

# Microstructure and Mechanical Properties Studies of Poly(vinyl alcohol)–Lead Salts Complexes

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## SYNOPSIS

Poly(vinyl alcohol) (PVA) was found to form complexes with  $\text{PbCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ , and  $\text{Pb}(\text{CH}_3\text{COO})_2$ . Different complex compositions were prepared by casting technique. Microdomains were observed in the case of the  $\text{PbCl}_2$ –PVA system. Complexes of  $\text{PbCl}_2$ –PVA system are semicrystalline over the entire composition range.  $\text{PbCl}_2$ –PVA complexes are stable to temperatures greater than  $350^\circ\text{C}$  in comparison to  $225^\circ\text{C}$  of pure PVA. The general features of the microdomains depends upon the temperature and the salt concentration. The hardness properties of the binary mixture were found to change in a nonlinear mode exhibiting a maximum value with the increase of the  $\text{PbCl}_2$  content and in a linear mode for the other salts. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Polymeric materials possessing good performance characteristics may be prepared not only via the synthesis of novel chemical compounds but also through processes of structural modifications. The introduction of ions into polymeric materials is a useful way to alter the supermolecular structure of polymers, and thus to produce various changes in chemical and physical properties.<sup>1</sup> The potential application of these materials in high density batteries,<sup>2</sup> in electrochemical display and sensors,<sup>3,4</sup> as flame retardants,<sup>5,6</sup> and as dehydrogenation catalysis,<sup>7</sup> has stimulated considerable investigations of fundamental factors governing the behavior of these systems. There are a number of studies on metal–polymer complexes. But, studies on ion-containing polymers have been mainly directed to structural and mechanical properties.<sup>8–13</sup>

In the present work we investigated complex formation between poly(vinyl alcohol) (PVA) and lead chloride ( $\text{PbCl}_2$ ), lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) and lead acetate ( $\text{Pb}(\text{CH}_3\text{COO})_2$ ). Structural investigations and hardness properties were carried out for com-

plexes prepared at different temperatures. Melting points of the pure PVA and its complexes were also measured.

## EXPERIMENTAL

PVA is a commercial material polymer obtained from BDH Limited (Polyox WSR-301,  $M_r$  approximately  $7.2 \times 10^4$ ) in powdered form. Lead salts were supplied by BDH chemical LTD (Poole, England).

Films were prepared by cast technique. To form films, a known weight of PVA was dissolved in distilled water, and the appropriate quantity of lead salt was also dissolved in the same solvent. The solutions were mixed and the mixture was stirred for several hours at room temperature, and then cast in flat glass petri dish. Films were dried in an air oven regulated at different temperatures. They were maintained at the specific temperature for several days, after which they could be peeled from the petri dish. The  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Pb}(\text{CH}_3\text{COO})_2$  complexes were colorless and those of  $\text{PbCl}_2$  were semitransparent. In general, the films were flexible. However, excess salts (more than 10 wt %) tended to make the polymer complex films brittle.

