

Thermal properties and morphology of cassava starch grafted with different content of polystyrene

Kaewta Kaewtatip · Varaporn Tanrattanakul ·
Katalin Mészáros Szécsényi · Jelena Pavličević ·
Jaroslava Budinski-Simendić

Received: 18 December 2009 / Accepted: 1 April 2010 / Published online: 6 May 2010
© Akadémiai Kiadó, Budapest, Hungary 2010

Abstract The interest in replacing synthetic polymers by biodegradable materials from renewable resources is steadily increasing. In this work, cassava starch grafted with different content of polystyrene (PS) was synthesized via free-radical polymerization using suspension polymerization technique. Thermal data of pure starch and the grafted starch with different content of PS were collected by simultaneous thermogravimetric (TG)–differential scanning calorimetry (DSC) setup in open alumina pans. Separately, typical DSC measurements were conducted in standard aluminum pans with lid. The data obtained by different methods are correlated and discussed. Morphology of cryogenic fracture surface of starch sample was studied by scanning electron microscopy. In order to obtain more reliable data about the processes taking place during the thermal treatment, the changes of surface morphology of starch treated at different temperatures are observed.

Keywords Cassava starch · Polystyrene · Grafted polymer · TG–DSC · DSC · Renewable resources

Introduction

Increasing attention and efforts of industrial researchers are nowadays devoted to a possible use of renewable feedstock both as energy source and as raw materials for the production of chemicals and polymeric materials. Particularly, food containers are very often produced by expanded polystyrene (PS) or coated paperboard and efforts are underway to produce similar items from polymers derived from renewable resources such as starch [1]. Natural polymers or biopolymers are produced in nature by living organism and by plants through biosynthetic processes involving CO₂ consumption, and are ultimately biodegraded and consumed in nature in a continuous recycling of resources. The starch is a biopolymer having some advantage, such as renewability and biodegradability, and is also abundant in all parts of the world and has a relatively low price. Starch is composed mainly of the two polysaccharides, amylose, and amylopectin. Amylose has a molecular mass of 10⁵–10⁶ g mol⁻¹ and amylopectin 2 × 10⁷ to 5 × 10⁸ g mol⁻¹. Depending on the botanical origin starch materials vary in composition, such as the amylose/amylopectin ratio and the degree and type of crystallinity, which affects both properties and processability [2]. The crystalline starch structure disappears when it is disposed to temperatures higher than 90 °C in the presence of a plasticizer, such as water. This transformation is called gelatinization [3]. It is possible to convert starch into a thermoplastic material, and for this purpose, it is necessary to disrupt the native semi-crystalline structure of starch. Disruption of the structure, i.e., gelatinization of the starch, is commonly achieved by heating starch in the presence of water. Potato starch has been shown to exhibit the highest swelling ability among the different types of starches due

K. Kaewtatip · V. Tanrattanakul
Bioplastic Research Unit, Department of Materials Science
and Technology, Faculty of Science, Prince of Songkla
University, Hatyai, Songkla 90112, Thailand

K. M. Szécsényi (✉)
Faculty of Sciences, University of Novi Sad, Trg Dositeja
Obradovića 3, Novi Sad 21000, Serbia
e-mail: mszk@uns.ac.rs

J. Pavličević · J. Budinski-Simendić
Faculty of Technology, University of Novi Sad, Bulevar Cara
Lazara 1, Novi Sad 21000, Serbia

