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Research Paper

Studying physico-mechanical properties of maleic acid grafted chitosan with metal as slow release fertilizers

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Abstract

Chitosan (CS) was successfully grafted with maleic acid (MA) in 1% acetic acid solution by using potassium persulfate (KPS) as the initiator. The grafting yield (GY) up to 84.25 % and grafting efficiency (GE) of 64.82 % were achieved. The formation of grafted chitosan was confirmed with usual spectroscopic methods and thermal analysis. The raw grafted chitosan was mixed with Na^{+}, Mg^{2+} and Ca^{2+} in aqueous hydroxide solution and K^{+} in aqueous chromate solution. The reaction mixtures were separated from excess unreacted maleic acid and characterized as a reacted grafted chitosan. The results showed a new form of maleic grafted chitosan after the reaction with metals. Also, grafted of CS with MA provide a promising set of materials for potential slow release fertilizer applications.

Keywords: *Grafting; Chitosan; Maleic Acid; Potassium Persulfate; Metal Ions.*

1. Introduction

Chitosan, poly [β-(1-4)-2-amino-2-deoxy- D-glucose], is the N-deacetylated form of chitin and has many useful features such as hydrophilicity, biocompatibility, biodegradability, antibacterial property, ion-chelating ability, and a remarkable affinity for many proteins and fats [1]. The deacetylated product, chitosan, has an amine functional group, which is strongly reactive with metal ions. The deacetylation degree will control the content of glucosamine and therefore the fraction of free amine groups available for metal binding. These groups are more reactive than the acetamide groups present on chitin. Also their solubility in acidic solutions differs, chitosan being soluble. The physicochemical properties of chitosan depend on various parameters such as degree of deacetylation and polymer weight [2]. Many researchers are now looking at the ability of this amino group to adsorb metal ions from industrial wastewater and leachates. The presence of heavy metal in environment is of major concern because of their transformation from relatively low toxic species into more toxic ones [3]. This review presents the developments in this area and identifies the defficiences in existing chitosan research by reviewing the equilibrium studies carried out to determine the capacity of chitosan for various metal ions [4]. To improve chitosan's performance as an adsorbent, crosslinking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycon, diglycidyl ether and isocyanates have been used [5]. Crosslinking agents do not only stabilize chitosan in acid solutions so that it becomes insoluble but also enhance its mechanical properties [6]. So the stability may be attained by chemical modifications. Chemical modifications that lead to the formation of chitosan derivatives, grafting chitosan and chitosan composites have gained much attention, extensively studied and widely reported in the literatures. Grafting of vinyl monomers onto chitosan is one way of achieving chemical modification of this amino polysaccharide. Several studies concerning graft copolymerization on chitin or chitosan have been reported. Redox initiators like Fenton's reagent, potassium persulfate, and cerium (IV) ammonium nitrate (CAN) have been found to be effective for this purpose [5-6]. Although maleic acid

is not an ordinary vinyl monomer, it has been reported to polymerize in water in the presence of potassium persulfate and poly (N-vinyl pyrrolidinone) [7].
The graft copolymer is an effective superabsorbent resin (SAR) and can absorb water 704 times its own dry weight [8]. Chitosan is easier to work with than chitin due to the protonation of amine groups in dilute acid solutions, especially acetic acid, leading to solubility [1].
In the present study, we report the grafting of chitosan with maleic acid in the presence of potassium persulfate as an initiator. Then, the grafted chitosan react with metal ions and all the samples were confirmed with usual spectroscopic methods and thermal analysis.

2. Experimental

2.1. Materials and apparatus

Chitosan, maleic acid and potassium persulfate were supplied from Aldrich. Acetic acid, 2-propanol and all other chemicals used in the experiments were obtained from Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (China).

