Carbohydrate Polymers 79 (2010) 296–300

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

The preparation and properties of dialdehyde starch and thermoplastic dialdehyde starch

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ARTICLE INFO

Article history:
Received 15 July 2009
Received in revised form 31 July 2009
Accepted 3 August 2009
Available online 9 August 2009

Keywords:
Dialdehyde starch
Starch re-crystallization
Re-crystallization (retrogradation)

ABSTRACT

Dialdehyde starch (DAS) is prepared by periodate oxidation of starch, and DAS with different aldehyde contents is plasticized by glycerol to obtain thermoplastic DAS (TPDAS). DAS is characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystalline starch is destroyed and oxidized to form amorphous DAS, while amorphous starch inside of starch granules is degraded. As a result, DAS containing 93.05% aldehyde content formes a ring shape. Compared to thermoplastic native starch, the re-crystallization of DAS can not take place in TPDAS during the storage period, because periodate oxidation has destroyed the crystallization of starch. With the increasing of aldehyde contents of DAS, the tensile strength and the resistance of both moisture absorption and water vapor permeability of TPDAS are improved. It is ascribed to the cross-linking of aldehyde groups in TPDAS.

1. Introduction

Currently, much interest has been raised in the development of environmentally friendly materials based on natural polysaccharides. Starch from a great variety of crops is one of the promising raw materials for the production of biodegradable materials (Petersen, Væggemose, & Bertelsen, 1999). As a multi-hydroxyl polymer, starch contains vast intermolecular and intramolecular hydrogen bonds, and exists in granule structure with about 15–45% crystallinity (Zobel, 1998). In the presence of plasticizers (e.g. water, glycerin and sorbitol) at high temperatures, starch crystallinity and hydrogen bonds can be destroyed, and be processed into continuous thermoplastic materials. However, polyols-plasticized starch tends to starch re-crystallization after being stored for a period of time and this re-crystallization embrittles TPS (Mathew & Dufresn, 2002; Van Soest & Knooren, 1997). To prepare starch-based materials with re-crystallization resistance and good mechanical properties, Ma and Yu (2004) have investigated the feasibility of small substance with amide group such as formamide, acetamide and urea to plasticize starch. These plasticizers can restrain starch re-crystallization because of the stronger hydrogen bond interaction between amide groups and starch than polyols. However, in views of food safety, these plasticizers containing amide groups are unfavorably applied to food packaging and edible films.

On the other hand, the modification of starch is a good choice to restrain starch re-crystallization. Dialdehyde starch (DAS) is used as cross-linking agent, which is produced by controlled periodate oxidative cleavage of the C-2 and C-3 bond of the anhydroglucose units of native starch (Martucci & Ruseckaite, 2009; Wongsagon, Shobsngob, & Varavinit, 2005). In this paper, DAS is prepared with periodate oxidation, which is plasticized by glycerol to obtain thermoplastic DAS (TPDAS). This work is focused on processing and characterization of DAS and TPDAS in terms of the effect of periodate oxidation on the interaction of starch molecules, the morphology, starch crystallization, mechanical properties, water absorption and water vapor permeability of TPDAS. It is worth noting that TPDAS can still be biodegraded, but the biodegradation rate of TPDAS is greatly influenced by aldehyde contents (Du et al., 2008).

2. Experimental

2.1. Materials

Potato starch is supplied by Manitoba Starch Products (Manitoba, Canada). Sodium periodate, sulfuric acid, anhydrous ethanol, hydroxylamine hydrochloride and glycerol are of analytical grade from Tianjin Chemical Reagent Company (Tianjin, China).

2.2. Synthesis of dialdehyde starch (DAS)

Sodium periodate solution (0.7 mol/L) is adjusted to pH 4.0 with sulfuric acid. Potato starch is added under vigorous mechanical

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doi:10.1016/j.carbpol.2009.08.005

Table 1
The aldehyde contents of DAS prepared at the different mol ratio of $NaIO_4$/starch.

	DAS15	DAS30	DAS50	DAS60	DAS80	DAS90
$NaIO_4$/starch (mol ratio)	0.1	0.3	0.5	0.7	0.9	1.1
Aldehyde content (%)	14.80	29.49	47.15	63.41	81.46	93.05

stirring. The molar ratios between sodium periodate and starch are 0.1, 0.3, 0.5, 0.7, 0.9 and 1.1, respectively. The reaction is kept at 37 °C for 4 h. The slurry is filtered and the product is washed with distilled water. After anhydrous ethanol is used to remove water, the powder is dried at 50 °C for 8 h. DAS with different aldehyde contents are obtained.

