

Thermal Decomposition of Cellulose/Synthetic Polymer Blends Containing Grafted Products.

V. Cellulose/Polystyrene Blends

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ABSTRACT: Homogeneous grafting of styrene onto cellulose was carried out in a dimethylacetamide/lithium chloride solvent system. The grafted products were added to cellulose/polystyrene (PS) blends as compatibilizers. The thermal decomposition behavior of the blends was investigated by thermogravimetry. The thermal stability of the blends decreased with an increase in grafted product content. The crystallinity of the blends decreased with grafted product content. The microphase-separated structures of the blends became finer with grafted product con-

tent. The glass transition temperatures for cellulose and PS in the blends were lowered with grafted product content. Differences in thermal decomposition behavior of the blends were correlated with compatibility. Thermogravimetry was effective for compatibility estimation in cellulose/PS blends containing grafted products. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2482–2487, 2010

Key words: thermal decomposition; cellulosic blends; compatibilizer; glass transition temperature; crystallinity

INTRODUCTION

Compatibility in polymer blends can be estimated from their glass transition temperatures, T_g .^{1–3} However, cellulose does not undergo a clear glass transition because of its hydrogen bonding ability. The difficulty in determining T_g for cellulosic blends has been reported.^{4–13} In a series of our previous work,^{5–8} the thermal decomposition behavior of the cellulosic blends containing compatibilizers was investigated. Differences in thermal stability of the blends were correlated with compatibility. We indicated the effectiveness of thermogravimetry for compatibility estimation in cellulosic blends.

It is necessary to investigate the thermal decomposition behavior of different cellulosic blends in order to correlate thermal stability with compatibility more precisely. In grafting, a graft copolymer and attendant homopolymer are synthesized simultaneously. A part of cellulose not participated in grafting remains. The difficulties for isolating cellulosic graft copolymers are well known.^{14,15} Thus we used the grafted products themselves as compatibilizers to vary the

graft copolymer content widely. In this work, styrene grafted cellulose products were added to the cellulose/polystyrene (PS) blends as compatibilizers.

EXPERIMENTAL

Grafting and sample preparation

Dimethyl sulfoxide (DMSO) containing paraformaldehyde has been used as a solvent for cellulose in our previous work.^{4–8,16–19} In this work, a dimethylacetamide (DMAc)/lithium chloride (LiCl) solvent system was used because of an insolubility of PS in DMSO. The homogeneous grafting of styrene onto cellulose in a DMAc/LiCl solvent system and characterization of the grafted products were performed similarly by the method described previously.^{16–20} The grafted products are characterized in Table I. It is presumed that, in homogeneous grafting, the molecular weight of the graft polymer is equal to that of the attendant homopolymer.^{14,15} Viscosity-average molecular weights, M_v , of the extracted PS thus were used as those of the graft polymers. M_v of cellulose and PS used for the blends were determined to be 146×10^3 and 195×10^3 from the intrinsic viscosity obtained with cadoxen²¹ at 20°C and toluene²² at 25°C, respectively.

The crude grafted products, DMAc/LiCl solution of cellulose, and DMAc solution of PS were blended to give proper ratios. The blends were cast onto

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TABLE I
Characterization of Grafted Products^a

Sample code	PS content/wt %			$M_v \times 10^{-3}$ of graft ^b	Number of grafts
	Overall	Graft polymer	Homopolymer		
g-PS 1	26.2	0.5	25.7	9.0	0.11
g-PS 2	48.2	3.2	45.0	2.0	2.0
g-PS 3	54.2	6.0	48.2	4.5	1.7

^a Viscosity-average molecular weight (M_v) of main chain cellulose is 146×10^3 .

^b M_v of the extracted PS homopolymer was used as that of the graft polymer.

glass plates at room temperature and dried at about 40°C under reduced pressure for 24 h. After being immersed in water for several days, the films were easily peeled off, air dried on filter papers at room temperature, and stored in a desiccator until use.

Measurements

A SEIKO SSC5000TA with a TG/DTA300 module was used for thermal decomposition measurements. The samples (ca. 20 mg) were preheated to 150°C at a heating rate of 10°C/min under nitrogen flow at 100 mL/min to evaporate adsorbed water. Measurements were carried out from room temperature to 600°C under the above conditions.

