/w) blend increases, but for PEO/starch (1 : 1 and 1 : 3 w/w) it slightly decreases. T_{onset} decreases for all compositions with increasing additive content and the same trend was found for the crystallization temperature, it leads to an increased supercooling effect during a heating-cooling cycle. The depression of the phase transition temperature implies that there is an interaction between the two components, which is in accordance with the crystallinity changes. For polymer blends in which one of the components crystallizes, a depression in the phase transition temperature, reflecting a change in the chemical potential of the amorphous phase because of a specific interaction, is expected when there is a degree of miscibility.¹⁶

For pure starch after gelatinization and drying no exoeffects or endoeffects in this temperature range were detected because of loss of order. Starch gelatinisation induces a number of changes in the starch granules, such as loss of order (birefringence, X-ray crystallinity), swelling, exudation of amylose, improved digestibility, granule disruption, enhanced solubility, and increased viscosity. From DSC studies, gelatinisation is an endothermic process, although it could involve the following two stages: (i) cleavage of existing hydrogen bonds (endothermic); (ii) formation of new bonds (involving water) to give a less ordered structure (exothermic).¹⁷

Donald and coworkers studied the occurrence and importance of liquid crystallinity in the organization of the starch granule. Within this model, the amylopectin is regarded as a side chain liquid crystalline polymer, in which the double helical clusters represent the rigid mesogen units which confer liquid crystalline ordering on the molecule. In the crystals, the mesogens are aligned, and there are long range

correlations between neighboring lamellar crystals, which give rise to the overall 9 nm repeat (smectic phase). An alternative packing (nematic) can be conceived, in which lateral organization within the lamellar crystals still holds, but the long range periodicity between layers is lost. Authors postulated that a necessary stage in the gelatinisation process will be the transition from the smectic to nematic state, accompanied by the loss of the 9 nm peak in the SAXS patterns (loss of lamellar order).^{18–20}

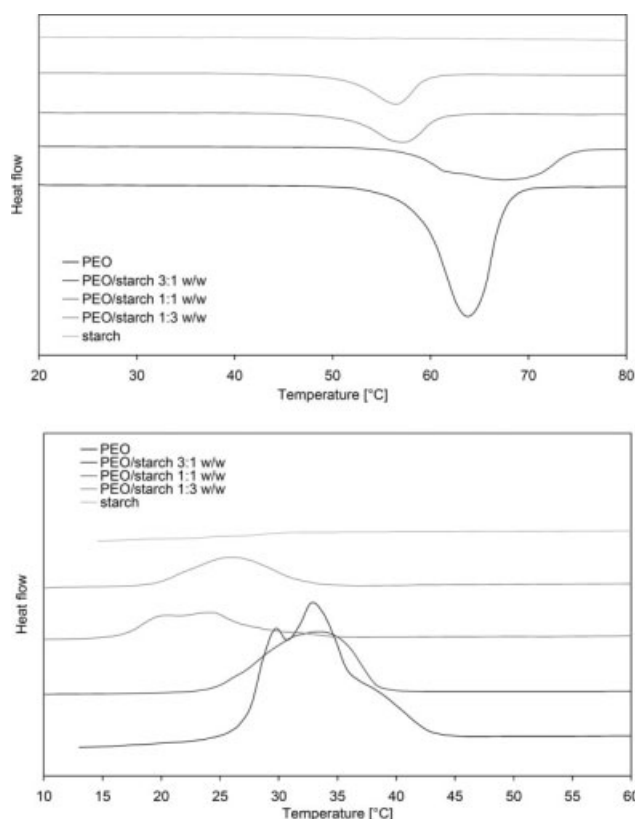


Figure 1 DSC curves (in dynamic mode, heating rate 10 K/min) for melting and crystallization processes of PEO/starch blends.