2.3. Preparation of thermoplastic DAS (TPDAS)

Five grams of DAS (or potato starch) and 2 g glycerol are added into 100 mL distilled water. The mixture is heated at 90 °C for 0.5 h with constant stirring. The mixture is cast into a dish and placed in an air-circulating oven at 50 °C until dry (about 6 h). The thermoplastic potato starch (TPS) and TPDAS films are preconditioned in a climate chamber at 25 °C and 50% RH for at least 48 h prior to the testing.

2.4. Determination of aldehyde contents

The aldehyde contents of DAS are determined according to Veelaert, de Wit, Gotlieb, and Verhé (1997) with some modification. DAS (0.2 g) is added in hydroxylamine hydrochloride (25 mL of a 0.25 M) solution. The pH is adjusted to 5 with NaOH (0.1 M) solution. The conversion of aldehydes into oximes continues at 50 °C for 2 h. The aldehyde content is determined with Eq. (1) by recording the consumption V_{sample} (mL) of NaOH (0.1 M), performing the reaction at a constant pH of 5. 0.2 g native potato starch is used as a control to record the consumption $V_{control}$ (mL) of NaOH.

$$\begin{aligned} \mathrm{CHO}(\%) &= \frac{0.1 \times (V_{sample} - V_{control})}{0.2 \times 1000} \times 100 \\ \mathrm{CHO}(\%) &= 8.1 \times (V_{sample} - V_{control}) \end{aligned} \tag{1}$$

Table 1 lists the aldehyde contents of DAS, which are prepared at the conditions of different molar ratios of sodium periodate/starch.

2.5. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of native starch and DAS are measured with a BioRad FTS3000 IR Spectrum Scanner (Hercules, CA, USA).

2.6. Scanning electron microscopy (SEM)

The samples are investigated with the scanning electron microscope Philips XL-3 (FEI Company, Hillsboro, Oregon, USA). Native starch and DAS powders are dispersed into ethanol using ultrasonication for 5 min. The suspension drops are drawn on a glass flake, dried to remove ethanol, and then coated with gold in vacuum for SEM. TPS and TPDAS are cryo-fractured in liquid nitrogen, and the fracture faces are coated with gold in vacuum for SEM.

2.7. X-ray diffractometry

Native starch and DAS powders are tightly packed into the sample holder, while TPS and TPDAS films are placed in a sample holder. X-ray diffraction patterns are recorded in the reflection mode in the angular range 5–40° (2θ) at ambient temperature by a BDX 3300 diffractometer, operated at a CuKα wavelength of 1.542 Å. Radiation from the anode, operated at 36 kV and 20 mA, monochromized with a 15 μm nickel foil. The diffractometer is equipped with 1° divergence slit, a 16 mm beam bask, a 0.2 mm receiving slit and a 1° scatter slit. Radiation is detected with a proportional detector.

2.8. Mechanical testing

The Testometric AX M350-10KN Materials Testing Machine is operated and a crosshead speed of 50 mm/min is used for tensile testing (ISO 1184–1983 standard). The data is averages of 5–8 specimens. In order to analyze the effect of relative humidity (RH) on mechanical properties of TPS and TPDAS, they are stored at RH 25 and 50%.

2.9. Water absorption

The water contents α_0 (dry basis) of TPS and TPDAS before the storage are determined gravimetrically by drying small pieces at 105 °C overnight. When the samples are stored for a period of time, water contents are calculated on the basis of original weight w_0, current weight w and α_0. Water content α is calculated with Eq. (2).

$$\alpha = \frac{w}{w_0}(1 - \alpha_0) - 1 \tag{2}$$

2.10. Water vapor permeability (WVP)

WVP tests are carried out by ASTM method E96 (1996) with some modifications (Yu, Wang, & Ma, 2008). The films are cut into circles, sealed over with melted paraffin, and stored in a desiccator at 25 °C. RH 0 is maintained using anhydrous calcium chloride in the cell. Each cell is placed in a desiccator containing saturated sodium chloride to provide a constant RH of 75%. Water vapor transport is determined by the weight gain of the permeation cell. Changes in the weight of the cell are recorded as a function of time. Slopes are calculated by linear regression (weight change vs. time) and correlation coefficients for all reported data are >0.99. The