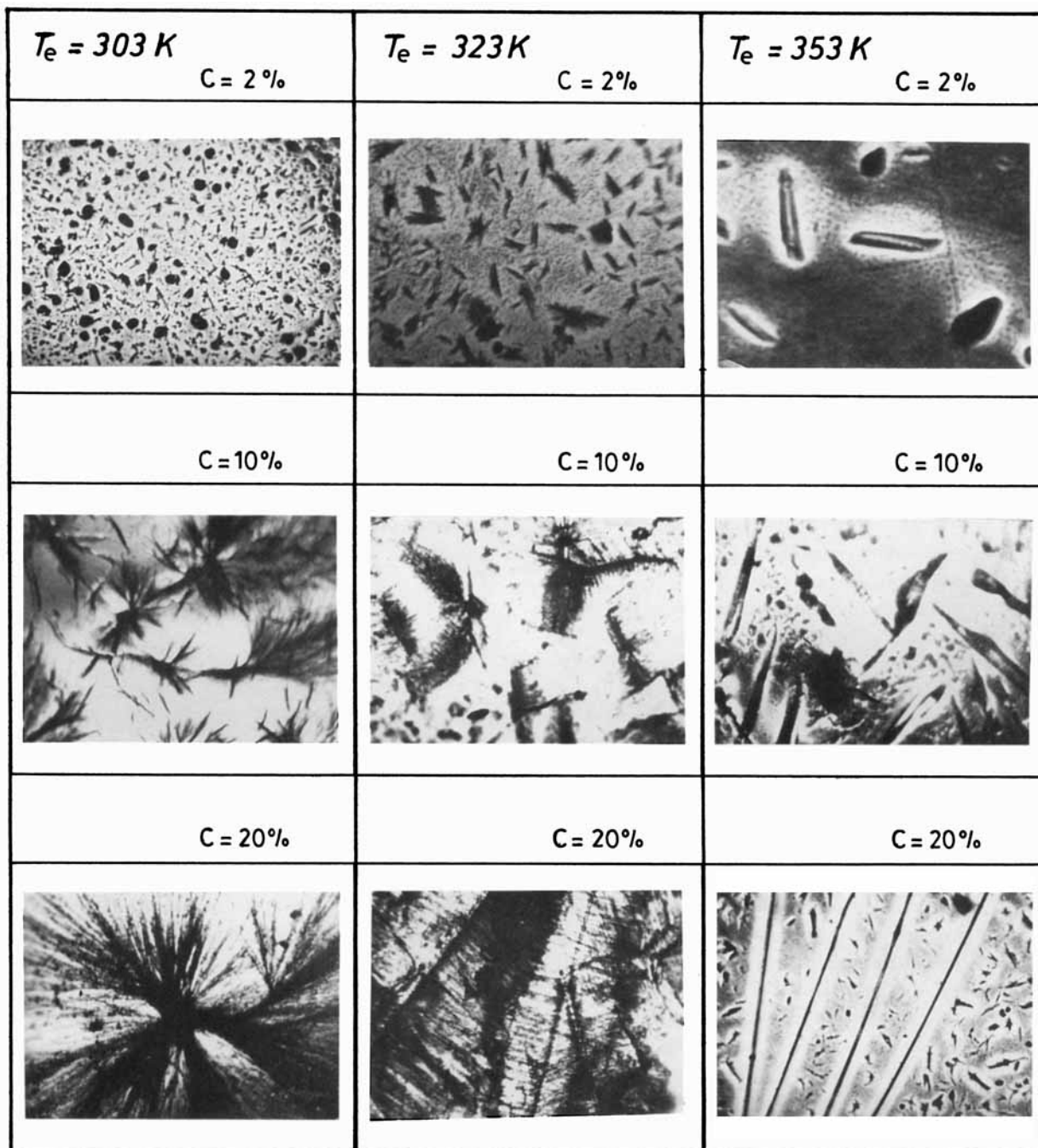
Surface morphology was examined using a polarized Zeiss Laboval 4 Optical Microscope. The wide