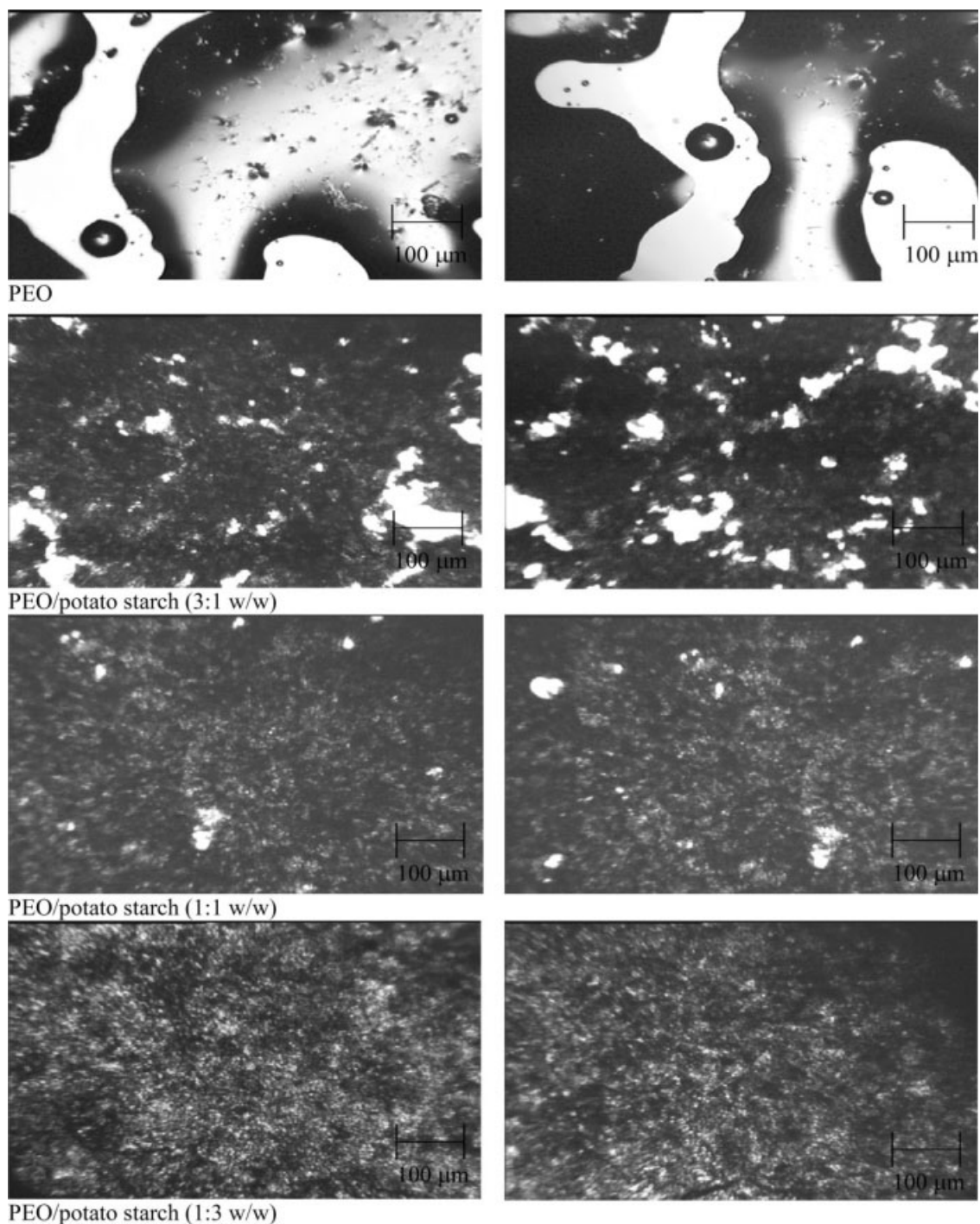
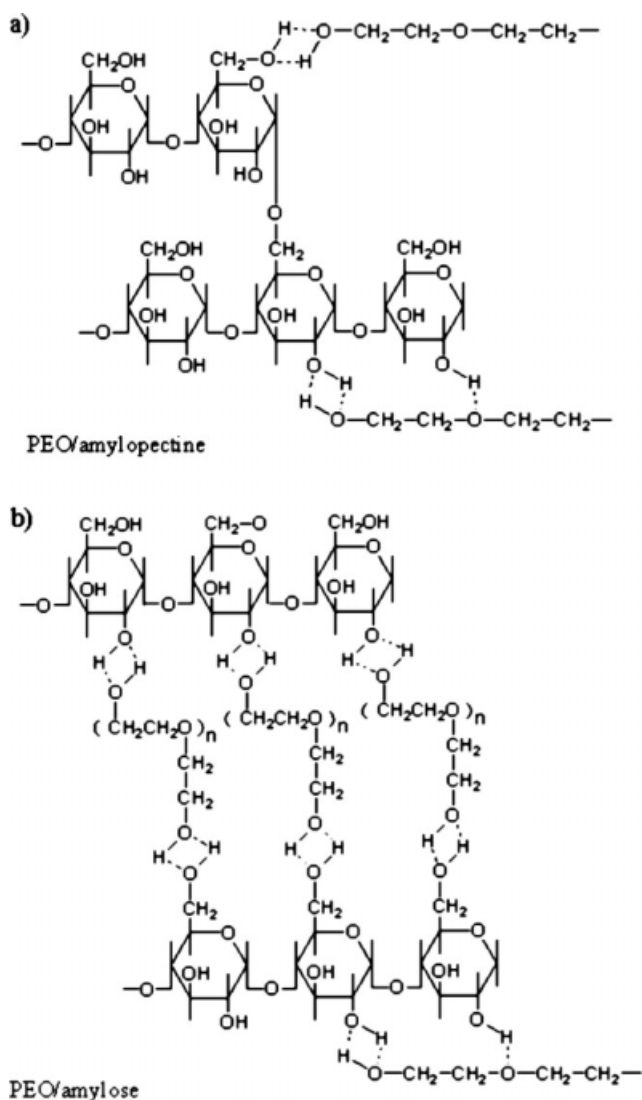