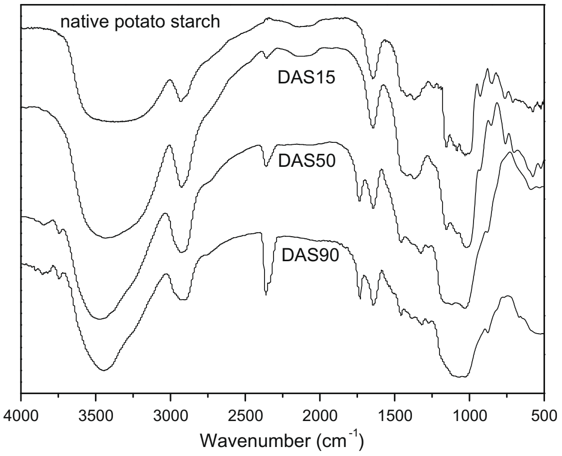

Fig. 1. FTIR spectra of native potato starch and DAS with different aldehyde contents.

water vapor transmission rate (WVTR) is defined as the slope (g/s) divided by the transfer area (m^2). After the permeation tests, film thickness is measured and WVP ($g\ Pa^{-1}\ s^{-1}\ m^{-1}$) is calculated as:

$$\mathrm{WVP} = \frac{\mathrm{WVTR}}{P(R_1 - R_2)} \cdot x \tag{3}$$

where P is the saturation vapor pressure of water (Pa) at the test temperature (25 °C), R_1 is the RH in the desiccator, R_2, the RH in the permeation cell and x is the film thickness (m). Under these conditions, the driving force $[P(R_1–R_2)]$ is 1753.55 Pa.

3. Results and discussion

3.1. FTIR

Fig. 1 shows the effect of aldehyde contents on the FTIR spectra of DAS. In the fingerprint region of FTIR spectra of starch, three characteristic peaks appear between 1000 and 1200 cm^{-1}, attributed to C–O bond stretching of starch (Ma, Yu, & Wang, 2007). The characteristic peak at 1640 cm^{-1} is related to the tightly bound water in the starch (Fang, Fowler, Tomkinson, & Hill, 2002). The characteristic peak for C=O groups at 1735 cm^{-1} is enhanced with the increasing of aldehyde contents of DAS. The periodate oxidation mainly breaks the C-2 and C-3 bond of the anhydroglucose units, and aldehyde groups are formed and take the place of C–OH groups at C-2 and C-3. With the increasing of aldehyde contents, the peak at 1150 cm^{-1} is weakened, which is attributed to C–O bond stretching of C–OH group in the anhydroglucose ring. Therefore, three characteristic peaks of C–OH groups gradually transfer into a broad band at the fingerprint regions of starch.

3.2. SEM

SEM micrograph of native starch granules and DAS with different aldehyde contents are shown in Fig. 2(a)–(d). Native starch presents spherical or elliptical granules with smooth surface, while the surface of DAS15 is slightly depressed with some wrinkles. The surface of DAS50 obviously sinks due to oxidated corrosion, which further makes DAS90 form a ring. It seems that the interior of starch granules are easily corroded, which is similar to hydrolyzed starch. According to Wang, Yu, and Gao (2007), the amorphous regions are mainly located inside of starch granules, while the crystalline areas mainly exist on the outside of the starch granule. The degradation of potato starch du to periodate oxidation is more obvious in the amorphous regions than at the crystalline areas. However, DSA still displays the smooth surface, which is very different from the rough surface of hydrolyzed starch.