Wide angle X-ray diffraction profiles were obtained for film specimens using a RIGAKU RINT3100SK diffractometer.

A Hitachi HU-11A transmission electron microscope (TEM) was used to observe microphase-separated structures. The samples were stained with osmic acid vapor for 24 h. The copolymer of *n*-butyl methacrylate and methyl methacrylate was used as an embedding medium. The embedded samples were cut into ultrathin sections of 50 nm thickness.

A SEIKO SDM5600H with a DMS200 module was used for dynamic mechanical measurements from -100 to 300°C at a frequency of 10 Hz, at a heating rate of 2°C/min. The samples (ca. $30 \times 6 \times 0.02$ mm³) were dried at about 40°C under reduced pressure for more than 24 h before use.

RESULTS AND DISCUSSION

Figure 1(a) indicates the thermogravimetric (TG) curves of the grafted product (g-PS 2) and cellulose (Cell)/PS (9/1) blends containing different amounts of g-PS 2. The weight of cellulose/g-PS 2/PS (9/0/1) blend without g-PS 2 decreases sharply at around 300°C and the second decrease occurs at around 430°C, indicating the presence of two thermal decomposition processes. As indicated previously,^{4-8,23,24} the weight decrease at around 300°C results from the decomposition of cellulose. The decomposition at around 430°C, thus, is assigned to that of PS. With an increase in grafted product content, the decomposition of cellulose and PS takes place at lower temperatures and become gently. The weight of g-PS 2 decreases at around

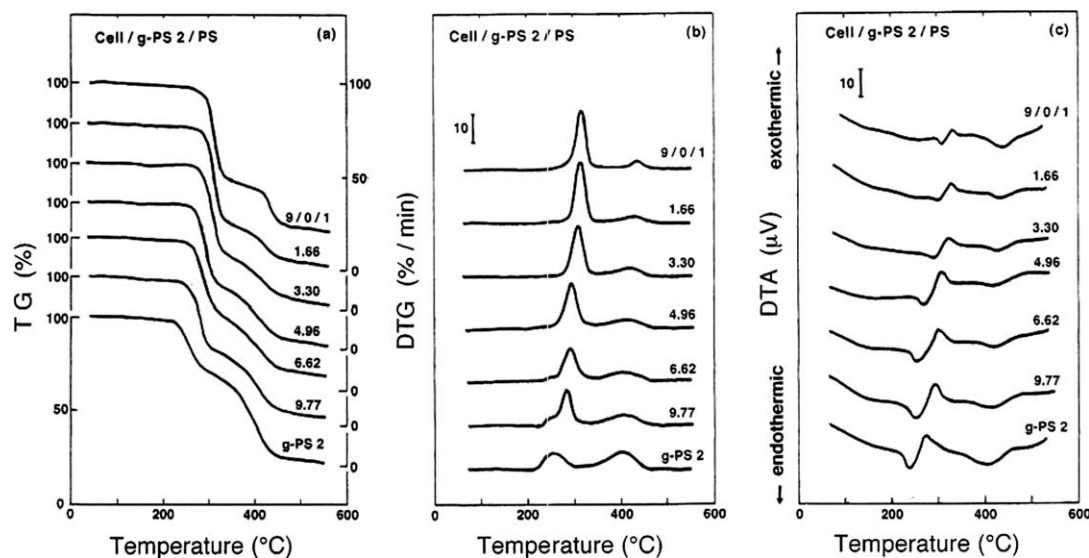


Figure 1 Thermograms of grafted product (g-PS 2) and Cell/PS (9/1) blends containing g-PS 2: (a) thermogravimetric (TG) curves; (b) derivative thermogravimetric (DTG) curves; (c) differential thermal analysis (DTA) curves.