to its higher content of phosphate groups [4]. This swelling capacity has been reported mainly to be a property of amylopectin. Starch-based materials can be very brittle. Both with regard to the properties and the processing ability of the material it is desirable to add a plasticizer. Glycerol is commonly used for this purpose, in order to convert starch into a thermoplastic material. Janarthanan et al. [5] studied the thermal behavior and surface morphology of PS grafted sago starch. Graft copolymerization, characterization, and degradation of cassava starch-*g*-acrylamide/itaconic acid super absorbents were investigated by Kiatkamjornwong et al. [6]. Pimpan and Thothong [7] synthesised the cassava starch-*g*-poly(methylmethacrylate) copolymers with benzoyl peroxide as an initiator. Starch processing can be performed with conventional methods used for synthetic polymers, e.g., extrusion and film blowing, but also by processes such as microwave treatment, baking in a hot mold, and freeze drying [8]. Porous structures of starch foams, have gained interest for packaging purposes and other disposable products. One challenge faced when working with starch-based materials is their sensitivity towards water and humidity, but when using these materials for absorption products, the water sensitivity could be taken as an advantage [9]. In our earlier research, a method for obtaining cassava starch (CS) grafted with PS was developed by suspension polymerization, using potassium persulfate (PPS) as an initiator. The optimum conditions giving the maximum percentage of grafted PS, PS-*g*-starch were determined [10]. The aim of the present publication was to study the thermal properties and morphology of CS grafted with different PS content.

Experimental

Materials

Cassava starch was kindly supplied by GSL General Starch Ltd., Thailand. The native CS had standard specification as follows. Maximum moisture content: 12.2%; maximum ash: 0.07%; fiber content: 0.1%; pH: 5.6; SO₂ content: 21.59 ppm; maximum viscosity: 630 Brabender units; sieve test: 99.61% after passing through 100 mesh. The starch was dried in an oven at 100 °C for 48 h and kept in a desiccator before its copolymerization. Styrene monomer was purchased from Fluka® and used after inhibitor was extracted with 5% sodium hydroxide aqueous solution and distilled water sequentially. The inhibitor-free styrene was dried with anhydrous calcium chloride and stored at 4 °C. PPS, toluene, and methanol were of analytical or reagent grade produced by Fisher Chemical®.

Preparation of CS grafted with PS (PS-*g*-starch copolymer)

The synthesis of copolymers is described in details in [10]. The conditions of PS-*g*-starch copolymer preparation and obtained *G* values are presented in Table 1. The *G*, % is the amount of the CS granules grafted with PS [11, 12] and it can be calculated using Eq. 1:

$$G, \% = \frac{w_2 - w_1}{w_1} \cdot 100 \quad (1)$$

where *w*₁ is the original mass of CS and *w*₂ the mass of unextractable products (after Soxhlet extraction).

Methods

Thermal data were obtained using TA Instruments' SDT Q600 TG/DSC thermal analyzer and Q20 DSC device. Simultaneous TG/DSC measurements were carried out up to 600 °C in nitrogen gas carrier (100 cm³ min⁻¹) in an open alumina pan with a corresponding empty referent pan at a heating rate of 10 °C min⁻¹ with sample masses of about 5 mg. For the pure starch sample the experiment was repeated in air under identical experimental conditions. Differential scanning calorimetry (DSC) measurements were accomplished in nitrogen atmosphere using standard aluminum pans with lid and pressure rating to 100 kPa. The samples with masses of 10.5 mg (±0.7 mg) were equilibrated at 30 °C. In the following step they were heated up to 160 °C with a rate of 10 °C min⁻¹, measuring the heat flow compared to an empty pan. The equipment was left to cool down to room temperature. In the next step the run was repeated under the same experimental conditions up to 250 °C. The results of the second run were evaluated. The mass of the covered pan with the sample was measured before and after the first run as well as after the second run, in order to determine the extent of water evaporation.

For visual observation of the thermal changes, a Koffler's hot stage apparatus was employed. To describe more precisely the changes due to the thermal treatment of starch, we have examined the surface morphology of starch as supplied, that of which was previously heated to 160 °C

Table 1 Amount of PPS and the reaction time for the materials with different *G* in PS-*g*-starch copolymer at 50 °C in 100 g of water and the starch-to-styrene monomer ratio of 25:75

Reaction time/h	Amount of PPS/g	<i>G</i> /%
2	0.6	10.50
2	0.2	15.41
1	0.4	21.68
2	0.4	34.00

(evaporation of the surface water) and the one, which was treated to 250 °C, by scanning electron microscopy (SEM) JEOL JSM-6460 at magnifications from 10^3 to 2×10^6 at 25 kV. For SEM morphological investigations, the fracture surfaces of samples were coated with gold using BAL-TEC SCD 005 instrument. This “Sputting coater” procedure was applied at 50 mA, under vacuum at 10^{-6} torr for 120 s. The brightness and contrast of the digitised SEM micrographs were adjusted using standard software.

