Influence of Surface Photocrosslinking on Properties of Thermoplastic Starch Sheets

Jiang Zhou, Yunhai Ma, Jian Zhang, Jin Tong

Key Laboratory for Terrain-Machine Bionic Engineering, College of Biological and Agricultural Engineering, Jilin University, Changchun 130022, China

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ABSTRACT: The surface of glycerol plasticized thermoplastic starch (TPS) sheets was modified by photocrosslinking under ultra violet (UV) irradiation. Sodium benzoate was selected as photosensitizer and induced onto sheet surface layer by soaking the sample sheets in photosensitizer aqueous solution. The effects of concentration of the photosensitizer aqueous solution, soaking time and moisture content in sheets before UV irradiation on the photocrosslinking were investigated. Water contact angle, moisture absorption, and mechanical properties were measured to characterize the influence of the surface photocrosslinking modification on the properties of TPS sheets. The obtained results showed that the surface photocrosslinking treatments markedly reduced the water sensitivity of TPS sheets and enhanced their tensile strength and Young's modulus but decreased the elongation at break. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 112: 99–106, 2009

Key words: thermoplastic starch; surface modification; ultra violet irradiation

INTRODUCTION

The development of thermoplastic starch (TPS) has received considerable attention over the last two decades due to its biodegradability, renewability, and low cost.[1–3] However, the hydrophilic nature of TPS seriously limits its wider applications.

Numerous studies have been done in an attempt to overcome the hydrophilic nature of TPS. Blending TPS with biodegradable synthetic polymers is a common method to reduce water sensitivity of TPS.[4–8] However, due to lack of compatibility between hydrophilic TPS and hydrophobic polymers, the mechanical properties of the blends generally became poorer.[5,7] Coating water resistant layers at the surface of TPS products is another approach. Prepolymers having -NCO groups,[9] zein,[10] and chitosan[11,12] were used for coating. A hydrogenated-carbon coating reduced the hydrophilic character of TPS films significantly.[13] The coating method also needs to enhance the interfacial adhesion between the surface layer and TPS substrate. Surface chemical modification is another method that can be used to reduce the hydrophilic character of TPS surface. By introducing hydrophobic groups to substitute the superficial hydroxyl groups of TPS,[14,15] the surfaces of TPS became more hydrophobic while the bulk composition and characteristics of the material were not changed. However, organic solvents were generally needed in these surface chemical modifications, this could increase the processing cost and give rise to environmental/health concerns.

The hydroxyl groups on glucose rings in the amylose and amylopectin molecules are responsible for the hydrophilicity of TPS materials. Crosslinking modification uses reagents having multifunctional groups to react with the hydroxyl groups in starch molecules and creates intermolecular bridges.[16] It is known that, through crosslinking, easy swelling and gelatinization of native starch can be inhibited, and crosslinking modified starch granules are even insoluble in boiling water. These suggest that crosslinking modification may improve water resistance of TPS materials.

Indeed, crosslinking technologies have been used to modify TPS materials. By adding crosslinking agents in starch slurry and preparing films by casting, crosslinking treatments were applied to solution cast TPS films.[17–20] Post-treatments through irradiation of ultra violet (UV)[20–23] and electron beam[24,25] were used to crosslink the extruded or compression molded TPS films and sheets. Gamma irradiation was also applied to treat the casting solutions to prepare crosslinked starch films.[26]

Comparing with bulk crosslinking, surface crosslinking modification of TPS provides an approach to

Correspondence to: J. Zhou (jiang.zhou@jlu.edu.cn).
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reduce surface hydrophilic characteristics of the materials without changing their bulk composition. In UV photocrosslinking, the amounts of photosensitizers used in a surface modification would be significantly lower compared with a modification of bulk material. Furthermore, the intermolecular bridge networks in the surface layer induced by photocrosslinking should be easier to be formed than that throughout whole bulk of the material. Author's previous work[27] showed that surface photocrosslinking by using sodium benzoate as photosensitizer reduced hydrophilicity and improved water resistance of gelatinized corn starch sheets. In this article, glycerol plasticized TPS sheets were modified by surface photocrosslinking through UV irradiation and the influence of the surface modification on physical and mechanical properties of the TPS sheets were studied.

