

Effect of post cross linking by sodium hexameta phosphate on the performance of starch/polyvinyl alcohol blend films

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(Acceptance Date 25th March, 2013)

Abstract

In this paper, the starch/PVA blend films were prepared by solution casting method. The blend is further post cross-linked by using sodium hexametaphosphate (SHMP). The extent of crosslinking is measured by swelling degree (SD) and gel mass (GM) analysis. It was seen that concentration of SHMP and sodium carbonate had considerable effect on the crosslinking reaction. With the increase in concentration of SHMP from 2 % to 12 %, GM was increased to 32.8 %. Whereas, with the increase in concentration of sodium carbonate from 0.5 % to 12 %, SD was decreased to 88.4 %. Decrease in swelling degree is favorable for cross-linking reaction. Starch/PVA blend films showed 30% increase in tensile strength after crosslinking with SHMP. Cross-linking with SHMP also improved the moisture resistance of starch/PVA blend films. The cross-linked starch/PVA blend films showed 27 % less water absorption than the non cross-linked starch/PVA blend films.

Key words: Starch/PVA blend films, swelling degree, gel mass, mechanical properties.

Introduction

Starch is a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds. It consists of two types of molecules, the linear and helical amylose and the branched amylopectin. Starch can act as a filler in thermoplastics due to its biodegradability, renewability and low cost¹⁻³. But, pure starch film lacks strength, water resistability

and thermal stability⁴⁻⁶. Therefore, various process have been tried in literature to modify the starch such as, glycerol^{7,8}, ultraviolet irradiation⁹, surface octanoylation by octanoyl chloride¹⁰, reaction with isocyanates, epoxy functions and stearoyl chloride¹¹. The film forming capacity of modified starches is also studied by various researchers¹²⁻¹⁴ and it was found that it improved after modification.

Recently starch has been blended with biodegradable synthetic polymers such as poly lactic acid (PLA), poly ϵ -caprolactone (PCL) and poly vinyl chloride (PVA) as it promoted good film formation^{15,16}. Out of completely biodegradable polymers, PVA can be blended with starch as PVA has good film formation, excellent physical properties, chemical resistance, good biocompatibility and high thermal stability. It can be completely degraded by a soil bacteria *psuedomonas* but degradation of pure PVA is very slow under the presence of plasticizer glycerol. It is the largest synthetic water soluble material produced in the world¹⁷ and biodegradable in nature and it is well suited for making blends with starch^{18,19}. Thus, starch/PVA blend is the most popular biodegradable polymer but it still lacks in mechanical strength and is hydrophilic in nature.

Cross-linking is an efficient and commonly used technique to increase the water resistance of starch/PVA blend. The polymer without crosslinking has free chains and due to the presence of the freechains the films uptake moisture and swells up, which makes it poor for further usage. When polymer chains are linked together by cross-links, they lose some of their ability to move as individual polymer chains. As crosslinking increases, free chains of the polymer is reduced and polymer tends to uptake less moisture. Crosslinking of starch/PVA blend films was done by various methods, ultra violet (UV) irradiation^{20,21}, citric acid²², epichlorohydrin²³, boron complexes²⁴, maleic acid²⁵, gelatin hydrogels²⁶, sodium trimetaphosphate²⁷.

In this paper, the modification of the starch/PVA blend films was carried out by

crosslinking the films with SHMP. The crosslinked films have been optimised by Gel mass and swelling degree analysis. The degree of swelling and gel mass of the films can also be determined using various other solvents such as (hydrocarbons, halogenated hydrocarbons, ethers, ketones, esters, alcohols, nitriles and nitro compounds). Mechanical properties and water absorption of the blend films were also examined.

2. Experimental

2.1 Materials:

Corn starch and α -Amylase were purchased from Sukhjit Starch and Chemicals Ltd. Phagwara (India), PVA and glycerol were obtained from SD fine chem Limited, Mumbai (India). SHMP and sodium carbonate were supplied by Nav Bharat chemical limited Jalandhar (india). Dimethyl sulphoxide (DMSO) was purchased from Merck Chemicals Limited, Mumbai (India). All these chemicals were of reagent grade.