Results and discussion

Thermogravimetric (TG) curves of native CS and PS-*g*-starch copolymer with different *G*, % (PS content) are shown in Fig. 1. Simultaneous TG/DSC measurements reveal for all samples that the first change belongs to the evaporation of the adsorbed water with derivative thermogravimetric (DTG) maximum at about 80 °C. The amount of water is about the same for all samples (about 9%) up to 160 °C. The adsorbed water content of CS and PS-*g*-starch copolymer determined by TG measurements is in the agreement with the literature data obtained in air-oven drying at 105 °C [13]. It refers to the highly hygroscopic nature of CS and its grafted polymer powders, as is usual for the materials containing starch in the powder form [14].

In the range from 160 to 250 °C a very small mass loss is observed ($\sim 0.5\%$), most probably due to the evaporation of structural water. A similar dehydration pattern was found in potato starch [2]. In order to see if the gas carrier has some influence on the thermal changes before the starch decomposition temperature is achieved, the mass loss was followed also in air (the TA curves are not presented). It was found that the thermal stability of starch is somewhat lower in air (onset: 250 °C) compared to that in nitrogen (onset: 275 °C), but it has no influence on the dehydration mechanism. All other measurements were

conducted in an inert atmosphere of nitrogen avoiding thus the interference of uncontrolled oxidation processes during the decomposition in air at higher temperatures.

The decomposition of CS and the PS-*g*-starch copolymer with different *G*, % begins above 290 °C onset preceded with a small mass loss of about 2% at 268 ± 1 °C DTG maximum for the grafted samples and at 284 °C for native CS (see Fig. 2), respectively. This mass loss, being observed in the pure CS as well as in its grafted samples, most probably belongs to the loss of starch amylopectin $-\text{CH}_2\text{OH}$ groups and is overlapped with further decomposition steps of the starch up to 350 °C with DTG peak temperatures of 307 ± 1 °C. The highest difference between the decomposition temperatures belongs to the pure starch and the grafted sample with PS content of 5%. The next DTG maximum of CS is also higher with 8 °C compared to all other samples. When CS is grafted with higher PS content than 5%, above 400 °C a new DTG peak appears with increasing intensity that most probably belongs to the presence of PS (Fig. 2). However, neither the position nor the intensity of this peak could be used to determine the PS content of the sample. In blends containing about the same amount of CS and PS components might be possible to predict their approximate composition on the basis of TG data [15]. Above 350 °C the decomposition of CS and its grafted polymers turns in an exothermic process even in nitrogen.

In spite of the different level of the heat flux, DSC decomposition pattern (Fig. 3) of the sample with 5% PS is more similar to the pure CS than to samples with higher PS content. This similarity is clearly seen in Figs. 2 and 3. The different thermal behavior of the sample with the highest PS content is visible in all three figures. Similar results were found in thermal studies of PS grafted sago starch [5]. Due to the relatively slow heating rate [16], DSC curves show no obvious transitions, neither of those for CS nor for PS. It is very difficult to detect the baseline shift of starch glass transition due to the low heat flow value compared

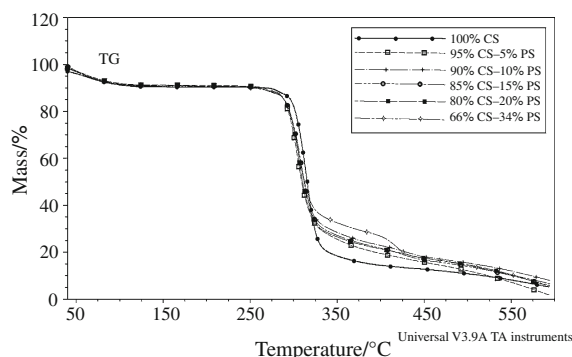


Fig. 1 TG curves of native cassava starch and PS-*g*-starch copolymer with different *G*, % obtained by simultaneous TG/DSC measurements