EXPERIMENTAL

Materials

The raw material, corn starch, was purchased from Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (Changchun, China). The photosensitizer, sodium benzoate, from Tianjin Guangfu Institute of Fine Chemicals (Tianjin, China) was used as received without further purification. Dimethylsulfoxide (DMSO), from Tianjin Dodi Chemical Industry Co. Ltd. (Tianjin, China), was used as a solvent for determining swelling degree (SD) and gel mass (GM) of surface modified sheets.

Preparation of TPS sheets

The corn starch was premixed with glycerol in a weight ratio of starch to glycerol at 85/15. The mixture was then kept in a sealed plastic bucket for 24 h to equilibrate the glycerol distribution. A twin-screw corotating extruder [CET-35, Coperion Keya (Nanjing) Machinery Co. Ltd., China] with 35.6 mm diameter and a 38 L/D ratio screws was used for the extrusion processing of TPS. The barrel sections 1–6 were maintained at 60, 80, 100, 120, 90, and 75°C, respectively. Starch/glycerol mixture was fed into the extruder through a twin-screw feeder [Coperion Keya (Nanjing) Machinery Co. Ltd., China] at a feed rate of 75 g/min. Extra water was added into the extruder by a peristaltic pump (Baoding Longer Precision Pump Co. Ltd., China) to give overall water content of 35% w/w. A die plate heated to 75°C was used to form the extrudate into a ribbon with 80 mm width and 10 mm thickness. The TPS sheets with thickness of about 0.35 mm were prepared by compressing the extruded ribbons at 80°C with a press. The prepared sheets were slowly dried to moisture content (MC) about 12% and sealed in zip plastic bags for experimental use.

Surface photocrosslinking modification

The photosensitizer aqueous solutions with different concentrations were prepared by dissolving sodium benzoate in distilled water. Small pieces of the TPS sheets (25 mm × 20 mm) were conditioned at 57% RH to moisture equilibrium and then soaked in photosensitizer aqueous solutions for various periods of time. When the sheets were taken out, the excess solution on the surfaces was dripped. The sheets containing sodium benzoate in surface layer were then exposed to UV light at normal atmospheric condition for surface modification. A UV mini-crosslink machine (Scients03-II, Ningbo Xinzhi Biological Science and Technology Co. Ltd., China) was used for UV exposure. The size of exposure chamber is 34 cm wide, 29.5 cm deep, and 15 cm high. There are five parallel tube lamps (28 cm long, 10 W each, emitting at 254 nm) on the top of the chamber. The samples were put at the bottom of the chamber for irradiating to a desired dose (J/cm^2) by using the energy setting system equipped in the UV mini-crosslink machine. This setting system uses a radiometer to measure irradiation dose continuously, and the irradiation stops automatically when the energy dose at the bottom of the chamber reached the set value.

Characterization

Degree of crosslinking

The degree of crosslinking was characterized by measuring SD and GM. Determinations of SD and GM were carried out following the procedure described by Delville et al.[21] The UV irradiated sheets were conditioned at 57% RH for moisture absorption equilibrium then immersed in DMSO in which the TPS sheet is originally soluble. The insoluble part (swollen sheet) was filtered out, wiped lightly and weighed (the amount was referred to as m_s) in an analytical balance with a precision of 0.1 mg. After that, the insoluble part was first rinsed in water and then in ethanol to remove the DMSO. The insoluble part was dried at 80°C for 6 h and reconditioned at 57% RH then weighed (the amount was referred to as m_d). The surface area normalized SD and GM were calculated by following formulas:

$$\text{Normalized SD} = (m_s - m_d)/(m_d \times A)$$

$$\text{Normalized GM} = m_d/A$$

where A is the surface area of sample sheet for photocrosslinking modification.

Contact angle measurements

Contact angle measurements were carried out by using a contact angle instrument, Contact Angle System

OCA20 (Dataphysics, Germany), and the Sessile and Captive drop method was applied. All the samples were conditioned at 57% RH for moisture equilibrium before measurements. A droplet of distilled water (3 μL) was placed on the sheet surface. The contact angles were measured on both sides of the drop and averaged. Each reported contact angle was the mean value of at least five measurements taken at different positions on the sheet. The measurements were made at room temperature in a closed box.

Stereomicroscopy

A stereomicroscopy, SteREO Discovery V12 (Zeiss, Germany), was used to observe the surface topographies of the control and surface photocrosslinking modified TPS sheets.