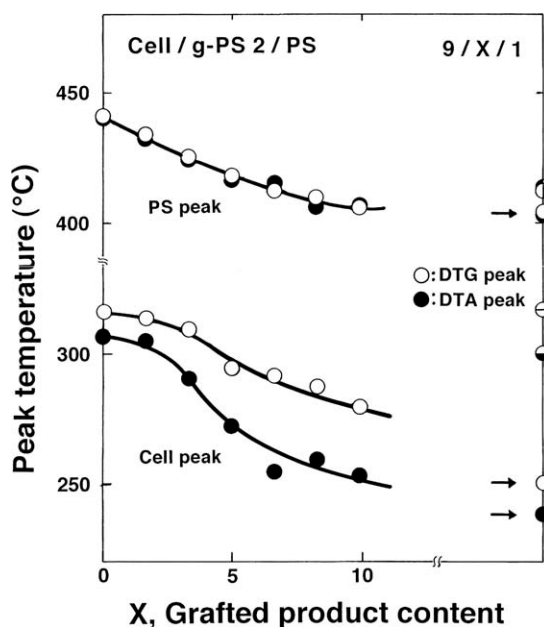


Figure 2 Dependence of DTG and DTA peak temperatures for Cell/PS (9/1) blends on g-PS 2 content: (○, ●) PS; (⊖, ⊙) cellulose.

220°C and then gradually over the temperature range 300–400°C.

Differences in thermal decomposition behavior of the blends can be seen more clearly from the derivative thermogravimetric (DTG) curves in Figure 1(b). All samples indicate two peaks. As noted above, the peaks at lower and higher temperatures correspond to the decomposition of cellulose and PS, respectively. We use these peak temperatures as a measure of thermal stability. Both peaks shift to lower temperatures and become broad with an increase in grafted product content.

Figure 1(c) shows the differential thermal analysis (DTA) curves of the same samples. The endothermic peaks associated with the decomposition of cellulose and PS are observed. We can also use these peak temperatures as a measure of thermal stability. Both peaks shift to lower temperatures with the addition of g-PS 2, being consistent with the data shown in Figure 1(b). It is clear that the addition of grafted product makes the cellulose/PS blend thermally unstable.

The dependence of DTG and DTA peak temperatures on grafted product content is revealed in Figure 2. No difference in both peak temperatures for PS observed at higher temperatures is recognized. Both peak temperatures fall gradually with an increase in grafted product content. The peak temperatures for PS homopolymer and PS in g-PS 2 are observed at around 410°C but those for PS in (9/0/1) blend are at around 440°C, suggesting an increase in thermal stability of PS in the blend. In our previ-

ous work,^{5–8} the thermal stability of synthetic polymers, except for poly(hydroxyethyl methacrylate) (PHEMA),⁸ in the blends hardly depended on the grafted product content. It is of interest to note an increase in thermal stability of PS. The differences in thermal stability of PS in blends have been reported.^{25–27} In blends of PS with poly(vinyl chloride), the thermal stability of PS was increased.²⁵ In blends of PS with poly(ethylene glycol), on the contrary, the decomposition of PS was accelerated.²⁶ In blends of PS with poly(methyl methacrylate) (PMMA), no evidence of interaction in the decomposition of blends was indicated.²⁷ On the other hand, the difference in both peak temperatures for cellulose observed at lower temperatures is recognized. The DTG peak temperature is slightly higher than the DTA peak temperature. The dependence of both peak temperatures on grafted product content is similar to each other, but that of DTA peak temperature is slightly sensitive to an increase in grafted product content.

The amounts of g-PS 2 required to influence the thermal stability of cellulose/PS blends with different compositions are compared in Figure 3. The difference in the dependence of both DTA peak temperatures for cellulose and PS on grafted product content is not obvious, but the cellulose/PS (9/1) blend is slightly sensitive to the addition of g-PS 2. In our previous work,^{5–8} four synthetic polymers were blended with cellulose. The cellulose/synthetic polymer composition dependence of thermal stability differed with the synthetic polymers blended.

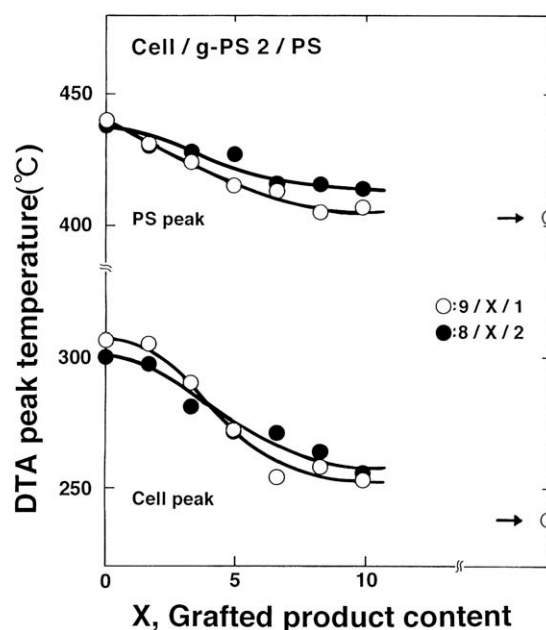


Figure 3 Dependence of DTA peak temperature for Cell/PS blends with different compositions on g-PS 2 content: (○) 9/X/1; (●) 8/X/2.