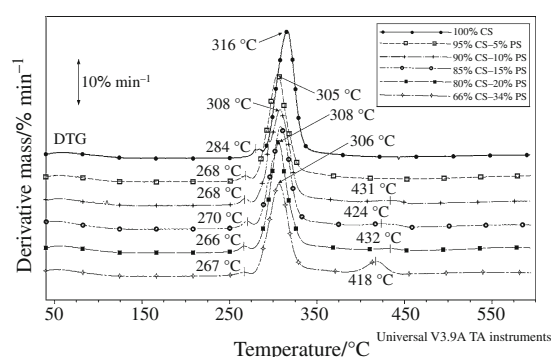


Fig. 2 DTG curves of pure cassava starch and PS-*g*-starch copolymer with different *G*, % obtained by simultaneous TG/DSC measurements

with that for the conventional polymers. The glass transition temperature depends on the water content of the sample. In addition, its position is the function of experimental conditions [17]. Pure PS (not presented) has a glass transition, T_g , at 107.5 °C.

The evaporation of the adsorbed water takes place in a relatively wide temperature interval and may overlap other processes related to structural changes. To separate the different processes, DSC curves of pure CS and its grafted derivatives using DSC Q20 TA Instruments device in standard aluminum pans with lid, were measured. By this way, the enthalpy of the dehydration in so called “self-generated atmosphere” was determined [18, 19]. In order to obtain a self-generated atmosphere and to remove the previous thermal history, samples were heated under identical regime in pans with lid up to 160 °C, cooled to the room temperature and the measurement was repeated. The first run shows no peaks except of the steady endothermic water evaporation. The pans were weighted to determine the mass of the evaporated water. The amount of adsorbed water agrees with the mass allowed by the vapor pressure at 160 °C and still remains the structural one. The mass loss in covered pan during the first run for grafted sample with 15% PS amounts $7.0 \pm 0.1\%$. At 250 °C (before the decomposition of the starch or the grafted polymer begins) the complete mass loss agrees with that found in open pan in simultaneous TG/DSC measurements ($8.9 \pm 0.9\%$) within the experimental error. The difference in DSC curves recorded to 250 °C without and with a thermal pretreatment of this sample is presented in Fig. 4. The solid line corresponds to DSC curve of the grafted sample ($G, \% = 15\%$) without thermal pretreatment. The broad peak refers to a prolonged water evaporation joined with the melting, probably due to the fusion of the different crystal regions of starch granules [20].

The sample previously heated up to 160 °C with much lower water content, at the second run shows two (dashed

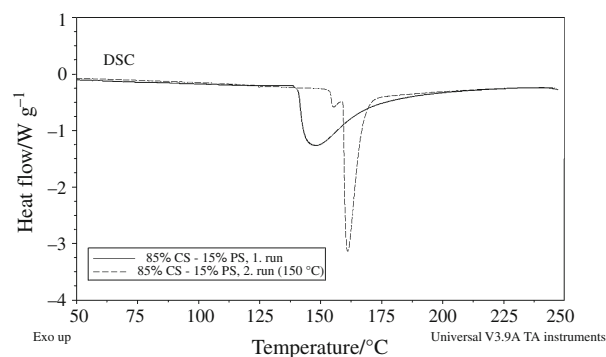


Fig. 4 DSC curves in standard pan with lid obtained in the first and second run, i.e., without and with a thermal pretreatment to 160 °C

line in Fig. 4) or sometimes more (see DSC traces of the preheated samples in Fig. 5) endothermic peaks, one of them being very sharp. Namely, starch granules with different crystal regions undergo different dismantling action of water [21] and are usually separated only in the samples with low water content [22]. The very sharp peak in the self-generated atmosphere in the covered pan is supposed to be due to the gelatinization of starch. The interactions before gelatinization affect all phase transitions in starch dispersions [23], which in principle should be valid for all complex starch systems. On the contrary, this intensive peak is missing when the thermal curves are recorded in open pan (see Fig. 6).