Figure 2 PLM microphotographs of PEO and PEO/starch blends taken at 75°C.

Results of DSC and microscopic investigations show that the presence of starch causes that PEO phase transition behavior depends on the ratio of the components—in studied blends solid–solid phase transition for PEO/starch 1 : 3 and 1 : 1 w/w has been observed; for PEO/starch blend 3 : 1 w/w solid–solid phase transition with a partial melting of PEO unbounded through hydrogen bonds with starch has been revealed at the temperature above phase change temperature – Figure 2.

In case of PEO/starch blends principal role play intermolecular hydrogen interactions between hydroxyl groups in PEO chains and starch – Scheme 1.

During gelatinization in water hydrogen bonds are continuously broken and reformed throughout the heating period, the dissociating water molecules force their way into the micellar network of hydroxyl groups which entrap and bind them; free water is consumed or 'bound', and viscosity increases until the peak viscosity is reached.



Scheme 1 Hydrogen interactions in PEO/starch blends: (a) PEO/amylopectine, (b) PEO/amylose.

The energy supplied by increased temperature and the shear from agitation then begin to destroy the O—H...O links holding the bound water molecules to the starch hydroxyl groups, and the viscosity rapidly decreases.²¹

Generally, the bond energy of a hydrogen bond in starch systems is in the weak category (~ 10 – 50 kJ/mol). The bond length is longer than that of the O—H bond, being about 170 p.m. compared with 97 p.m.. In a series of rheological studies, it has been found that amylose was the dominant gel-forming component in starch and that the water content was critical in the resultant gel structure and properties.²²

In PEO/starch blends under investigation water-starch hydrogen bonds were partially replaced by PEO/starch intermolecular hydrogen bonds. One can assume that in the PEO/starch blends character and heat of phase transition will depend on the

strength and amount of hydrogen bonds in blends. The depression of heat of phase transition and crystallinity of the blends implies that there is a strong intermolecular interaction between starch and PEO. Similar effect was reported by Ding et al.²³ for PEO/cellulose diacetate systems—they found that in the chemical bonded material, the steric effect and drag effect were much larger than that in the blend, so the number of segments that could crystallize decreased, which led to the decline of enthalpy. Similarly, the extent of defects in the crystalline regions in the bonded material was much higher than that in the blended material, and the crystal size in the bonded material was smaller than that in the blend. Thus, the transition temperature of the bonding materials was lower than that of the blend.