2.2 Film Preparation Method:

The starch/PVA blend films were prepared by solution casting method. PVA solution was prepared by adding 12 g of PVA into 100 ml of distilled water and heated at a temperature at 80 °C for 45 minutes till dissolution. 18 g of corn starch and 3 g of glycerol were mixed together in 100 ml of distilled water and heated at 80 °C for a period of 1 h to carry out gelatinization. PVA solution and gelatinized starch were mixed. The temperature of starch/PVA mixture was maintained at 80 °C with constant stirring for 3 h. After this, the prepared solution of starch/PVA mixture

was poured onto the petri dish and allowed to dry in oven for 24 h at 50°C and the fully dried membranes were peeled off from the petri plates.

2.3 Crosslinking of films for SD and GM Analysis:

The starch/PVA blend films prepared, were conditioned at 50°C for 2 h. After conditioning, samples (25mm x 25mm) of starch/PVA blend films were post crosslinked by soaking the films in Na₂CO₃ solution (with varied concentrations and for different periods of time) and further they were dipped in SHMP solutions (with varied concentrations and for different periods of time). After treating the blend films with SHMP, blotting paper was used to remove excess SHMP solution from the surfaces of the blend films. Crosslinking reaction was completed by placing the samples of the blend films in oven for varied reaction time ranging from 1 h to 12 h at 50°C.

2.4 Swelling degree and Gel mass:

The degree of crosslinking was determined by measurement of film swelling degree (SD) and gel mass (GM). This test was done according to the procedure described in research paper (Delville et al. 2002). The crosslinked film pieces (25mm x 25mm) were conditioned at 40°C for 1 h and weighed (W₁). After conditioning, the crosslinked films were soaked in DMSO (20ml for each film) at 25°C for 24 h. DMSO solution was used as free chains of starch/PVA blend are completely soluble in DMSO whereas, crosslinked chains do not dissolve. After 24 h, the insoluble part of the crosslinked starch/PVA blend was

filtered out, dried with blotting paper to remove excess DMSO and weighed (W₂). Washing of insoluble part was done, first by soaking in water and then in ethanol in order to remove excess DMSO. The insoluble part is then dried at 80°C for 24 h and reconditioned at 57% RH before weighing (W₃). It (W₃) represents the weight of the crosslinked starch/PVA network alone.

The swelling degree (SD) is given by:

$$SD = \frac{W_2 - W_3}{W_3} \approx \frac{W_2}{W_3} \quad \text{As, } W_3 \ll W_2$$

Gel mass (GM) is defined as the ratio of weight of starch/PVA crosslinked network to the initial weight of the starch/PVA network and free chains. It is the measure of the amount of starch/PVA molecules involved in the crosslinking. Gel mass (GM) is given by:

$$\%GM = \frac{W_3}{W_1} \times 100$$

2.5 Mechanical properties:

Tensile strength (TS) and elongation at break (%E) were measured on universal testing machine (NEXYGEN, Lloyd Instruments Limited, England) at a crosshead speed of 1.2mm/min, according to ASTM D882 method. Dumbbell shaped specimens (width of 5mm and 40 mm length) were cut and the thickness of the film was measured by a mechanical scanner (digital thickness gauge 'Mitutoyo', Tokyo, Japan) at six random positions. The average thickness of each specimen was less than 1mm. All the tests were carried out at

room temperature (25°C) under controlled conditions²⁸

2.6 Water absorption measurements:

Water absorption measurements were done according to the ASTM D570-81 method. Film pieces (30mm x 30mm) were conditioned at 50°C for 3 h and weighed (W_{dry}). Dried films were immersed in distilled water at room temperature (25°C) for 24 h. After 24 h, samples were removed from the beakers containing distilled water, dried by wiping gently with blotting paper and subsequently weighed (W_{wet}) to determine water absorbed by the films. The water absorption (W_a) is given by :

$$\% W_a = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$

2.9 Enzymatic degradation:

Enzymatic degradation studies were carried out at 37°C, pH=7, using α -Amylase for 96 h. The dried samples were cut into 30mm x 30mm, weighted (W_o), and immersed in conical flasks containing α -amylase (20 ml) with an enzymatic activity of 328.9 KNU/g. The flasks were placed in aincubator shaker with the rate of 160 rpm at 37°C. After 24 h intervals, the residue was washed with distilled water, and dried at 80°C to a constant weight and weighed (W_1).