DSC curves registered in pans with lid show no correlation between the PS content neither with the heat flux nor the peak temperature (see Fig. 5). In order to find the reason for the missing correlation, we checked the repeatability of the measurement. We carried out the measurements for the sample with 15% PS content (mass $10 \text{ mg} \pm 10\%$) under almost identical conditions, six times. Except that all the peaks were detected, their position changed randomly referring to the high sensitivity of the measurement to very small differences in experimental

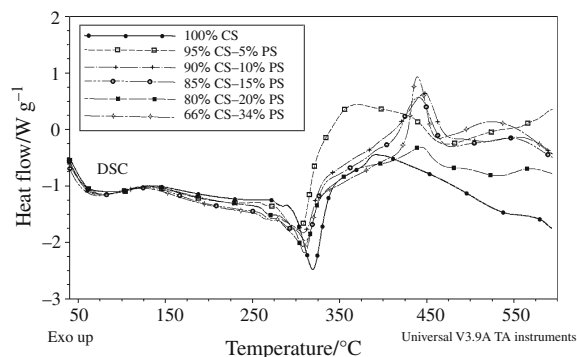


Fig. 3 DSC curves for pure cassava starch and its grafted modification with different $G, \%$ obtained by simultaneous TG/DSC measurements

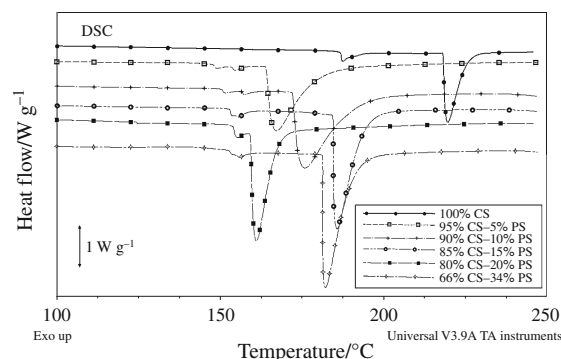


Fig. 5 DSC curves of cassava starch and polystyrene grafted samples obtained in aluminum pan with lid

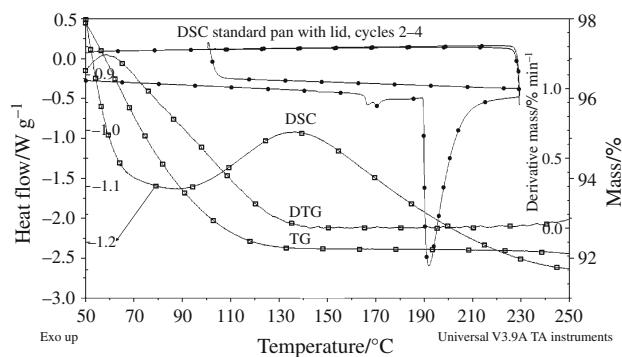


Fig. 6 TG, DTG, and DSC curves of native cassava starch sample obtained in open and covered vessels with thermal pretreatment

conditions (e.g., the mass and correspondingly, the water pressure change in the pan with lid). The decomposition pattern in this mass range in open pans is not sensitive to the sample mass. After the complete evaporation of water, the structural changes are irreversible [10, 24–26]. The simultaneous TG/DSC curves and the corresponding DSC curve of the second and further runs (Fig. 6) support this proposition.