2.2. Grafting of chitosan

The grafted polymerization was prepared as previously described in the literature [9-11] and as the following: Chitosan (5.0g,) dissolved in 1% acetic acid solution (200g), by stirring, in the water bath at 70°C. After soluble, a known amount of potassium persulfate (0.2g, 0.74mmol in 10 ml of distilled water) was added as an initiator. After 5 mins., a solution of maleic acid (20g, 172.31mmol in 50ml of distilled water) was added by dropping for 30 mins. The mixture was left for 3 hours at 70°C in nitrogen atmosphere under continuous stirring. 2-propanol was used to precipitate the product. The product was dried at room temperature. The homopolymer of maleic acid was removed from the graft copolymer by exhaustive Soxhlet extraction with acetone for 36 h. The final copolymer was then dried to a constant weight in an oven at 60°C. The grafting yield (GY %) and grafting efficiency (GE %) was calculated as follows [12] :

$$\text{Grafting Efficiency } (\text{GE }\%) = \frac{Wg}{Wg + Wi} \times 100$$

$$\text{Grafting Yield } (\text{GY }\%) = \frac{Wg - Wi}{Wi} \times 100$$

Where, Wg = Weight of grafted copolymer
Wi = Weight of homopolymer

2.3. Reaction of metal with raw grafted chitosan

An unknown mass of CS-g-MA was mixed with Na^+, Mg^{2+} and Ca^{2+} in aqueous hydroxide solution and K^+ in aqueous chromate solution. The reaction was continued until obtained the pH 7 for every reaction. 2-propanol was used to precipitate the product. The product was then dried at room temperature.

2.4. Tests

FT-IR data were recorded on a Perkin Elmer 2000-FTIR spectrophotometer in frequency range of 4000-400 cm^{-1} and in solid state with samples embedded in KBr discs. DSC was carried out using a Perkin Elmer Differential Scanning Calorimeter DSC. The samples were tested under N_2 atmosphere at a scanning rate ± 20 $^oCmin^{-1}$. The thermal gravimetric analysis (TGA) was conducted on a TGA/SDTA 851e under nitrogen flow. The heating rate was 20°C/min. For SEM, the samples were gold sputtered and observed at an accelerating voltage of 10 kV, in order to avoid membrane degradation. For EDX analysis, samples were carbon sputtered and the correspondent cross-sections were analyzed at an accelerating voltage of 10 kV. EDX quantification of metal/carbon/oxygen/nitrogen intensity ratio was normalized to 100% at the surface, for each sample.

3. Results and discussion

3.1 Grafting efficiency (GE) and grafting yield (GY)

Based on the calculations, the grafting yield (GY) up to 84.25 % and grafting efficiency (GE) of 64.82 % were achieved. According to this, chitosan was successfully grafted to maleic acid.

3.2. FT-IR spectra

The IR spectra of the chitosan and the grafted chitosan with maleic acid are shown in Fig. 1. Fig. 1a showed that the main characteristic peaks of chitosan are at 3432 cm^{-1} (O–H stretch), 2887 cm^{-1} (C–H stretch), 1637 cm^{-1} (N–H bend), 1384 cm^{-1} (C–N stretch) and 1161 cm^{-1} (asymmetric stretching of the C–O–C bridge)[13].