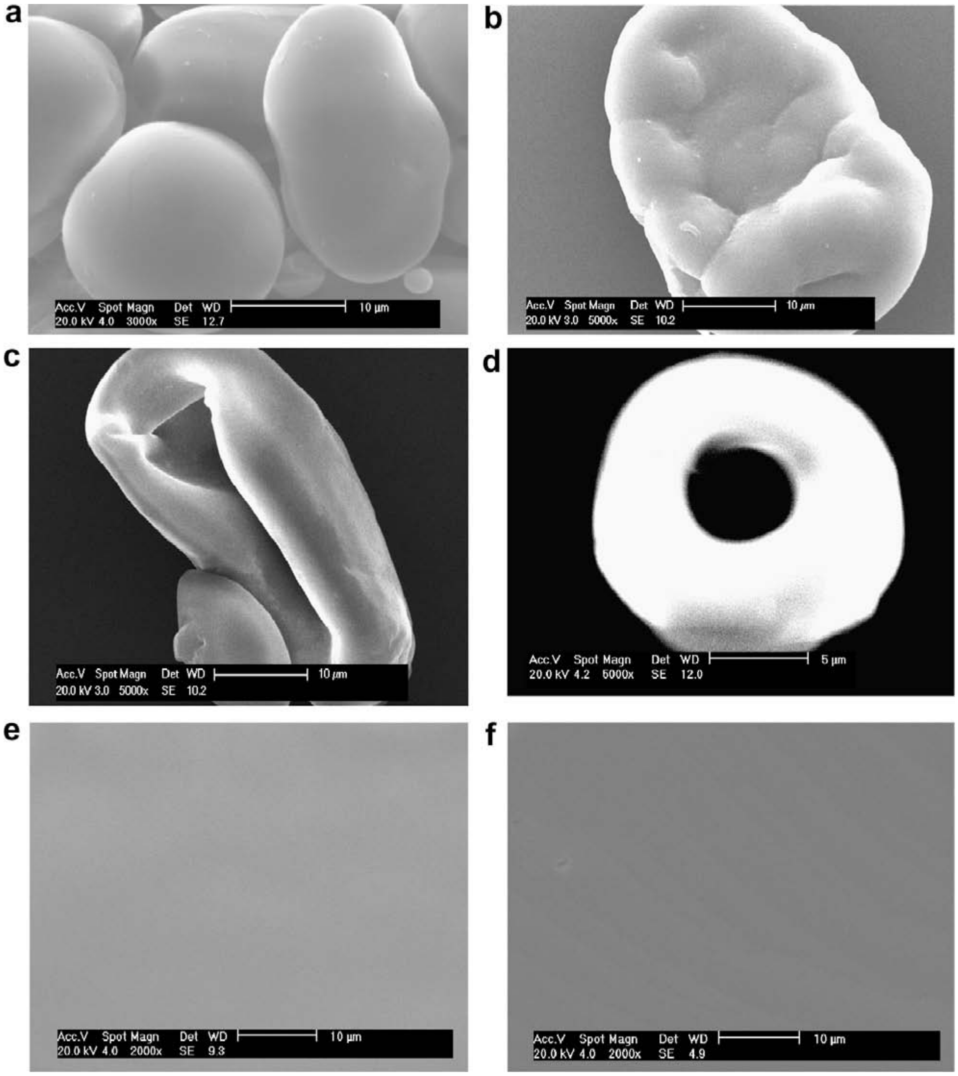

Fig. 2. SEM micrographs of starch, DAS, TPS and TPDAS. (a) Potato starch, (b) DAS15, (c) DAS50, (d) DAS90, (e) TPS and (f) TPDAS50.

As shown in Fig. 2(e) and (f), a continuous phase of TPS or TPDAS is formed without any residual granules by the action of high temperature, water and glycerol. It is well known that glycerol can enter starch granular interior, disrupt intermolecular and intramolecular hydrogen bonds and make granular starch plasticization (Ma, Jian, & Chang, 2008).

3.3. X-ray

The diffraction patterns of native starch and DAS are presented in Fig. 3. Native potato starch exhibits the typical B-type pattern (Fiedorowicz & Para, 2006). When the mol ratio of $NaIO_4$/starch reaches 0.5, DAS shows no crystal peak of starch. It implies that periodate oxidation can destroy the crystalline regions of starch granules. As shown by SEM in Fig. 2(b)–(d), the periodate oxidation makes the degradation of amorphous starch easy. Therefore, the crystalline starch can be oxidized to form amorphous DAS, while amorphous starch inside of starch granules can be degraded. As a result, DAS90 formed a ring.

There are no crystals of native starch in newly prepared TPS, because glycerol and water can replace starch intermolecular and intramolecular hydrogen bonds and destruct the crystal of native starch. However, TPS plasticized with glycerol (as shown in Fig. 3(b)) tends to re-crystallization after being stored for 70 day, and this re-crystallization embrittles TPS (Ma, Yu, & Wan, 2006). Glycerol can not form enough strong and stable hydrogen bonds with starch, and then make starch molecules from interacting and crystallizing again (Ma & Yu, 2004). However, in Fig. 3(b) no obvious starch molecular crystallization appears in TPDAS when they are stored at RH 50 for 70 day. Because periodate oxidation has destroyed the crystallization of starch, the re-crystallization of DAS can not take place during the storage period.