Additionally, the processes were observed using a Koffler's hot stage apparatus. As the sample was only covered with glass in order to secure the self-generated atmosphere, a wet starch sample was used. Around 130 °C the excess of water boiled off. Above 160 °C the gelatinization was observed in a temperature range of 10 °C when the sample completely dried. If the dry sample was wetted again, on the second run only the boiling of the excess water could be observed, without the gelatinization of the sample. Gelatinization results in a complete thermal destruction of the native starch. Depending on the further thermal treatment of the amorphous phase, recrystallization may take place [27]. However, under the conditions we have carried out the measurements, the structure of the samples changed irreversibly. The granules lose their crystallinity, but maintain their individuality [20]. In blends with plasticizers the irreversible order–disorder transition related to starch gelatinization is not necessarily apparent [28].

SEM analysis

In order to obtain more reliable data about the processes taking place during the thermal treatment of the samples we have observed the surface morphology changes in the function of temperature pretreatment. As the observed gelatinization is the property of the starch component, Fig. 7a shows the SEM image of the untreated pure starch sample. Figure 7b shows the image of the same sample heated up to 160 °C, while Fig. 7c illustrates the surface of

the sample which was heated up to 250 °C after cooling down to room temperature from 160 °C. The granules of the sample are round, oval or irregular shape and wide distribution of sizes. The average size of the particles is increasing with increasing temperature. The most important change can be observed in Fig. 7b. Namely, when the sample is heated up to 160 °C bubbles are appearing on the surface of the particles. The bubbles disappear when the sample is heated further to 250 °C (Fig. 7c). The explanation of this phenomenon is most probable related to the evolution of the structural water emerging to the surface of the particles. This is in the accordance with DSC curves. In the temperature range near to 160 °C, DSC curves in the aluminum pans with lid show two or more peaks belonging to the evaporation of the mobile water and

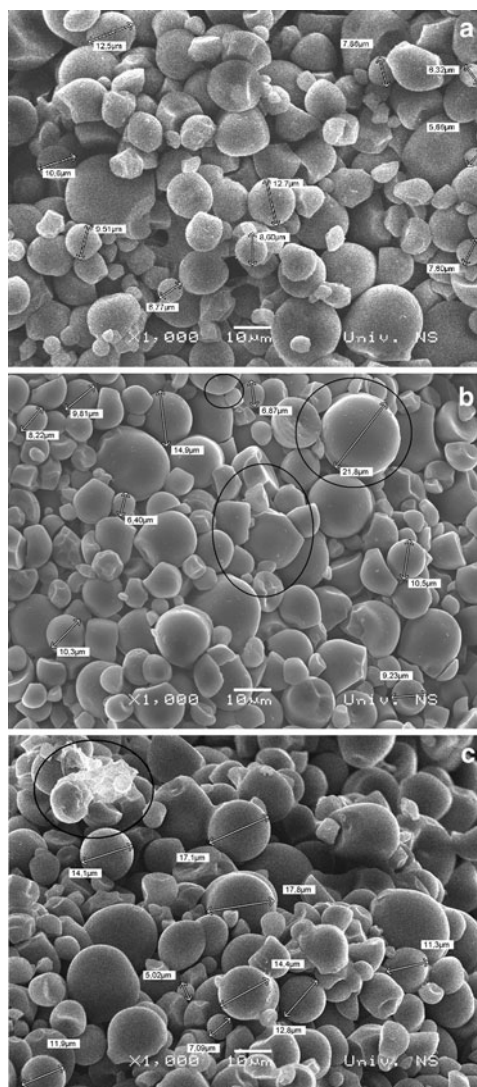


Fig. 7 SEM images of cassava starch without thermal treatment (a), heated up to 160 °C (b), and treated up to 250 °C, the circle is showing the traces of the former gelatinization (c)

capillary active water including the beginning of the removal of structural water. Above 160 °C the gelatinization of the samples takes place, manifesting in a very sharp, intensive DSC peak. The trace of the gelatinization can be observed in Fig. 7c (marked by a circle). When the sample is heated up to 250 °C, the bubbles almost completely disappear from the surface of the particles, referring to its nearly complete dehydration. Except of the somewhat larger average size of the particles, no significant changes are visible on the surface morphology of the sample. This is also in the accordance with its thermal behavior. The similar surface morphology is referring to a similar chemical composition. Namely, the decomposition temperature of the CS and that of its grafted copolymers is above 250 °C.

