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Original Research Article

Optical properties of polymethyl methacrylate/polyvinyl chlorideblends

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ABSTRACT
We evaluated the optical parameters of doped polymer blends (PVC / PMMA). The energy gap (E_{opt}), absorption edge, optical permittivity, refractive index, constant B, $(n_0B)^{-1}$, and N/m* are composition-dependent. Increase the dopant concentration. The refractive index (n_0) was calculated in the range of 400 to 1000 nm and its linear or nonlinear behavior was also investigated with increasing Iodine content. The ratio of carrier concentration to the effective mass (N/m*) was evaluated.

1. Introduction

Polymer composites have grown steadily in importance over the past decade. The incorporation of transition metal salts into polyvinyl polymers, either pure or mixed in multiphase systems, can lead to large changes in various parameters of the polymers [1-3]. The study of the optical absorption spectra of solids provides important information about the band structure and energy gap of crystalline and amorphous materials. Analysis of the low-energy part of the absorption spectrum provides information about the vibrations of the atom, while the high-energy part of the spectrum provides information about the electronic state of the atoms.

The refractive index is an important parameter for the design of optical components such as prisms, windows, and optical fibers [4]. Polyaniline is used in light-emitting diodes in pure or doped form photovoltaic, sensors and supercapacitors [5]. Polyaniline is widely used as a research material due to the low cost of the monomer, ease of processing, and excellent stability [6, 7]. In transparent he studied conductive metal oxide thin films. Such transparent conductors are applied in a variety of active and passive electronic and optoelectronic devices [8], from aircraft windows to charge-coupled imaging devices [9]. Photoconductivity is one of the important classes of electro-optical properties of materials. Such studies are of interest because of the wide range of technical applications and the complexity of the phenomenon [10]. Sangwar and Mohari [11] studied the electrical, thermal, and optical band gaps of polypyrrole-filled PVC: PMMA thin films, using ammonium persulfate and p-toluenesulfonic acid as oxidants, Polypyrrole was prepared from pyrrole monomer by a chemical oxidation process, as a dopant.

Patel et al. [12] studied PVC/PMMA polymer blends were characterized by Fourier Transform Infrared Spectroscopy (FTIR), UV-VIS spectroscopy, and mechanical analysis. Ahmed [13] used a solution casting technique to create transparent films from (PMMA/PVAc) mixtures of different concentrations. To show the effect of UV radiation, we performed FTIR transmission spectra on the samples. In addition, absorbance measurements were taken at room temperature over the wavelength range 190-900 nm before and after exposure to UV and filtered radiation using a xenon arc lamp.

The work was extended to also include changes in the optical parameters such as band tail width and bandgap energy of the samples. In addition, refractive indices were calculated for samples from reflection and absorption spectra before and after exposure to UV and filtered radiation. The results indicated that no absorption minima are found in the visible wavelength range, indicating that all samples are colorless. Moreover, the increase in the refractive index values after 24 hours of exposure to UV light could be attributed to the increase in local density due to photo-induced cross-linking.

2. Objectives

The general theory of light absorption by amorphous semiconductors proposed by Mott et al. [14, 15] shows that

there are some Similarities between the energy band structure of crystalline and glassy non-metallic materials. Crystalline materials exhibit well-defined energy bands with sharp conduction and valence band edges. Glassy materials exhibit band-tailing into the normally forbidden gap [16].

Absorption at slightly higher energies (related to absorption coefficient $\alpha \geq 10^4$) can provide information about the combined density of states at the valence and conduction band edges. There are two types of optical transitions that can occur at edges in crystalline semiconductors, direct or indirect the theory of such transitions was advanced by Davis et. al [17] presentation. Both involve the interaction of electrons in the valence band with electromagnetic waves, facilitated across the fundamental gap to the conduction band.

For indirect transitions, however, there is also a simultaneous interaction with lattice vibrations. Therefore, an electron's wave vector can change during an optical transition, and the momentum change can be absorbed or emitted by the photon (radiation gives the electron negligible momentum). For amorphous materials, localized electronic states within the mobility gap are fundamentally considered. The matrix element $D(E)$ of the optical transitions between yes in different bands has the same value regardless of whether the initial states and the states are localized.

Furthermore, the density of states at the band edges is assumed to be a linear function of energy. Furthermore, transitions are unlikely if both the initial and final states are localized [17]. Mort et. al [15] have reported the general theory of optical absorption in amorphous semiconductors.