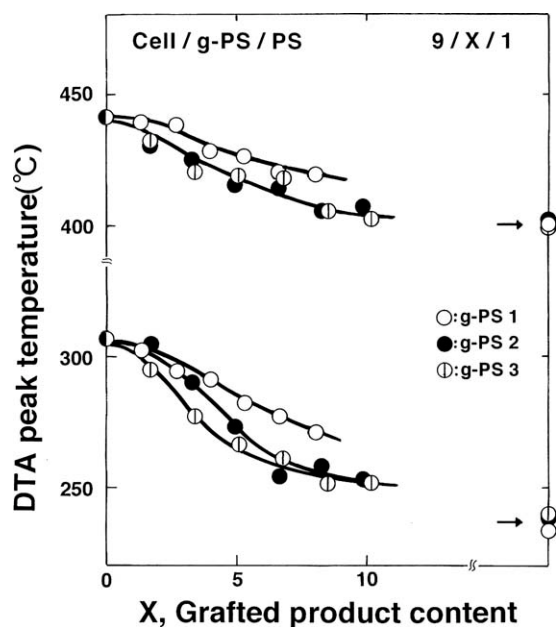


Figure 4 Dependence of DTA peak temperature for Cell/PS (9/1) blends containing different grafted products on grafted product content: (●) Cell/PS (9/1).

Two polymers, i.e., PMMA⁵ and poly(acrylonitrile),⁶ showed the same composition dependence as PS. However, in other cases, i.e., poly(methyl acrylate)⁷ and PHEMA,⁸ the blends with lower cellulose content were sensitive to the addition of grafted product. It is difficult to explain the difference in the dependence of thermal stability on the cellulose/synthetic polymer composition at the present stage.

Three kinds of grafted products were added to the cellulose/PS (9/1) blend. The dependence of DTA peak temperatures on the grafted product content is shown in Figure 4. The grafted product content dependence slightly varies with the grafted product. The addition of g-PS 3 is most effective of three grafted products. As characterized in Table I, the graft polymer content in g-PS 3 is highest of three grafted products but the grafting efficiency is 11% at the most. A comparison of these data with our previous work⁵⁻⁸ indicates that the amount of grafted product required to affect the thermal stability of cellulose/PS blends is largest of our results. In our work, the crude grafted products themselves were added to cellulose/synthetic polymer blends as compatibilizers. The grafted products contain cellulose, attendant homopolymer, and graft copolymer. It is inevitable that the grafted product with lower grafting efficiency, i.e., that with lower graft copolymer content, is less suitable for compatibilizer.

Figure 5 indicates the X-ray diffraction patterns of g-PS 2 and cellulose/PS (9/1) blends containing g-PS 2. The peak intensity at lower degrees decreases with an increase in grafted product content, suggesting a decrease in crystallinity. Thermal stability of cellulose

mainly depends on crystallinity.²⁸⁻³¹ It can be supposed that PS chains hinder the crystallization of cellulose chains to result in lower thermal stability of the blends.

Figure 6 shows TEM micrographs of g-PS 1 and cellulose/PS (8/2) blends containing g-PS 1. The dark domains indicate the cellulose phases stained with osmic acid. The microphase-separated structures of g-PS 1 are fine and interfaces between cellulose and PS domains are not clear. The microphase-separated structures of the blends become finer with the addition of g-PS 1. It is clear that the thermal stability of the blends with fine microphase-separated structures decreases. The low crystallinity and fine microphase-separated structure imply good compatibility of cellulose with PS in the blends. The thermal stability of the blends with good compatibility thus decreases remarkably.