Moisture absorption

Moisture absorption was measured by storing the samples at room temperature in desiccators with controlled relative humidities which were maintained by using saturated salt solutions according to standard practices (ASTM E 104-85). The chosen salts were LiCl, $MgCl_2$, NaBr, NaCl, and KNO_3, and the corresponding humidities at room temperature are 11, 33, 57, 75, and 93% RH. Before putting the sheet samples into the desiccators, they were fully dried in an oven at 80°C and weighed in an analytical balance with a precision of 0.1 mg. The back surface (the one not facing the UV lamps during irradiation) and the four edges of the sheet samples were covered with white vaseline (Tianjin Shuangsheng Chemical Factory, China) to ensure only the UV irradiated surface was exposed to the chosen humidity environment and weighed again. The purpose of vaseline coatings was to examine how the surfaces with different crosslink extents affect the kinetics of moisture sorption. To build a moisture sorption kinetic curve, a set of dried samples were put in a desiccator with a given humidity, after being stored for predetermined time, some of them were taken out and weighed. The weighed samples were replaced in the desiccators for the equilibrium measurements. The equilibrium was considered to be reached when the weight gain <1% since the last weighing. The MC was calculated using the measured wet weight, W_w, and the dry weight, W_d, by:

$$MC = (W_w - W_d)/W_d$$

Mechanical properties

The specimens, 50 mm long dumbbells with 4 mm neck width, were cut from the prepared sheets. After surface photocrosslinking modifications, all the specimens were conditioned at 75% RH and room temperature to the equilibrium. The tensile tests were carried out by using an Instron Universal testing Machine model 1121 (Instron) at a crosshead rate of 2 mm/min. Tensile strength, Young's modulus and elongation at break were obtained. At least five specimens were measured for each sample at the same experimental conditions and the average values were taken.

RESULTS AND DISCUSSION

Photocrosslinking reaction

The sensitizer, sodium benzoate, used here is known to be decomposed under UV irradiation and to produce radicals, the crosslinking reaction occurs through a radical mechanism by hydrogen abstraction.[21,28] The starch macromolecular network formed by crosslinking due to UV irradiation can be characterized by the SD and GM. Surface area normalized GM is directly related to the mass of starch macromolecules involved in the crosslink network and the surface area normalized SD is related to the density of the newly created network.

Effect of concentration of photosensitizer aqueous solution

The concentration of photosensitizer aqueous solution determines the sensitizer content in the surface layer of TPS sheets. The work of Delville et al.[21] showed that, for bulk crosslinked TPS sheets, a very low photo-additive content (0.1%) is sufficient to crosslink starch, and no improvement was observed by increasing the amount of photo-additive. Author's previous work also demonstrated that, for the surface photocrosslinking of gelatinized corn starch sheets, the 0.75% sodium benzoate aqueous solution gave rise to the highest crosslink extent (characterized by lower SD and higher GM) in the investigated concentration range from 0.1 to 2.0%.[27] Therefore, the concentration of sodium benzoate aqueous solution varying from 0.5 to 1.0% was chosen in this study.

Figure 1 shows the normalized SD and GM as a function of UV irradiation dose for the sheets soaked in the sodium benzoate aqueous solutions with different concentrations for 90 s. It can be seen that the concentration of photosensitizer aqueous solutions significantly affects the values of both normalized SD and normalized GM. When irradiated with a higher UV dose (>20 J/cm^2), the concentration of 0.75% gave rise to a lower SD and a higher GM compared with the concentrations of 0.5 and 1.0%. This means a higher crosslink extent has been

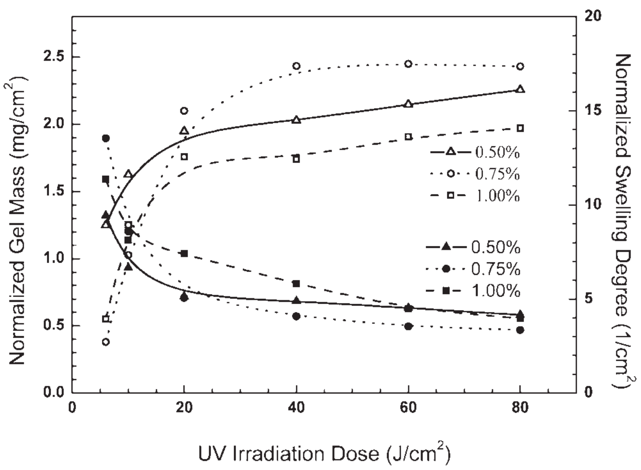

Figure 1 Changes of normalized swelling degree (solid symbol) and gel mass (open symbol) against UV irradiation dose for the TPS samples soaked in sodium benzoate aqueous solutions with different concentrations for 90 s.