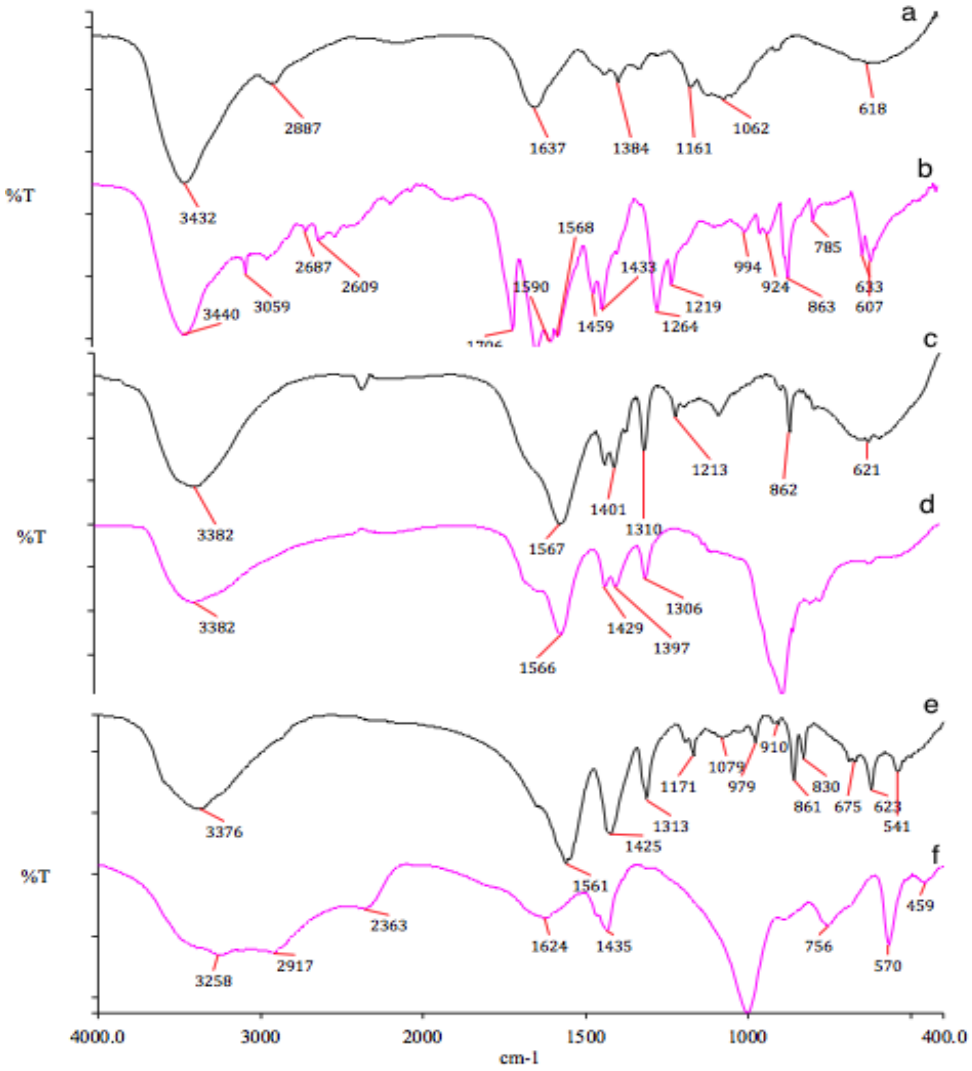

Fig. 1: FT-IR Spectrum of (A) Chitosan, (B) CS-G-MA, (C) Na^{+}, (D) with K^{+}, (E) Ca^{2+}, and (F) Mg^{2+}

For the spectrum of grafted chitosan, in Fig.1b, some new absorption peaks appeared. The peak at 1706 cm^{-1} corresponds to the C=O vibrations of maleic acid introduced onto the chitosan [1]. The peaks at 1219 cm^{-1} and 1264 cm^{-1} corresponded to the C-O stretch of the acid. At 3059 cm^{-1}, 2687 cm^{-1} and 2609 cm^{-1} attributed to OH stretch of the acid. The peaks at 1459 cm^{-1} and 1433 cm^{-1} indicated the OH bend of the acid. For the spectrums of grafted chitosan react with metals, Fig. 1c-d and Fig. 1e-f shown that the peak of carbonyl group are shifted from 1706 cm^{-1} to 1510-1650 cm^{-1}. Fig. 1c, band at 1567 cm^{-1} corresponds to the sodium carboxylate group. For Fig. 1d, band at 1566 cm^{-1} corresponds to the K carboxylate group. At Fig. 1e, band at 1561cm^{-1} correspond to Ca carboxylate group. For Fig. 1f bands at 1624 cm^{-1}correspond to the Mg carboxylate group. The results revealed that grafted chitosan was reacting with metal [14].

3.3. Differential scanning calorimetry (DSC)

DSC curves of CS, CS - g- MA and CS- g- MA–Metals are shown in Figures 2 and 3. All the DSC curves showed the single T_g value, which confirmed the miscibility of grafting maleic acid with chitosan. From the data in Table 1, T_g value of chitosan, which was 92.92 ^{o}C, increased to 135.00 ^{o}C after grafted with maleic acid. Then the values decreased to 124.00 ^{o}C, 120.00 ^{o}C, 79.13 ^{o}C and 94.58 ^{o}C after grafted chitosan react with Na^{+}, Mg^{2+}, Ca^{2+} and K^{+}. Tm value of chitosan increased after grafted with maleic acid from 118.00 ^{o}C to 164.94 ^{o}C.