The weight loss rate is given by :

$$\text{Weight loss rate(\%)} = \frac{W_o - W_1}{W_o} \times 100$$

3. Results and Discussion

3.1 Crosslinking reaction:

The prepared starch/PVA blend films were post crosslinked by SHMP and sodium carbonate. The various conditions used for various experiments such as, concentration of SHMP, concentration of sodium carbonate, reaction time and soaking time in SHMP are shown in Table 1.

Table 1. Experimental conditions of the films

Starch/ PVA (%w/w)	SHMP Crosslinking (Treating conditions)	Na ₂ CO ₃ (Treating conditions)	Time of reaction (h)
60:40	2%, 60 s	3%, 60 s	2
60:40	4%, 60 s	3%, 60 s	2
60:40	6%, 60 s	3%, 60 s	2
60:40	8%, 60 s	3%, 60 s	2
60:40	12%, 60 s	3%, 60 s	2
60:40	3%, 60 s	0.5%, 60s	2
60:40	3%, 60 s	1%, 60 s	2
60:40	3%, 60 s	2%, 60 s	2
60:40	3%, 60 s	4%, 60 s	2
60:40	3%, 60 s	6%, 60 s	2
60:40	3%, 60 s	8%, 60 s	2
60:40	3%, 60 s	12% 60 s	2
60:40	3%, 10s	3%, 60 s	2
60:40	3%, 30s	3%, 60 s	2
60:40	3%, 60s	3%, 60 s	2
60:40	3%, 90s	3%, 60 s	2
60:40	3%, 120s	3%, 60 s	2
60:40	3%, 60 s	3%, 60 s	1
60:40	3%, 60 s	3%, 60 s	2
60:40	3%, 60 s	3%, 60 s	3
60:40	3%, 60 s	3%, 60 s	4
60:40	3%, 60 s	3%, 60 s	6
60:40	3%, 60 s	3%, 60 s	8
60:40	3%, 60 s	3%, 60 s	12

3.1.1 The effect of varying concentration of SHMP on SD and GM:

The measurement of swelling degree (SD) and gel mass (GM) for the films plays an important role in determining the degree of crosslinking between the components, of the films²⁹. Fig. 1 showed the values of SD and GM of the samples soaked in 3% sodium carbonate for 60 s and then in different concentrations of SHMP for 60 s and heated at 50 °C for 1 h for the crosslinking reaction to take place. It was observed that as the concentration of SHMP increased from 2% to 12%, SD showed decreasing trend and GM showed increasing trend. However, at higher concentrations of SHMP, there was no change in the values of SD and GM. This is because at higher concentrations of SHMP, more macromolecules will participate in crosslinking reaction forming a network with higher number of crosslinks, which reduces molecular mobility of the starch/PVA blend films³⁰.

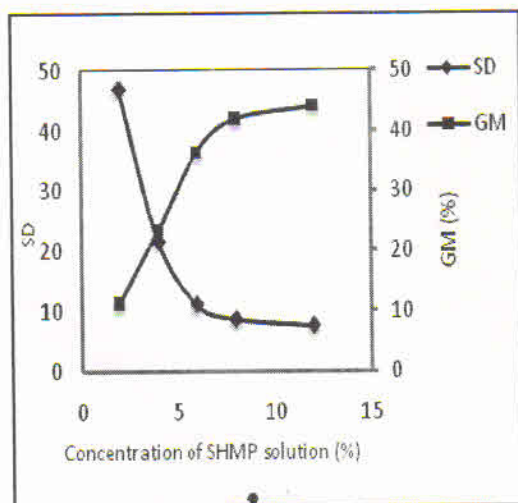


Fig 1: Effect of concentration of SHMP on Swelling degree and Gel mass

3.1.2 The effect of varying concentration of Na_2CO_3 on SD and GM:

Starch/PVA blend films were dipped in different concentrations of sodium carbonate solution for 60 s and then in 3 % SHMP solution for 60 s and heated the crosslinked starch/PVA blend at 50 °C for 1 h in order to complete the crosslinking reaction. Results showed that with the increase in the concentration of sodium carbonate from 0.5% to 12%, SD decreased and GM increased till 6% concentration of sodium carbonate (Fig. 2). After 6 % concentration of sodium carbonate there was no change in GM and SD. This is because at low concentration of sodium carbonate, hydroxyl groups of starch/PVA blend films were changed into oxygen anions and these anions promoted crosslinking reaction of the starch/PVA blend films. But higher concentration of sodium carbonate had no impact on crosslinking of the starch/PVA blend films due to saturation of hydroxyl groups.