Conclusions

Starch powder and its PS grafted powders are hygroscopic and contain about 9% water. In open alumina pans the evaporation of differently bond water molecules takes place in a wide temperature range up to about 250 °C. The chemical decomposition of the samples begins at about 260 °C, most probably with the departure of starch amylopectin -CH₂OH groups. The decomposition pattern of the CS and its grafted copolymers with different PS content measured in open pans is very similar up to 350 °C. The peak characteristic for PS component appears above 400 °C in samples containing more than 10% of PS with increasing intensity in both DTG and DSC curves.

To separate the type of water molecules, DSC measurements were conducted in standard aluminum pans with lid. At the first step the samples were heated to 160 °C. The amount of the evaporated water was determined by weighting the pan after cooling it down to room temperature and found to be about 7% in all samples. The run was repeated up to 250 °C. By this way, the differently bonded water molecules could be separated. In addition, in 160–190 °C temperature range a very sharp endothermic peak, missing in the measurements using open pans, appears. It was found to belong to an irreversible gelatinization at low (<2%) water content, in a self-generated atmosphere.

The surface morphology of starch granules treated in aluminum pan with lid at different temperatures was investigated by SEM. It was found that the morphology does not change significantly due to the different thermal history. However, on the surface of the granules treated to 160 °C “bubbles” are visible, referring to the emerging of structural water molecules to the surface of the granules. When in the followed cycle the same sample is heated up to 250 °C, the remaining water creates a self-generated atmosphere, suitable for the gelatinization of the sample.

After gelatinization the granules maintain their individuality when cooled down to room temperature.

Acknowledgements We would like to thank Faculty of Science in Prince of Songkla University and Faculty of Technology in University of Novi Sad for their financial support.

References

- Chiellini E, Cinelli P, Ilieva VI, Imam SH, Lawton JW. Environmentally compatible foamed articles based on potato starch, corn fiber and poly(vinyl alcohol). *J Cell Plast.* 2009;45:17–32.
- Zhao S, Wang C-Y, Chen M-M, Sun J-H. Mechanism for the preparation of carbon spheres from potato starch treated by NH₄Cl. *Carbon.* 2008;47:331–47.
- Mihai M, Huneault A, Favis BD. Foaming of polystyrene/thermoplastic starch blends. *J Cell Plast.* 2007;43:215–36.
- Sjöqvist M, Boldizar A, Rigdahl M. Processing and properties of expanded starch materials. *J Cell Plast.* 2009;45:51–66.
- Janarthanan P, Zin WMD, Yunus W, Ahmad MB. Thermal behaviour and surface morphology studies on polystyrene grafted sago starch. *J Appl Polym Sci.* 2003;90:2053–8.
- Kiatkamjornwong S, Sonsuk M, Wittayapichet S, Prasassarakich P, Vejjanakroh P. Degradation of styrene-g-cassava starch filled polystyrene plastics. *Polym Degrad Stab.* 1999;66:323–35.
- Pimpan V, Thothong P. Synthesis of cassava starch-g-poly(methylmethacrylate) copolymers with benzoyl peroxide as an initiator. *J Appl Poly Sci.* 2006;101:4083–9.
- Taggare P. Starch as an ingredient: manufacture and applications. In: Eliasson AC, editor. *Starch in food.* Boca Raton, FL: CRC Press; 2004. p. 369.
- Graaf RA, Janssen LP. Properties and manufacturing of a new starch plastic. *Polym Eng Sci.* 2004;41:584–94.
- Kaewtatip K, Tanrattanakul V. Preparation of cassava starch grafted with polystyrene by suspension polymerization. *Carbohydr Polym.* 2008;73:647–55.
- Singh V, Tiwari A, Pandey S, Singh SK. Microwave-accelerated synthesis and characterization of potato starch-g-poly(acylamine). *Starch.* 2006;58:536–43.
- Fang Y, Chen P, Zhang W, Luo W. Synthesis and properties of starch grafted poly[acrylamide-co-(acrylic acid)]/montmorillonite nanosuperabsorbent via γ -ray radiation technique. *J Appl Poly Sci.* 2005;96:1341–6.
- Ren G-y, Li D, Wang L-j, Özkan N, Mao Z-h. Morphological properties and thermoanalysis of micronized cassava starch. *Carbohydr Polym.* 2010;79:101–5.
- Rodriguez A, Sain M, Jeng R. Thermal characterization of starch-based polymers produced by *Ophiostoma* spp. *J Therm Anal Calorim.* 2009;98:317–23.
- Chartoff RP, Sircar AK. Thermal analysis of polymers. In: Mark HF, editor. *Encyclopedia of polymer science and technology.* New York: John Wiley & Sons, Inc; 2005. p. 31.
- Liu P, Yu L, Liu H, Chen L, Li L. Glass transition temperature of starch studied by a high-speed DSC. *Carbohydr Polym.* 2009;77:250–3.
- Yu L, Christie G. Measurement of starch thermal transitions using differential scanning calorimetry. *Carbohydr Polym.* 2001;46:179–84.
- Paulik J, Paulik F. Simultaneous thermoanalytical examinations by means of the derivatograph. In: Wendlandt WW, editor. *Comprehensive analytical chemistry, vol. XII, thermal analysis.* Amsterdam: Elsevier; 1981. p. 54.
- Paulik F, Besseney-Paulik E, Walther-Paulik K. Differential thermal analysis under quasi-isothermal, quasi-isobaric conditions