A deeper insight into the phase transition behavior of polymer blends offers MTDSC. This technique offers extended temperature profile capabilities by e.g. sinusoidal wave superimposed to the normal linear temperature ramp. The modulated temperature and resultant modulated heat flow can be deconvoluted using a Fourier transform to give reversing and nonreversing components.²⁴ The reversible and non-reversible signals reveal the thermodynamic and kinetic characteristics, respectively, of transitions.

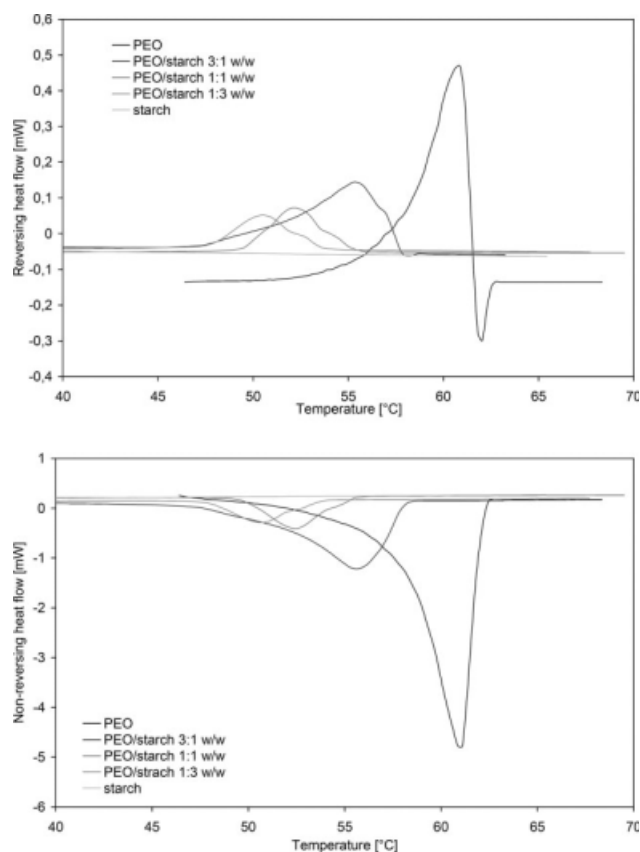


Figure 3 MTDSC profiles for melting of PEO, starch and PEO/starch blends.