reached when using the 0.75% sodium benzoate aqueous solution. The above results indicated that, for sodium benzoate aqueous solution, a concentration of 0.75% is sufficient to crosslink the surface layer of the TPS sheets. A higher concentration of photosensitizer aqueous solution would result in higher photosensitizer content onto the surface layer of the TPS sheets. An excessive amount of the photosensitizer could increase UV energy absorption and decrease UV penetration depth into the exposed sample, which would lead to a lower crosslink extent characterized by normalized GM. Although there may exist an optimum concentration around 0.75% which could crosslink the starch molecules more efficiently, no further investigations were made to explore it.

It can be seen from Figure 1 that, in the lower UV irradiation dose range (<20 J/cm^2), the decreasing of SD and the increasing of GM with UV irradiation dose were more quick than that in the higher irradiation dose range. These indicated that the surface crosslink reaction was fast at beginning but slowed down afterwards. The reason could be attributed to the decrease of starch macromolecular mobility with progress of the crosslink reaction. The formation of intermolecular bridges induced by crosslink reaction and sample water loss during UV irradiation could lead to decrease of starch macromolecular mobility and reduce the crosslink reaction kinetics.

Effect of soaking time

The soaking time of the sample sheets in sodium benzoate aqueous solution determines the thickness of the surface layer containing photosensitizer which in turn affects the depth range that starch macromolecular network can be formed. Figure 2 shows the normalized SD and GM as a function of UV irradiation dose for the sheets soaked in 0.75% sodium benzoate aqueous solution with different periods of time. Basically, the shapes of the kinetic curves for different soaking times were similar and possessed the common feature described in Figure 1. However, it was found that the kinetic curves of 10 s soaking in sodium benzoate aqueous solution was much flatter than that of 30 and 90 s soakings. Thirty-second soaking gave rise to a lower final value of normalized SD and a higher final value of normalized GM in the investigated conditions.

The effect of soaking time on the normalized SD and GM is complicated. A lower SD was not always corresponding to a higher GM. This is understandable. Shorter soaking gave rise to a thinner surface layer containing the photosensitizer, which will result in a lower GM value due to less of starch macromolecules involved in the crosslink reaction, but the SD could reach a relative lower value if both photosensitizer content and UV irradiation dose are enough to create a high crosslink density network. Since the photosensitizer distribution is not uniform along the depth from the surface and UV intensity declines with the penetration depth, crosslink density in the crosslinked surface layer may exist in a gradient. The effect of soaking time on the final crosslink extent characterized by normalized SD and GM is dependant on the concentration of photosensitizer aqueous solution, the UV irradiation dose and the UV penetration depth in the system, whereas the UV penetration depth is influenced by photosensitizer content in the system.

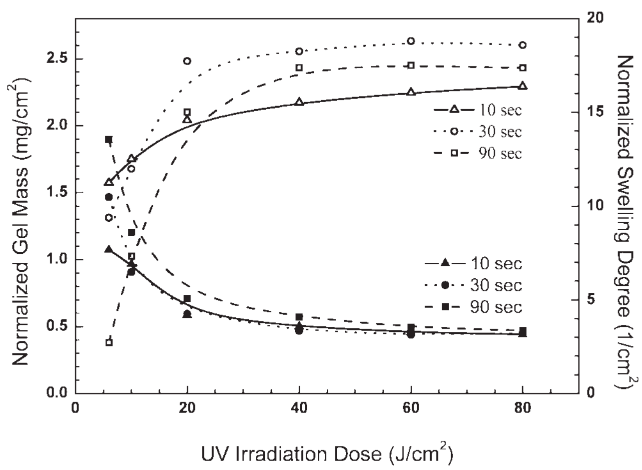

Figure 2 Changes of normalized swelling degree (solid symbol) and gel mass (open symbol) against UV irradiation dose for the TPS samples soaked in 0.75% sodium benzoate aqueous solution for different periods of time.