Table 1: Thermal Properties of CS-G-MA and (CS-G-MA) M Films.

Polymer	Step Stage	Temperature Range (°C)	Weight Loss %	Residue %	IDT[b] °C	T_g [a] °C	T_m [a] °C
CHITOSAN	1	29.38-202.36	12.69	87.29	310	92.92	118.00
	2	202.36-897.27	55.57	31.73			
CS-g-MA	1	29.80-161.91	21.65	78.33	180	135.0	164.94
	2	161.91-300.90	40.95	37.37			
	3	300.90-895.47	16.49	20.89			
CS-g-MA-Na	1	29.42-143.56	18.26	82.20	80	124.0	127.41
	2	143.56-900.33	38.81	43.39			
CS-g-MA-Mg	1	29.94-257.51	42.83	57.19	122	120.0	127.84
	2	257.51-900.62	8.19	49.00			
CS-g-MA-Ca	1	29.78-104.71	4.14	96.04	180	79.13	187.26
	2	104.71-247.26	14.24	81.81			
	3	247.26-900.91	20.39	61.41			
CS-g-MA-K	1	29.54-195.70	13.45	86.93	74	94.58	487.51
	2	195.70-347.24	4.58	82.35			
	3	347.24-557.98	8.37	73.99			
	4	557.98-688.45	2.28	71.71			
	5	688.45-899.84	7.91	63.80			

a) Determined from DSC curves.

b) Determined from TGA curves.

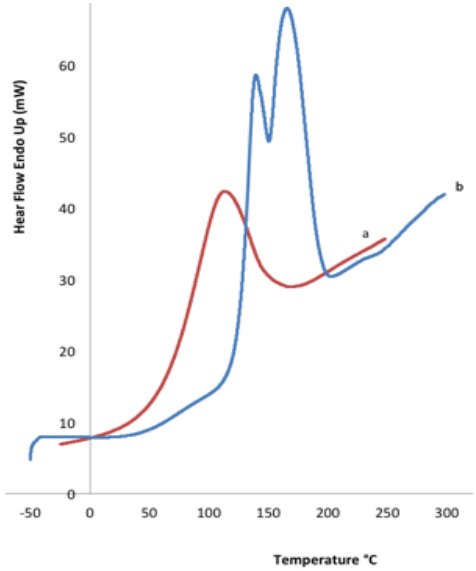

Fig. 2: DSC of CS (A) and CS-G-MA (B)

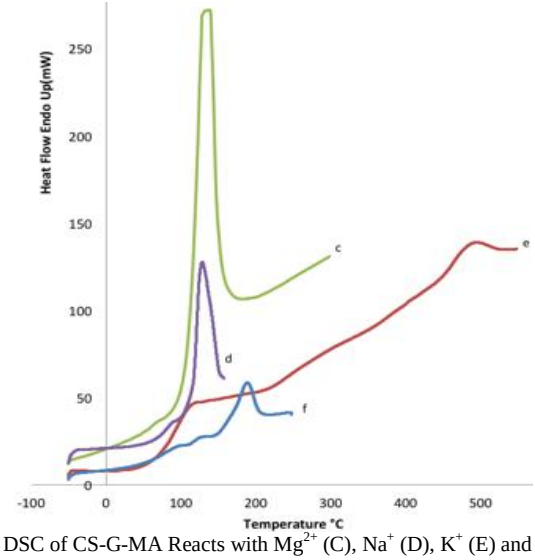

Fig. 3: DSC of CS-G-MA Reacts with Mg^{2+} (C), Na^{+} (D), K^{+} (E) and Ca^{2+} (F)

The value of Tm for grafted chitosan react with Na^+ and Mg^{2+} decreased to 127.41 ^oC and 127.84 ^oC. For reaction with Ca^{2+} and K^+, the value of Tm increased to 187.26 ^oC and 487.51 ^oC. All these value showed that the reactions were successfully occurred.