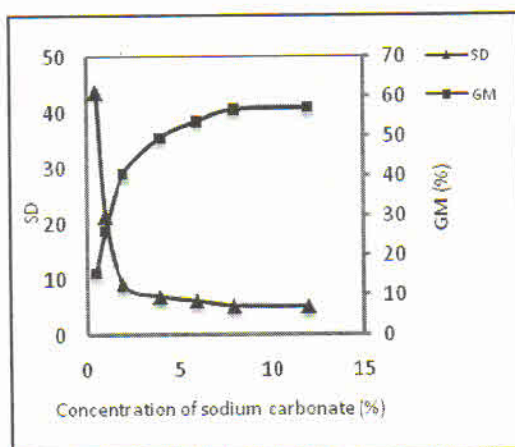


Fig. 2. Effect of varying concentration of sodium carbonate on swelling degree and gel mass

3.1.3 The effect of varying reaction time on SD and GM:

The starch/PVA blend films were immersed in 3 % sodium carbonate for 60 s and then in 3 % SHMP for 60 s. After that, the films were placed in an oven at 50°C for varied reaction time from 1 h to 12 h, for the crosslinking reaction to finish. Results showed that SD and GM are function of crosslinking reaction time (Fig. 3). SD increases initially with increasing reaction time, but after 8 h of reaction time, both SD and GM becomes constant. As the reaction time of crosslinking is increased, crosslinking density increased at first, but after 8 h of reaction time the molecular mobility decreased due the saturation of crosslink bonds and evaporation of moisture which reduces the formation of more crosslinks at higher reaction time.

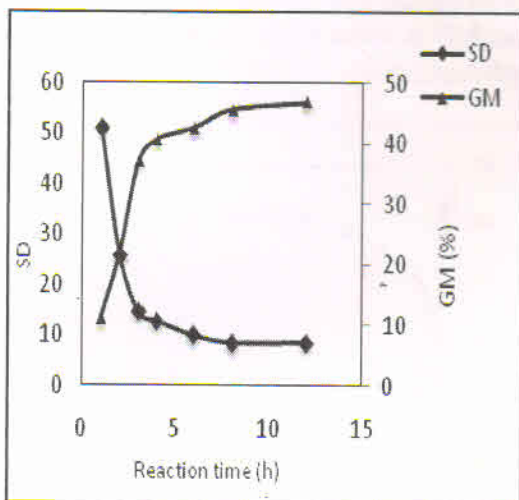


Fig. 3. Variation of swelling degree and gel mass with the reaction time

3.1.4 The effect of varying reaction time on SD and GM:

The starch/PVA blend films were soaked in 3 % sodium carbonate for 60 s and then in 3 % SHMP for various periods of time and heated at 50°C for 1 h. The results showed that variation in soaking time of starch/PVA blend films in SHMP had a significant effect on the crosslinking reaction between starch/PVA blend films (Fig. 4). It was seen that, with the increase in the soaking time in SHMP, crosslinking increases to some extent between starch/PVA blend films. But, after 60 s there was no influence of soaking time in SHMP on the crosslinking density of starch/PVA blend films due to the formation of thicker SHMP layer on the surface of starch/PVA blend films which reduces further crosslinking reaction. Therefore, longer soaking time in SHMP had no considerable change on SD and GM.