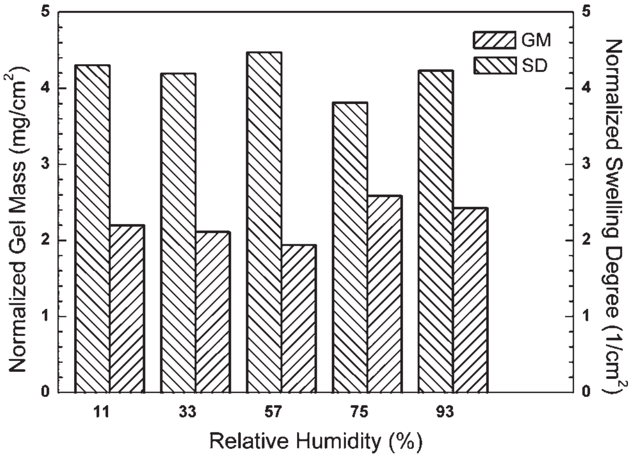

Figure 3 Normalized swelling degree and gel mass for the TPS samples conditioned to equilibrium at various humidities after soaking in 0.75% sodium benzoate aqueous solutions for 90 s then irradiated with 40 J/cm^2 UV dose.

Effect of moisture content

For the bulk crosslinked TPS sheets, the effects of plasticizer (glycerol or water) on the UV photocrosslinking have been documented.[21] Crosslinking necessitates a compromise between the macromolecular mobility enhanced by the presence of the plasticizers (especially of water) and the probability of macroradicals combining. It is difficult to evaluate the water content in the surface layer containing photosensitizer for the studied cases. However, since the sheets were conditioned in 57% RH to equilibrium before soaking in the photosensitizer aqueous solution, the difference of water sorption should be negligible for the sheets with the same soaking time. Although no reconditioning after soaking is easier, more convenient and saving time in practical applications, further experiments were carried out to study the role of water content in the surface photocrosslink reaction. Sheets were conditioned in 11, 33, 57, 75, and 93% RH for moisture equilibrium after soaking in 0.75% sodium benzoate solution for 90 s, then irradiated with 40 J/cm^2 UV dose. The data of normalized SD and GM were presented in Figure 3. The sample reconditioned at 75% RH gave rise to a lower SD and a higher GM than others. Compared with the data in Figure 3 with that of the no reconditioning sheets, it may conclude that the effect of water content on the crosslink extent was not significant for the investigated cases.

Water contact angle

One of the primary aims of surface photocrosslinking modification of TPS sheets is to investigate how the surface modifications influence the surface hydrophilic character of the material. Contact angle measurements provide a quantitative characterization of material surface energy. An increase in water contact angle indicates an enhancement of hydrophobic character of surface and a lower value for the polar component of the surface energy.

Table I showed the water contact angles of the control sheet and the surface crosslinked sheets prepared at different conditions. The results in Table I showed that, when using photosensitizer aqueous solutions with concentrations of 0.5 and 0.75%, the surface modifications with lower UV irradiation dose gave rise to higher values of surface water contact angle. However, with increasing of UV irradiation dose, the water contact angle showed a trend of declining and decreased to the values less than that of the control one. These results were not expected, because the crosslink extent was increased markedly with increasing of UV irradiation dose especially for the first 20 J/cm^2 exposure. The surface hydrophilic character of the surface crosslinked sheets should be reduced with increasing of crosslink extent, and a higher value of water contact angle should be yielded.

In the process of the surface modifications by soaking the TPS sheets in a photosensitizer aqueous solution and exposing them under UV irradiation,

TABLE I
Water Contact Angles of the Control Sheet and Those Soaked in Different Concentrations of Sodium Benzoate Aqueous Solutions for 90 s and Exposed Under Different UV Doses

UV dose (J/cm^2)	Control	Concentration 0.5%	0.75%	1.0%
0	75.14 ± 2.37	–	–	–
6	–	81.97 ± 4.57	84.17 ± 1.65	72.76 ± 2.26
10	–	82.93 ± 6.00	90.63 ± 1.99	68.95 ± 2.48
20	–	60.40 ± 4.79	73.15 ± 5.80	58.30 ± 1.70
40	–	60.90 ± 4.25	69.33 ± 2.17	57.54 ± 2.75
60	–	58.95 ± 1.28	69.50 ± 4.09	62.98 ± 1.43
80	–	61.93 ± 5.86	60.70 ± 4.86	61.90 ± 1.02