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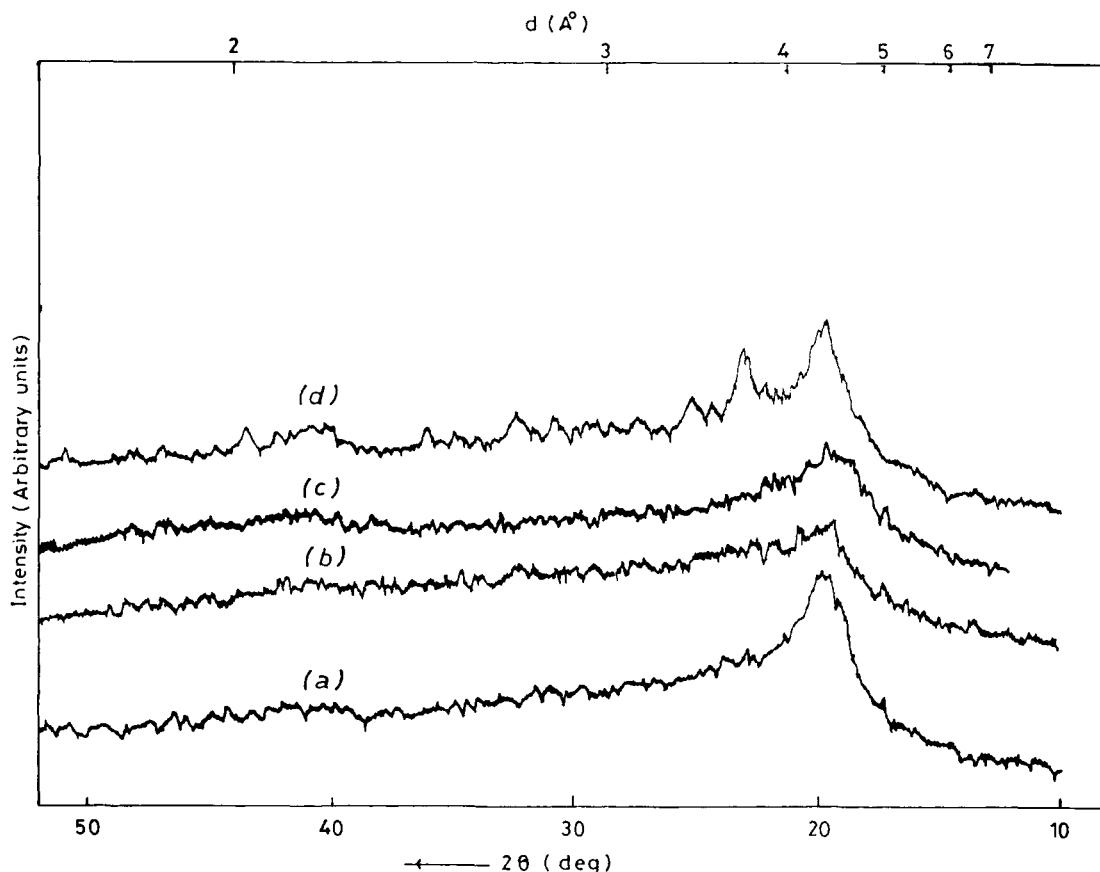
angle X-ray diffractions (WAXD) were recorded using a Philips PW 1729 X-ray diffraction instrument.

Microhardness investigations were carried using a Vicker tester adopted with a square-pyramidal diamond indenter. The microhardness value (MH)

was derived from the residual projected area of indentation according to  $MH = KP/d^2$ ,  $d$  being the length of the impression diagonal,  $P$  the contact load applied, and  $K$  a factor equal to 1.854. A loading cycle of 0.1 min was used. Loads of 0.5 and 1 N were employed to eliminate the instant elastic contribu-



**Figure 1** Polarized light micrographs represents the formation stages of microdomains grown in PVA-PbCl<sub>2</sub> complexes prepared at different evaporation temperatures ( $T_e$ ) and different PbCl<sub>2</sub> content ( $C$ ).



**Figure 2** X-ray diffraction patterns of: (a) pure PVA, (b) 5 wt %,  $\text{Pb}(\text{NO}_3)_2$ -PVA, (c) 5 wt %  $\text{Pb}(\text{CH}_3\text{COO})_2$ -PVA, and (d) 5 wt %  $\text{PbCl}_2$ -PVA complexes at 303 K.

tion. About 10 indentations were made on the surface of about  $0.25 \text{ cm}^2$  area to characterize the value of MH. The accuracy of MH is believed to lie within 1%.