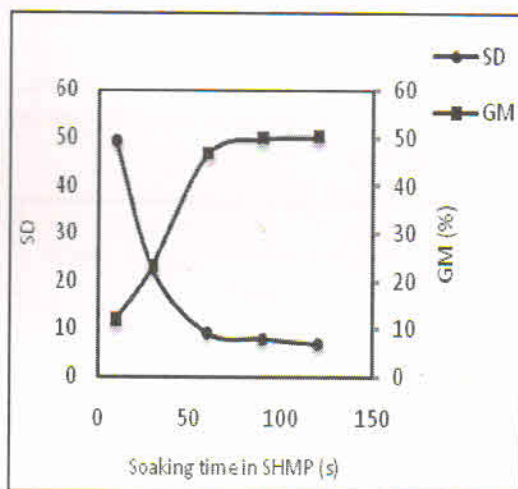


Fig. 4. Variation of swelling degree and gel mass with soaking time in SHMP

3.1.5 Optimisation:

Swelling degree (SD) and gel mass (GM) were optimized by crosslinking the starch/PVA blend films using sodium carbonate

solution and SHMP solution at different experimental conditions. It was seen that starch/PVA blend films had maximum crosslinks when the blend films were soaked in 6 % sodium carbonate solution for 60 s and then in 8 % SHMP solution for 60 s. The starch/PVA blend films were heated at 50°C for 1 h to give the maximum crosslinking density. Deviating from any of the above condition will give lower crosslinks between the starch/PVA blend.

3.2 Mechanical properties of the films:

The tensile strength and percentage elongation of the PVA/NS blend films with and without crosslinking are shown in Fig. 5. The tensile strength of NS film was 1.41 N/mm² which is much less than PVA film (14.28 N/mm²). Whereas, PVA/NS blend film showed tensile strength 3.52 N/mm², which is greater than NS film. The remarkable increase in tensile strength of PVA/NS blend film is due to the formation of intermolecular bonds between PVA and starch. The PVA/NS crosslinked blend films showed 30 % more increase in tensile strength than the PVA/NS non crosslinked blend films. The increase in tensile strength of PVA/NS crosslinked film is due to the formation of macromolecular crosslinks which increases the tensile strength at the cross-section of the film.

Percentage Elongation at break (Fig. 6) was maximum for PVA film (561.41 %) and it decreased to 110.84 % in non crosslinked PVA/NS blend film. But after crosslinking, the percentage elongation of the PVA/NS blend films reduced by 20 %. The decrease in percentage elongation at break for the crosslinked PVA/NS film was due increase in bonds and increased rigidity of the PVA/NS blend films and

therefore caused decrease in elongation at break.

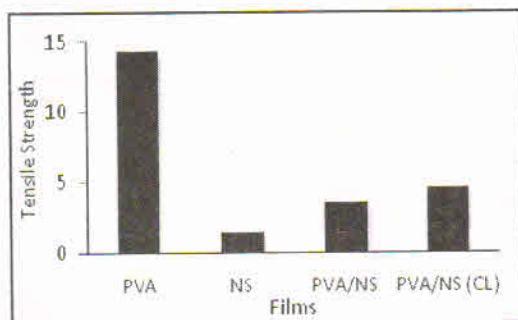


Fig. 5. Tensile strength of PVA/NS blend films

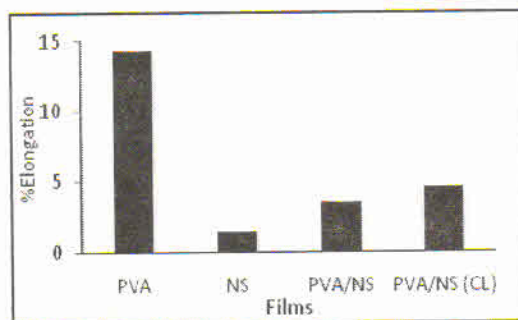


Fig. 6. Percentage elongation of PVA/NS blend films

3.3 Water absorption measurements:

Water absorption is the most important factor for the biodegradable materials³⁰. NS films showed the maximum water absorption (89.7 %) whereas, PVA/NS blend films has water absorption 10 % less than the NS films as shown in Fig. 7. After post crosslinking of PVA/NS blend films by SHMP, The water absorption tendency is reduced by 34 % than the PVA/NS blend films which were not post crosslinked. Therefore, SHMP was used to

improve the properties of PVA/NS blend films, as it forms inter and intra ester linkages which crosslink starch molecules and thereby reducing the hydroxyl groups in the blend films.