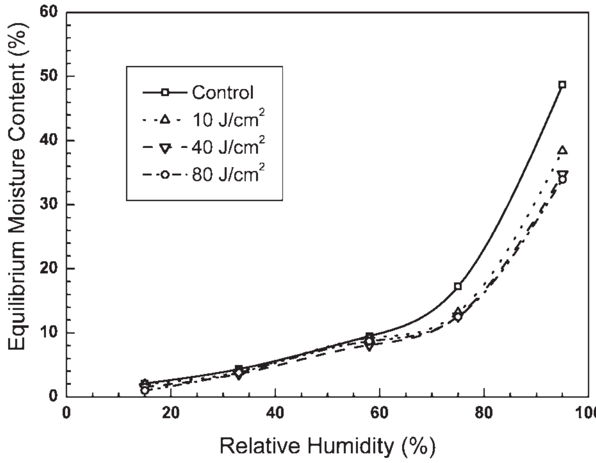

Figure 4 Moisture absorption isotherms at RT for the control sheet and those soaked in 0.75% sodium benzoate aqueous solution for 90 s and exposed under different UV doses.

the sheet surface layer was subjected to swelling, drying, and shrinking. Surface toughness may be changed and, even more, micro-cracks could be formed at the surface during the above treatments. All of these could lead to the water contact angle changing with photocrosslinking treatment conditions because surface contact angle correlates with the surface roughness. The surface morphologies of the control and surface crosslinked sheets were examined by a stereomicroscope. No micro-cracks were observed on the surfaces of the crosslinking modified sheets. Therefore, for the surface modified sheets, the decrease of water contact angle with UV irradiation dose should not be attributed to possible formation of surface micro-cracks. However, examinations of the surface morphologies gave an impression that the surface roughness of the crosslinking modified sheets seems increasing with UV irradiation dose. The decrease of water contact angle with UV irradiation dose may be due to the changes of surface roughness. Actually, it is difficult to make the wettability measurements with water and hydrophilic substrate when the substrate is not smooth enough. But the data in Table I help to appreciate the averages, deviations, and variations for comparisons.

Moisture absorption

The equilibrium MCs of the control and surface crosslinked sheets in various humidities at room temperature were shown in Figure 4. It can be seen that, after surface modification, the sheets showed a notable lower moisture uptake than the control one in the common moisture absorption region (50–80% RH). This effect was particularly pronounced in the high RH range. At 93% RH, the equilibrium MC of the sheet modified with 80 J/cm^2 UV irradiation dose decreased about 30% compared with that of the control one, which is significant.

Moisture absorption kinetics was examined at 93% RH, the data were presented in Figure 5. Basically, moisture absorption was quick in the first 10 h conditioning, afterwards the curves turned into level. However, the influence of surface photocrosslinking modification on the moisture absorption kinetic curves was dramatic. Compared with the control sample, the moisture absorption kinetic curves of UV crosslinked ones were shifted lower. The effect of UV irradiation dose on the initial part of the kinetic curves was not significant, but the final values of moisture uptake in the surface modified sheets decreased with UV irradiation dose. These results suggested that although surface photocrosslinking modification did not give rise to a notable improvement in moisture absorption rate of the TPS sheets, it did reduce the moisture uptake ability of the sheets dramatically.

Mechanical properties

Mechanical properties are important criterion for many practical applications of TPS. The formation of starch macromolecular network in the sheet surface layer could change the mechanical properties of the sheets. It is worthy to examine the influence of surface photocrosslinking modifications on the sheet mechanical properties.

Figures 6 and 7 shows the mechanical properties of the control and the surface crosslinked sheets at room temperature and 75% RH. The surface crosslinked sheets were prepared by soaking them in

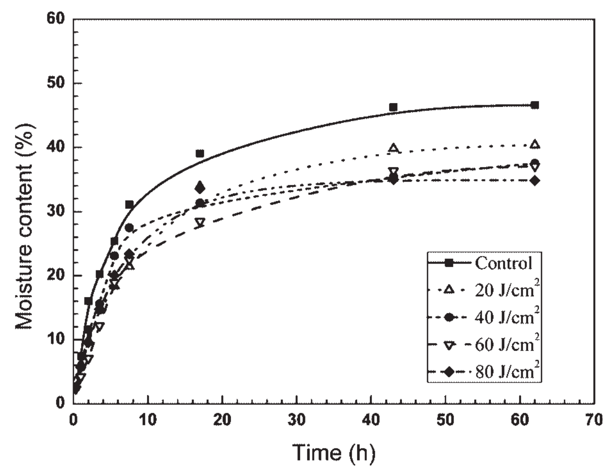

Figure 5 Moisture absorption kinetics at RT and 93% RH for the control sheet and those soaked in 0.75% sodium benzoate aqueous solution for 90 s and exposed under different UV doses.