## RESULTS AND DISCUSSION

### Surface Morphology and Microstructure

Films formed from PVA blended with  $\text{Pb}(\text{NO}_3)_2$  or  $\text{Pb}(\text{CH}_3\text{COO})_2$  were colorless, transparent, and optically homogenous as observed by optical microscope. Complexes of PVA with  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Pb}(\text{CH}_3\text{COO})_2$  salts of weight percentage ranging from 1 to 10 yielded flexible and easily processed films. The formation of such homogeneous solid solutions indicates extremely high compatibility of PVA with both  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Pb}(\text{CH}_3\text{COO})_2$ . Hence PVA seems to solvate the above mentioned salts. This solvated complex reduces interchain interaction of PVA. The surface morphology of  $\text{PbCl}_2$ -PVA complexes are clearly different from those

of PVA blended with both  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Pb}(\text{CH}_3\text{COO})_2$ .

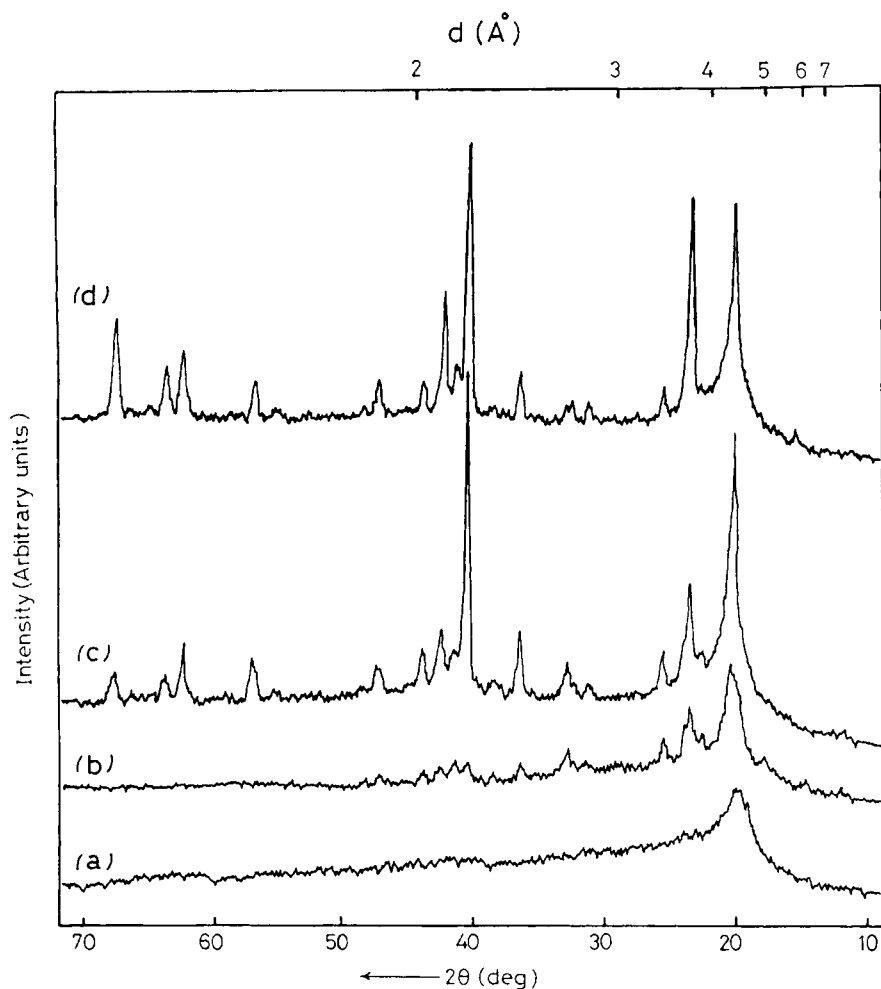
Optical microscopy (OM) examination of  $\text{PbCl}_2$ -PVA cast films substantiated multiphases as given in Figure 1. The general feature of the domains can be characterized by the existence of spherulites, clusters, and rod-like structures dispersed in the matrix of the complex film. It was revealed that the feature structures depend on both the salt concentration and the temperature of the solvent evaporation.