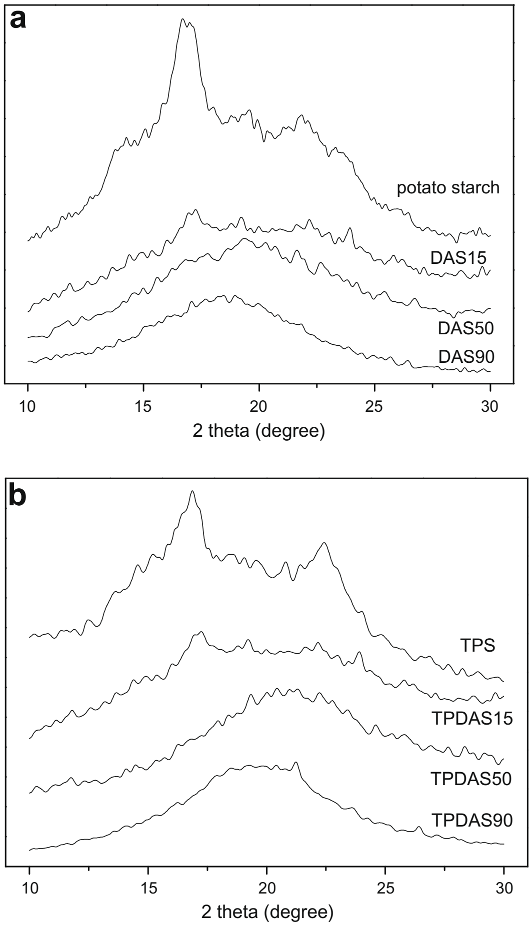

Fig. 3. X-ray diffraction patterns of native potato starch and DAS with different aldehyde contents (a), TPS and TPDAS stored at RH 50% for 70 days (b).

3.4. Mechanical properties

As shown in Fig. 4, with the increasing of aldehyde contents of DAS, the tensile strength of TPDAS increased, but the elongation at break decreased. The C-2 and C-3 aldehyde groups of the anhydroglucose units in DAS could form inter- and intramolecular hemiacetal and acetal cross-linking in the processing of DATPS (Veelaert et al., 1997). DAS with the higher aldehyde contents are more likely to form these cross-linking, contributed to the reinforcement of TPDAS.

Fig. 4 also reveals that the tensile strength and elongation at break of TPDAS are so different, when TPDAS are, respectively, stored at RH 25% and RH 50%. At the lower RH, TPDAS exhibit the higher tensile strength, while TPDAS has the better elongation at break at the higher RH. In fact, water plays a role of plasticizer, which can weaken the interaction of DAS molecules. Therefore, tensile strength is decreased, but elongation at break is improved, when TPDAS absorb more moisture at the higher RH.

3.5. Water absorption

As shown in Fig. 5(a), native starch and DAS reach the balance of water absorption after they are stored at the environment of RH 75% for 13 days. And water absorption of DAS improves with the increasing of aldehyde contents. The hydrophilicity of aldehyde groups made DAS absorb more moisture at the same storage time. The balance water contents are, respectively, 15.79%, 17.14%, 17.63% and 19.33% for native starch, DAS30, DAS60 and DAS90.

However, Fig. 5(b) represents the water absorption of TPS and TPDAS at RH 75%. With the increasing of aldehyde contents, water absorption of TPDAS exhibits the reverse order of DAS. The more the aldehyde contents of DAS are, the less the water absorptions of TPDAS are. Although DAS is more hydrophilic than native starch, the cross-linking in the processing of DATPS reduces the hydrophilicity of TPDAS. Therefore, TPDAS from DAS with higher aldehyde contents has better resistance of moisture.

3.6. WVP

As shown in Fig. 6, WVP of TPDAS films decrease with the increasing of aldehyde contents of DAS. Water vapor easily goes through TPS film with the highest WVP values of 16.4×10^{-10}

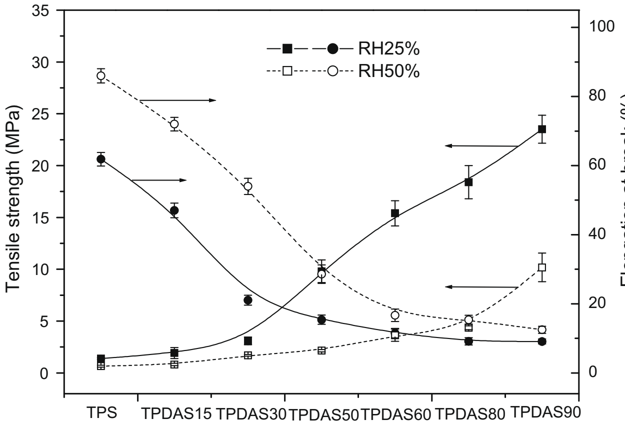

Fig. 4. The effect of aldehyde contents of DAS on tensile strength and elongation at break of TPS and TPDAS, stored at RH 25% and 50%.