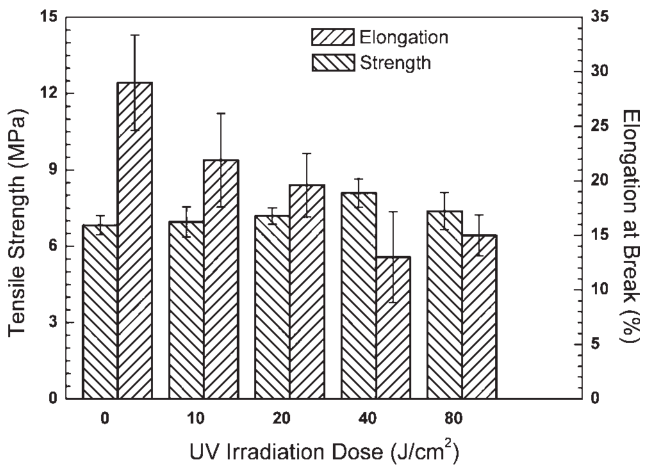

Figure 6 Effects of surface photocrosslinking modification on tensile strength and elongation at break of the TPS sheets.

0.75% sodium benzoate aqueous solutions for 90 s then exposed with different UV irradiation doses. Compared with that of the control, surface photocrosslinking modification increased the tensile strength and Young's modulus but decreased the elongation at break of the TPS sheets. It can be seen from Figures 6 and 7 that both tensile strength and Young's modulus initially increased with the UV irradiation dose, but declined at 80 J/cm^2 dose. The trend of the elongation at break changing with UV irradiation dose was reverse. Tensile strength and Young's modulus of the UV surface crosslinked sheets with 40 J/cm^2 irradiation dose were increased by 18 and 199% respectively, and elongation at break reduced by 55%. As demonstrated above, with increasing of UV irradiation dose, the crosslink extent in the surface layer increased and the equilibrium MC in the sheets decreased. These gave rise to the increasing of tensile strength and Young's modulus as well as the decreasing of elongation at break. Under higher UV irradiation dose, the macromolecular chain scission may occur, this could lead to the observed declines of tensile strength and Young's modulus of the sheets irradiated with 80 J/cm^2.

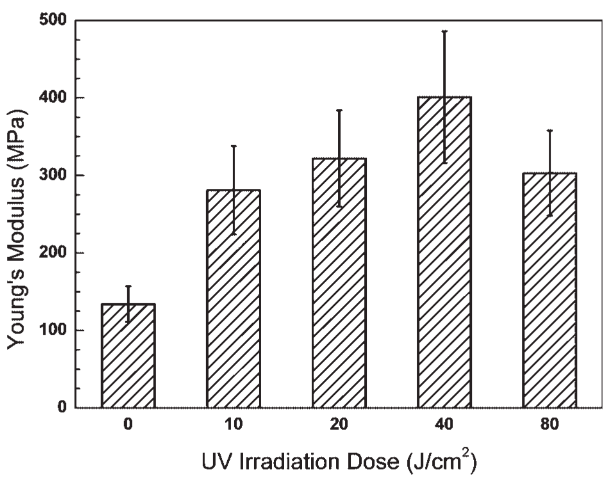

Figure 7 Effects of surface photocrosslinking modification on Young's modulus of the TPS sheets.

CONCLUSIONS

Glycerol plasticized TPS sheets were surface crosslinked by soaking the sheets in sodium benzoate aqueous solution and exposing them under UV irradiation. When irradiated with higher UV dose (>20 J/cm^2), the 0.75% sodium benzoate aqueous solution resulted in more efficient crosslink reactions compared with the concentrations of 0.5 and 1.0%. The influence of water content in sheets on surface crosslink extent is not significant for the investigated cases. Although the surface hydrophilic character of the TPS sheets, characterized by water contact angle, was not improved notably after surface photocrosslinking modification, the water uptake ability of the TPS sheets was significantly reduced especially in higher relative humidity range. The surface photocrosslinking modification increased tensile strength and Young's modulus but decreased elongation at break of the TPS sheets. The surface photocrosslinking technique provides a novel approach to lower water sensitivity of TPS materials and extend their possible applications.

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