3.4. Thermo gravimetric analysis (TGA)

The thermal stability and degradation behavior of chitosan, grafted chitosan and reaction of grafted with metals were evaluated by TGA under nitrogen atmosphere. From the TGA curves shown in Fig 4, the differences between the samples can be noted. All the data for step stage, temperature range, weight loss (%), residue (%) and Initial Degradation Temperature (IDT) are shown in the Table 1. Based on the data observed, initial degradation temperature of chitosan decreased from 310 ^oC to 180 ^oC after grafted. This indicated that the thermal stability of chitosan decreased after grafting.

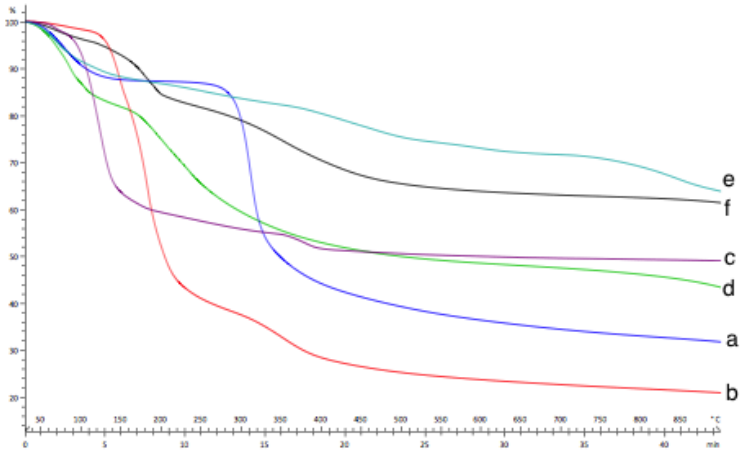

Fig. 4: TGA Curves for CS (A), CS-G-MA (B), and CS-G-MA Reacts with Mg^{2+} (C), Na^+ (D), K^+ (E), Ca^{2+} (F)

For grafted chitosan react with metal, initial degradation temperature decreased. CS-g-MA react with Na^+ showed that the IDT was 80 ^oC. IDT for CS-g-MA react with Mg^{2+} was 122 ^oC. Then, IDT for CS-g-MA react with Ca^{2+} was 180 ^oC. IDT for CS-g-MA react with K^+ was 74 ^oC. Based on results obtained, the thermal stability of grafted chitosan was decreased after reaction with metals ion.

3.5. Scanning electron microscope (SEM)

The scanning electron micrograph of chitosan, grafted chitosan and after react with metals is show in Figure 5 respectively. The grafted chitosan modified the surface of chitosan significantly and making it useful for reaction with metal. It was clearly seen that the fibrous nature of chitosan was modified after grafting [15]. SEM image of chitosan was smooth and no pores or semi-pores on the surface. Because of strong interactions between chitosan and maleic acid, SEM image of grafted chitosan showed rocks like structure, which provides larger surface area for better adsorption. The structure existed of small pores and indicated for better solubility. SEM image of grafted chitosan react with Na^+, Mg^{2+}, Ca^{2+} and K^+ are modified the image of grafted chitosan and the surface morphology changed dramatically. Reaction of the grafted chitosan with Na^+ changed to needle like structure. For reaction with K^+, the structure looked porous. Reaction with Ca^{2+}, the surface look strong with irregular structure and reaction with Mg^{2+} changed the structure to not uniform. These proved that metal was reacted with the grafted chitosan and the fibrous nature of chitosan was totally modified when it was chemically modified [15].

4. Conclusion

Chitosan (CS) was successfully grafted with maleic acid (MA) in the presence of potassium persulfate as an initiator. The grafting yield (GY) up to 84.25 % and grafting efficiency (GE) of 64.82 % were achieved. The grafting of chitosan and reaction of grafted chitosan with metals were strongly confirmed by FTIR. The morphological structure by SEM revealed that the grafted chitosan has improved solubility and fractured structure. Reaction of grafted chitosan with metals Na^+, K^+, Ca^{2+} and Mg^{2+} also modified the structure of grafted chitosan. Crystannility and thermal stability of the chitosan decreased after grafted and also when the grafted chitosan react with metals. Reactions of grafted chitosan with metals were successfully.