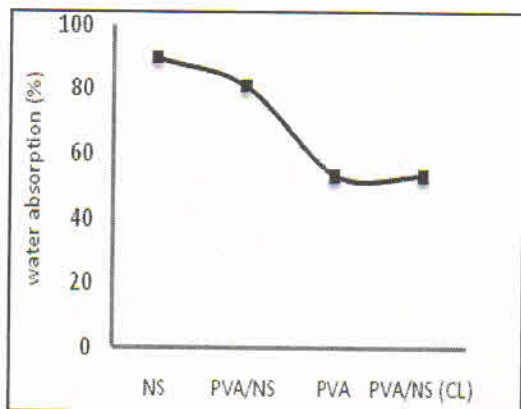


Fig. 7. Percentage decrease in water absorption of PVA/NS blend films

3.4 Enzymatic degradation:

The enzymatic degradation of PVA/NS blend films in α -amylase was observed and the results are shown in Fig. 8. NS film was most degraded due to increase in susceptibility to enzyme attack. Whereas, The enzymatic degradation rates of PVA/NS (CL) blend films were lower than NS film, as crosslinks due to SHMP forms a dense structure between starch and PVA, making the PVA/NS (CL) blend films more compact, which in turn reduced the diffusion of α -amylase in the blend. The PVA/NS blend films showed similar weight loss behavior as the PVA/NS (CL) blend films post cross-linked by SHMP. This indicates that crosslinking had no significant influence on biodegradability of the films.

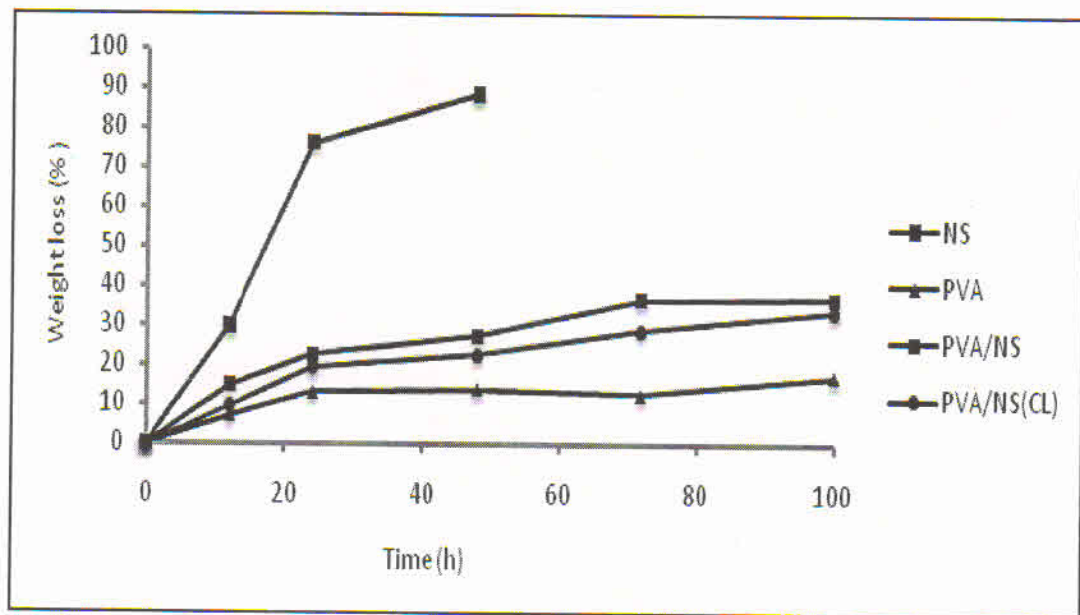


Fig. 8. Influence crosslinking on PVA/NS blend films weight loss rate by enzymatic degradation

4. Conclusion

Different PVA/NS blend films were prepared and cross-linked with SHMP. The Crosslinking density changes with the change in the concentration of SHMP and sodium carbonate. Soaking time in SHMP and sodium carbonate also affects the density of cross-links formed between the PVA/NS blend films. Mechanical properties showed that the crosslinking modification has increased the tensile strength of PVA/NS blend films by 30 % but decreased the elongation at break by 20 % because of the increase in intermolecular interactions after crosslinking with SHMP. The cross-linked starch/PVA blend films showed 27.38 % less water absorption than the non cross-linked starch/PVA blend films. Biodegradability of PVA/NS blend films was evaluated by enzymatic degradation test. The PVA/NS blend films showed similar weight loss behavior as the PVA/NS (CL) blend films (post cross-linked by SHMP). This indicates that crosslinking had no significant influence on biodegradability of the films.

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