A difficulty in determining T_g by differential scanning calorimetry (DSC) for cellulosic blends has been reported.⁴⁻¹³ In this work, DSC measurements were also performed. The glass transition at around 110°C for PS was observed but the dependence of T_g on grafted product content was not clear. Moreover, the glass transition at higher temperatures for cellulose was not recognized. Figure 7 indicates the temperature dependence of mechanical loss tangent for the cellulose/PS (9/1) blends containing g-PS 2. The (9/0/1) blend indicates three relaxation peaks. The peak at around -50°C is assigned to the relaxation

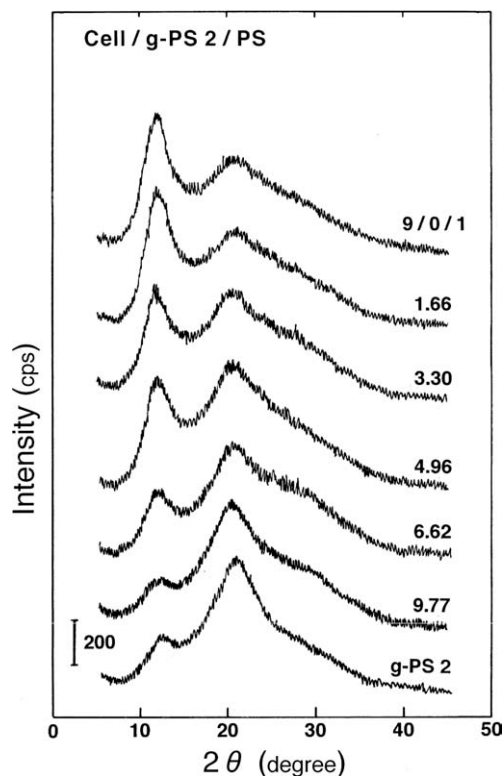


Figure 5 X-ray diffraction patterns of g-PS 2 and Cell/PS (9/1) blends containing g-PS 2.

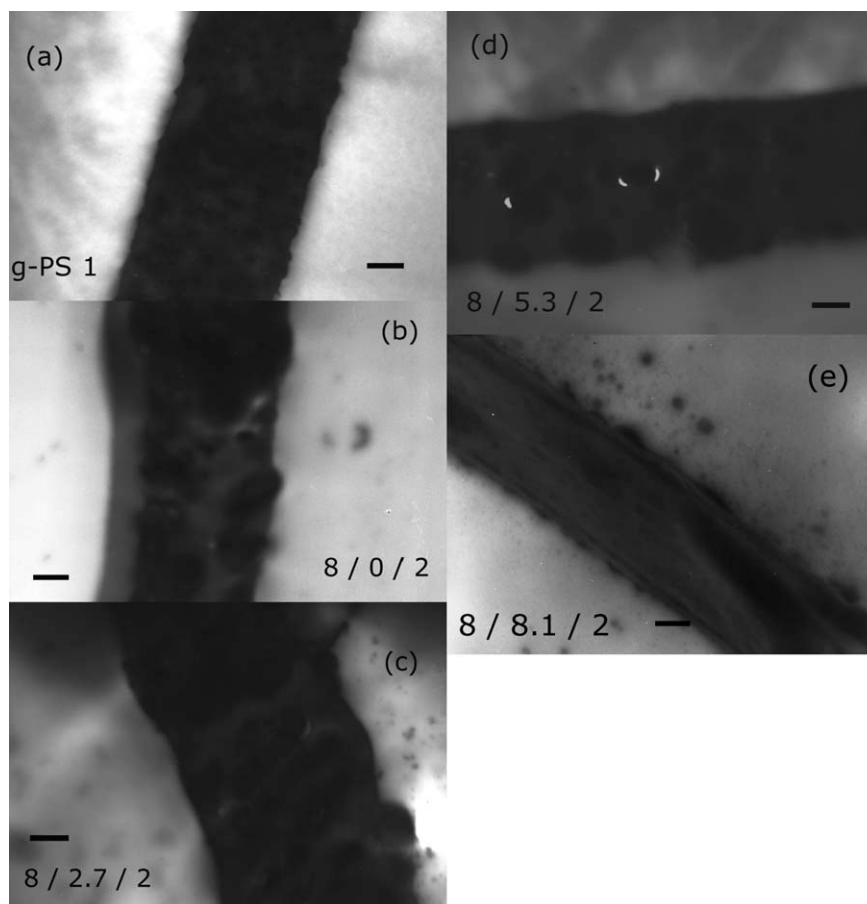


Figure 6 TEM micrographs of: (a) g-PS 1; (b) Cell/g-PS/PS (8/0/2); (c) Cell/g-PS/PS (8/8.1/2); (d) Cell/g-PS/PS (8/5.3/2); (e) Cell/g-PS/PS (8/8.1/2). Scale bar represents 2 μm .