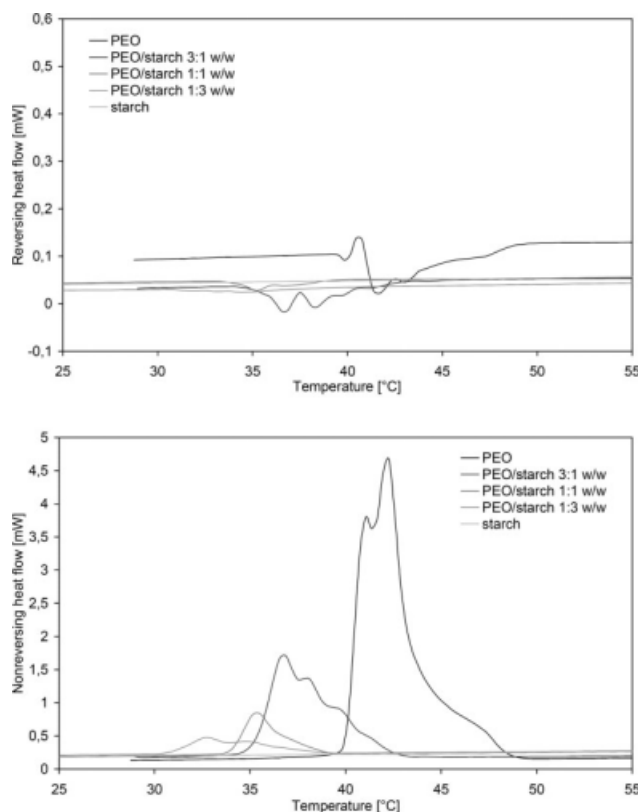


Figure 4 MTDSC profiles for crystallization of PEO, starch, and PEO/starch blends.

Examples of events associated with nonreversible signals are the endothermic relaxation of amorphous materials, gelatinisation, recrystallization, and protein denaturation. Reversible events include glass transition and simultaneous crystallization.^{25,26}

Results of the MTDSC measurements for melting and crystallization processes of PEO/starch blends are shown in Figures 3 and 4.

From Figure 4 it can be observed a strong influence of the amount of additive on the melting processes. For pure PEO (in comparison with PEO/starch blends) peaks are sharper and have larger intensity, as shown in total and nonreversing signal. Moreover,

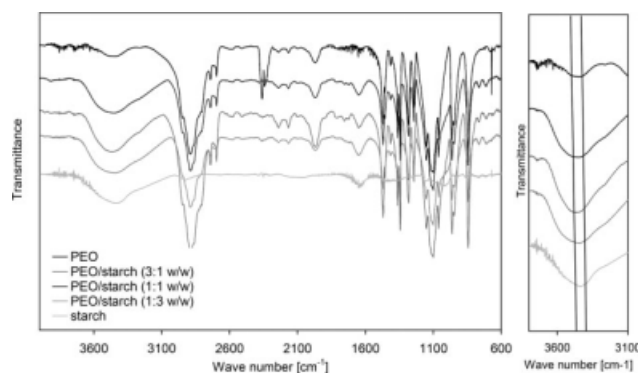


Figure 5 FTIR spectra for PEO, starch, and PEO/starch blends.

TABLE II
Frequency of Stretching Bands of the —OH Group of PEO, Starch and PEO/starch Blends

Sample	—OH frequency [cm^{-1}]
PEO	3449
PEO/starch 3 : 1 w/w	3471
PEO/starch 1 : 1 w/w	3467
PEO/starch 1 : 3 w/w	3433
starch	3430

a strong recrystallization effect (as evidenced by exothermic effect in reversing heat flow) during melting process has been observed. For PEO/starch blends peaks are broader and less intense because of lower PEO chains mobility, as they are bounded through hydrogen bonds with amylose/amylopectine.

FTIR spectra of the blends are presented in Figure 5.

Frequency of stretching bands of the —OH group of PEO, starch, and PEO/starch blends are presented in Table II.

A considerably shift of the stretching vibration bands of both the O—H group (proton-donor group) from starch and PEO has been found. It is an evidence for hydrogen bond interactions in PEO/potato starch blends, but quantitative aspects of this effect need to be investigated in more detail – such studies are in progress.

CONCLUSIONS

Novel biodegradable PEO/potato starch blends were obtained for thermal energy storage applications as form stable PCMs. Results of DSC and microscopic investigations showed that the presence of starch changes PEO phase transition behavior that depends on the ratio of the components – solid–solid phase transition for PEO/starch 1 : 3 and 1 : 1 w/w has been observed, whereby for PEO/starch blend 3 : 1 w/w solid–solid phase transition with a partial melting occurred. The heat of phase transition depends on the strength and amount of hydrogen bonds in blends—the depression of heat of phase transition and crystallinity of the blends implies that there is a strong intermolecular interaction between starch and PEO. MTDSC data reveal a strong recrystallization effect, evidenced by an exothermic peak in the reversing heat flow during melting process. A considerably shift of the stretching vibration bands of the proton-donor O—H group from starch and PEO has been found by FTIR.

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