The domain structures in the PVA- $\text{PbCl}_2$  complex were found to be reversible, that is, they dissolved in hot water and grow again on the evaporation of the solvent.  $\text{PbCl}_2$ -PVA complex are not soluble in hot alcohol while  $\text{PbCl}_2$  itself is dissolved. Further, it was found that such domains could not be formed in using dimethyl sulfoxide (DMS), alcohol, and water-alcohol mixture. Hence, the random sequence structure may be due to the formation of short-random sequences of PVA, or simultaneously formed PVA and  $\text{Pb}^{2+}$  complexes.

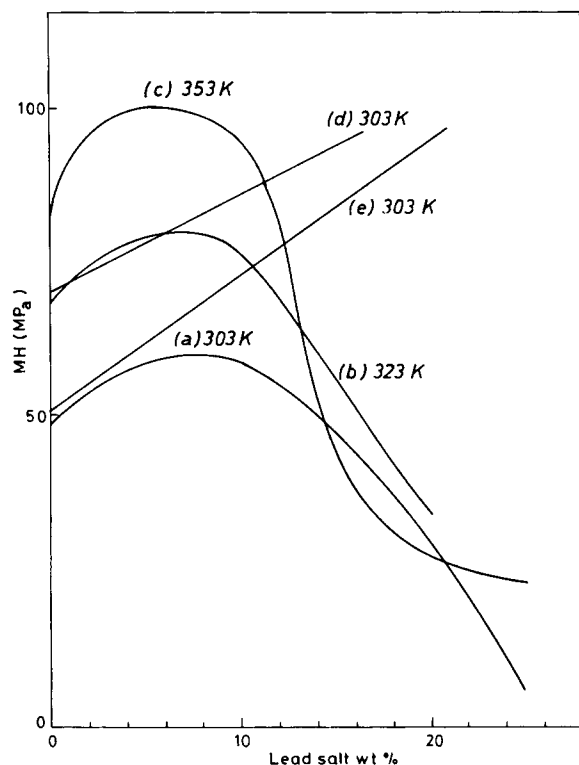
These observations are consistent with the WAXD results. No diffraction peaks but a large amorphous window as observed in the PVA, PVA-Pb(NO<sub>3</sub>)<sub>2</sub>, and PVA-Pb(CH<sub>3</sub>COO)<sub>2</sub> films, prepared at room temperature ( $T = 303$  K), as shown in Figure 2(a-c). On the other hand, a semicrystalline structure was observed in PVA-PbCl<sub>2</sub> complexes prepared at room temperature [see Fig. 2(d)]. It would appear that the presence of PbCl<sub>2</sub> salt in the polymer medium may effectively initiate the nucleation or the growth processes of the crystalline phases. PVA-PbCl<sub>2</sub> complexes prepared at evaporation temperatures, 353 K, for different PbCl<sub>2</sub> content [Fig. 3(a-d)], gave rise to a different crystalline bands due to better orientation. However, OM investigations showed that PVA polymer chains have the tendency for fiber formation at high prepared temperature. The rod-like structure could be caused

by transient cross-links of adjacent chains via the solvated cations that are coordinated to the oxygen atoms along the PVA chain. The higher degree of crystallinity is achieved by physical conditioning, that is hot drawing and heat treatment. Investigations revealed that the melting point of complexes formed from PVA and 5 wt % PbCl<sub>2</sub>, 5 wt % Pb(NO<sub>3</sub>)<sub>2</sub>, 5 wt % Pb(CH<sub>3</sub>COO)<sub>2</sub> are, respectively, 360, 370, and 395°C in comparison with 225°C of pure PVA.<sup>14</sup> It seems that nonflammability properties are imported to PVA by complexing with lead salts. Hence, PVA-lead salts complexes may be considered as flame retardants as in complexing PVA with other metals.<sup>6</sup>

OM and WAXD investigation revealed that the crystallization process in the PVA-PbCl<sub>2</sub> system can be visualized as a two stage process.<sup>15-20</sup> The primary process where the crystal growth leads to the for-



**Figure 3** X-ray diffraction patterns of: (a) pure PVA; (b) 5 wt %, (c) 10 wt % and (d) 25 wt % PbCl<sub>2</sub>-PVA complexes at 353 K.