$g\,m^{-1}\,s^{-1}\,Pa^{-1}$, while WVP value of TPDAS90 films reach to $4.0 \times 10^{-10}\,g\,m^{-1}\,s^{-1}\,Pa^{-1}$. Since the involvement of hydrophilic groups in cross-linking increased with the increasing of aldehyde contents of DAS, the hydrophilicity of TPDAS is decreased, and the cross-linking also decreases the interstice of DAS molecules. The decrement of the hydrophilicity and the interstice result in the decreasing of WVP with the increasing of aldehyde contents.

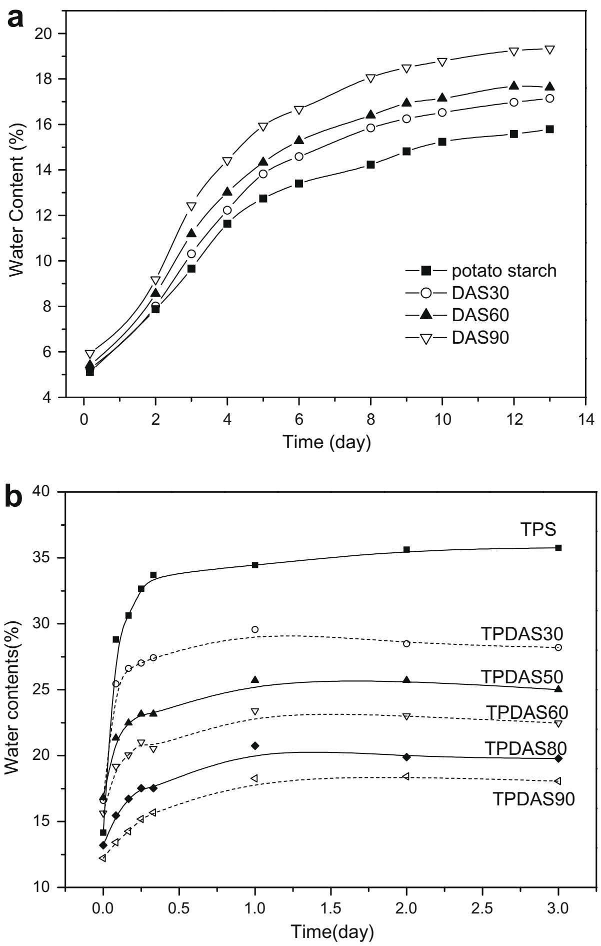

Fig. 5. Water absorption of native starch, DAS (a), and TPS, TPDAS (b).

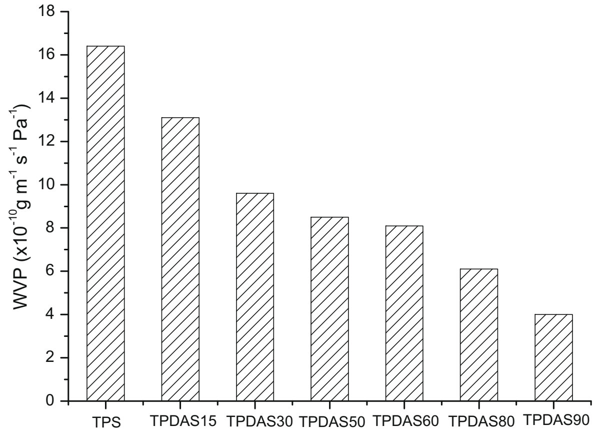

Fig. 6. The effect of aldehyde contents of DAS on water vapor permeability of TPDAS.

4. Conclusion

In this study, DAS with different aldehyde contents is plasticized by glycerol to prepare TPDAS. The periodate oxidation degrade amorphous starch inside of starch granules, and oxidized original crystalline fractions on the outside of starch granule. Compared to TPS, TPDAS exhibit the resistance of starch re-crystallization during the storage. DAS with the higher aldehyde contents are more likely to form the cross-linking, which contributes to the reinforcement and the decrement of the hydrophilicity, water absorption and WVP. TPDAS can be applied in the medical, agricultural, drug release and packaging fields as edible films, disposable or food packaging. In addition, DAS can also be used to prepare natural polysaccharide (starch, agar, alginate and chitin) composites.

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