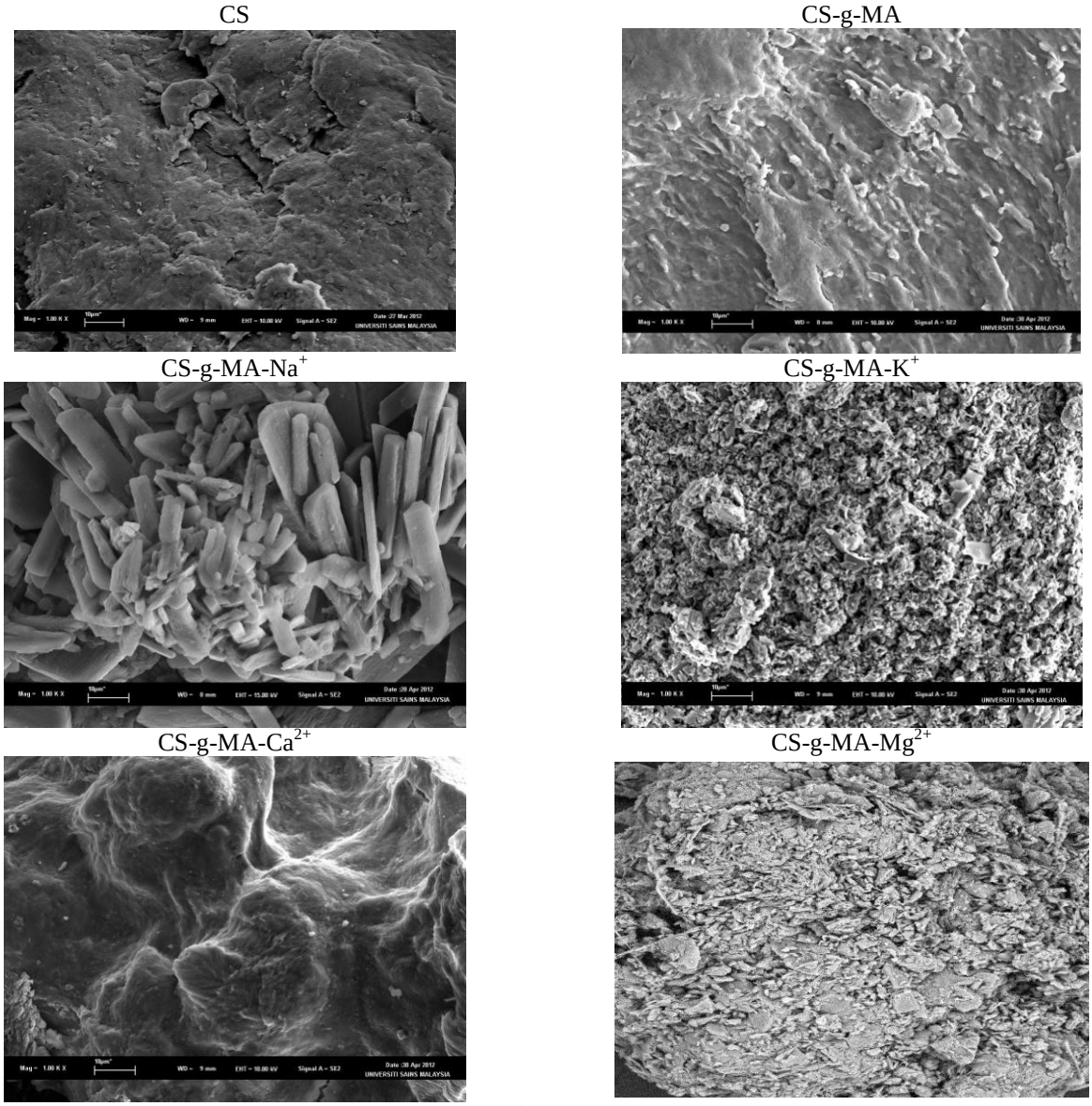

Fig. 5: Scanning Electron Micrographs of the Pure CS, CS-G-MA and CS-G-MA-Metals.

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