**Figure 4** Dependence of MH on PVA-lead salts concentration for films prepared at different temperatures.

mation of spherulites and the secondary may include lamellar thickening, leading to the formation of rod-like structures. On the other hand, the surplus of the dopant  $\text{PbCl}_2$  crystallizes at the later time.

In conclusion, the complexes of PVA with  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Pb}(\text{CH}_3\text{COO})_2$  salts showed homogeneous, amorphous materials. On the other hand, PVA- $\text{PbCl}_2$  complexes resulted in a multiphase structure, in which crystalline PVA and amorphous PVA with dissolved  $\text{PbCl}_2$  salts resulted.

### Hardness Investigations

The fact that  $\text{PbCl}_2$ -PVA complexes are semicrystalline, containing both amorphous and crystalline regions, makes conventional the MH technique suitable for their study.<sup>21</sup> Figure 4 shows the dependence of the MH of lead salts-PVA complexes on the composition of the mixture. Clearly the physical structure of the complex is greatly influenced by the formation temperature and lead salt concentration. As shown in Figure 4(a-c), the higher the formation temperature, the greater is the MH of the PVA- $\text{PbCl}_2$  complexes. This may be due to the desorption

of the water molecules that act as plasticizers at room temperature. On the other hand, the MH increases from 1 to 5 wt % of  $\text{PbCl}_2$ , has a maximum in the range 5-10 wt %. This increase in MH might be connected with the rise in the number of tie molecules connecting the better oriented matrix. Further increase of  $\text{PbCl}_2$  content led to a drastic decrease of MH that reached a value less than that of pure PVA with 20 wt % content. The decrease in MH may be partially connected with the formation of salt aggregation. On the other hand, in the PVA- $\text{Pb}(\text{CH}_3\text{COO})_2$  and PVA- $\text{Pb}(\text{NO}_3)_2$  complexes [Fig. 4(d,e)], the MH linearly increases with the salt concentration increase.

This observation provides the variations in surface mechanical properties of PVA-lead salts complexes affected by changes in processing, heat treatment, and microstructure. Hence, the surface hardness reflects its response to the intermolecular forces holding the chains within the polymer matrix.

### CONCLUSIONS

Our investigations clearly demonstrate that PVA forms complexes with  $\text{PbCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ , and  $\text{Pb}(\text{CH}_3\text{COO})_2$ . The presence of crystallinity in the  $\text{PbCl}_2$ -PVA system was confirmed by a polarized microscope and X-ray diffraction. The microdomains in this system can take different structural forms. OM investigations revealed the presence of supermolecular structures (spherulites, clusters, rod-like) in complexes prepared at different evaporation temperatures. The hardness properties of the binary mixtures of PVA and lead salts were studied. The MHs of the surfaces were found to depend on salt type, salt content, and temperature of preparation. For PVA blended with both  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Pb}(\text{CH}_3\text{COO})_2$  the MH increases linearly as the salt concentration increases. On the other hand, in the PVA- $\text{PbCl}_2$  complex, the MH changed in a nonlinear mode, reached a maximum, and then decreased as the salt content increased.

Generally, the complexes of PVA with  $\text{PbCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Pb}(\text{CH}_3\text{COO})_2$  may represent a new family of ionic conductors. Investigations regarding conductivity behavior and the principal factors that determine their electronic structures and their electrical properties are in progress.

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