- (Q-DTA). Examinations using “transformation-governed heating control” and “self-generated atmosphere” (TGHC–SGA). *Thermochim Acta*. 2003;402:105–16.
20. Schiraldi A, Piazza L, Fessas D, Riva M. From macromolecules to man. In: Kemp RB, editor. *Handbook of thermal analysis and calorimetry* (ser. ed.: Gallagher PK), vol. 4. Amsterdam: Elsevier; 1999. p. 839.
 21. Li G, Sarazin P, Favis BD. The relationship between starch gelatinization and morphology control in melt-processed polymer blends with thermoplastic starch. *Macromol Chem Phys*. 2008;209:991–1002.
 22. Steeneken PAM, Woortman AJJ. Identification of the thermal transitions in potato starch at a low water content as studied by preparative DSC. *Carbohydr Polym*. 2009;77:288–92.
 23. Habitante AMBQ, Sobra PJA, Carvalho RA, Solorza-Feria J, Bergo PVA. Phase transitions of cassava starch dispersions prepared with glycerol solutions. *J Therm Anal Calorim*. 2008;93:599–604.
 24. Hamdan S, Hashim DMA, Ahmad M, Embong S. Compatibility studies of polypropylene (PP)-sago starch (SS) blends using DMTA. *J Polym Res*. 2000;7:237–44.
 25. Ge XC, Xu Y, Meng YZ, Li RKY. Thermal and mechanical properties of biodegradable composites of poly(propylene carbonate) and starch–poly(methyl acrylate) graft copolymer. *Compos Sci Technol*. 2005;65:2219–25.
 26. Mano JF, Koniarova D, Reis RL. Thermal properties of thermoplastic starch/synthetic polymer blends with potential biomedical applicability. *J Mater Sci Mater Med*. 2003;14:127–35.
 27. Belopolskaya TV, Tsereteli GI, Grunina NA, Smirnova OI. Calorimetric study of the native and postdenatured structures in starches with different degree of hydration. *J Therm Anal Calorim*. 2008;92:677–82.
 28. Schlemmer D, de Oliveira ER, Sales MJA. Polystyrene/thermoplastic starch blends with different plasticizers. Preparation and thermal characterization. *J Therm Anal Calorim*. 2007;87:635–8.