caused by the motion of methylol groups in the glucose residues.^{32–35} The peaks at around 120 and 220°C correspond to the glass transition of PS and cellulose chains, respectively. With the addition of g-PS 2, both peaks at higher temperatures shift to lower temperatures. It is clear that the molecular motion of cellulose and PS chains is influenced by the addition of grafted product.

The dependence of the mechanical loss tangent peak temperatures on the grafted product content is revealed in Figure 8. Both peak temperatures for cellulose and PS are lowered with an increase in grafted product content. In our previous work,^{5–8} the peak temperatures for synthetic polymers shifted to higher temperatures with the addition of grafted products. It is difficult to explain the depression of peak temperature for PS at the present stage. A comparison of Figure 8 with Figure 2 shows that the dependence of both peak temperatures on the grafted product content is similar to each other. The changes in DTA peak temperatures, crystallinity, microphase-separated structures, and T_g are correspondent to each other. Therefore, the changes in thermal decomposition behavior of these blends are correlated with compatibility.

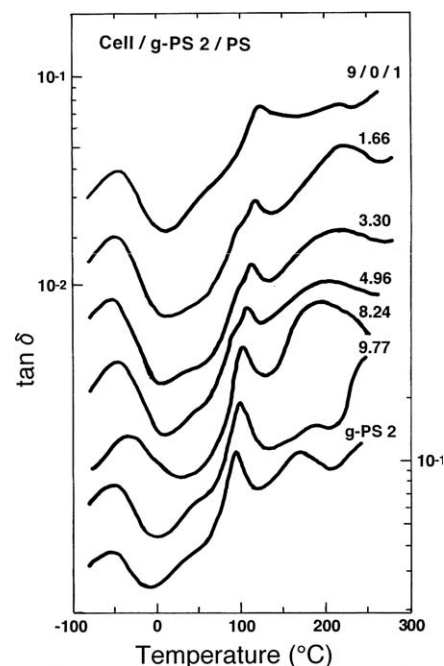


Figure 7 Temperature dependence of mechanical loss tangent for g-PS 2 and Cell/PS (9/1) blends containing g-PS 2.

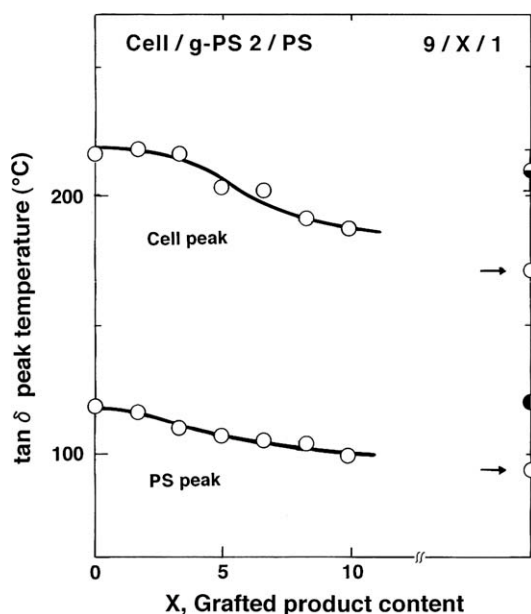


Figure 8 Dependence of mechanical loss tangent peak temperature for Cell/PS (9/1) blends on g-PS 2 content: (○) cellulose; (●) PS.

CONCLUSION

Styrene-grafted cellulose products were added to cellulose/PS blends as compatibilizers. The thermal decomposition behavior, crystallinity, microphase-separated structure, and T_g were investigated. Changes in thermal stability of the blends containing grafted products were correlated with compatibility. Thermogravimetry was found effective for compatibility estimation in cellulosic blends containing grafted products as compatibilizers.

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