The optical absorption coefficient α(υ) at a frequency υ is given by

$$\alpha(\vartheta) = \frac{4\pi\sigma_{min}}{cn_0\Delta E}\frac{h\vartheta - E_{opt}}{h\vartheta}^{r}. \quad (1)$$

The reflectance [17] can be calculated using the equation given by

$$T = (1 - R)\exp(-A). \quad (2)$$

The relation between the optical dielectric constant ($\in'$) and the square of wavelength (λ^2) is given by [18, 19]

$$\in' = \in'_{\infty}\frac{e^2}{\pi c^2}\frac{N}{m^*}\lambda^2. \quad (3)$$

3. Materials and methods

Preparation of sample

The polyvinyl chloride (PVC) of standard grade product supplied by Polychem Industries Mumbai and polymethyl methacrylate (PMMA) supplied by Dental Product of India Ltd., Mumbai was used for the study. The two polymers PVC (1.5 g) and PMMA (0.5 g) were taken in the ratio of 3:1 by weight. The 1.5 g of PVC in 20 ml of tetra hydrofuran (THF) and 0.5 g of PMMA in 10 ml tetra hydrofuran were dissolved separately. After complete dissolution, the two solutions were mixed together. Iodine was added in weight percent to prepare the iodine-doped blend films, 0.2%, 0.4%, 0.6%, 0.8%, 1.0%. Each was dissolved in 5 ml of THF to prepare an iodine solution.

The iodine solution was later mixed with a homogeneous solution of PVC and PMMA. The total volume of solvent was kept constant at 35 ml. The solution was heated at a constant temperature of 333 K for 2 hours to completely dissolve the polymer and obtain a clear solution. A glass plate (15 cm × 15 cm) was used as a substrate and washed thoroughly with hot water and then with acetone.

To achieve perfect leveling and thickness uniformity of the film, the film was prepared on a thoroughly cleaned optically flat glass plate while floating in a mercury bath. The entire assembly was placed in a dust-free chamber maintained at a constant temperature (313 K). Thus, films were prepared by isothermal evaporation technique [22, 23]. The film was heated at a constant temperature of 323 K for 12 hours and at room temperature for another 12 hours to remove traces of solvent. Finally, the film was peeled off from the glass plate. It was cut into appropriately sized pieces and washed with ethyl alcohol to remove the surface contaminants.

Thickness Measurement

For increased accuracy and resolution, a compound microscope was used in combination with an accelerometer to measure minimum counts of 13 µm and 3.3 µm at the magnification of 1:10 and 1:100, was used. A small section of the sample was taken and mounted vertically to obtain a clear cross-section of the thickness. The thickness of the film used in this study is approximately 80 µm.

4. Results

The absorbance 'A' and transmittance 'T' of simple were measured at both normal incidence over the spectral range 400-1000 nm using a CART 2390 double beam auto scanning spectrophotometer (within the Regional Sophisticated Instrumentation Centre, Chennai) The 'A' and 'T' on doping rates of iodine thin films are shown in Figure 1 and Figure 2.

The results for the various optical properties listed in Table 1 and the iodine percentage are shown in Figure 3. The observed behavior indicates a forbidden direct transition for amorphous materials.

Similar behavior was reported by Tembhurkar et. al [24] and Deshmukh et. al [25] reported. The values of optical energy gap E_{opt} obtained from the extrapolation of the linear range and the constant B from the slope of the curve shown in Figure 3 are given in Table 1 respectively. Note that the value obtained by E_{opt} increases with ancestry from J_{od}. Similar behavior was reported by Deshmukh et. al [25] observed. The value of the absorption edge [24] is calculated from Figure 2 and summarized in Table l.

Note that the values obtained for the absorption edge increase with the dopant percentage.

Table 1: Variation of Optical energy gap (E_{opt}), absorption edge, infinitely high-frequency dielectric constant (ε'_∞), refractive index (n_0), Constant B, the ratio of carrier concentration to the effective mass (N/m*) for different samples.

Sample PVC+PMMA+ % of dopant iodine	(E_{opt}) eV	Absorption edge (eV)	ε'_∞	Refractive index (n_0)	Constant B (cm^{-2} eV)	(N/m*) cm^{-3}	$(n_0B)^{-1}$ (cm^2 eV^{-1})
A1 0.2%	1.23	1.22	13.05	2.88	1.16×10^4	0.49×10^{21}	29.77×10^{-6}
B1 0.4%	1.26	1.24	12.37	2.81	1.02×10^4	0.28×10^{21}	34.79×10^{-6}
C1 0.6%	1.28	1.27	16.01	3.19	1.55×10^4	0.48×10^{21}	20.07×10^{-6}
D1 0.8%	1.31	1.30	10.41	2.69	1.15×10^4	0.46×10^{21}	32.27×10^{-6}
E1 1%	1.33	1.34	9.96	2.57	0.17×10^4	0.32×10^{21}	22.22×10^{-6}

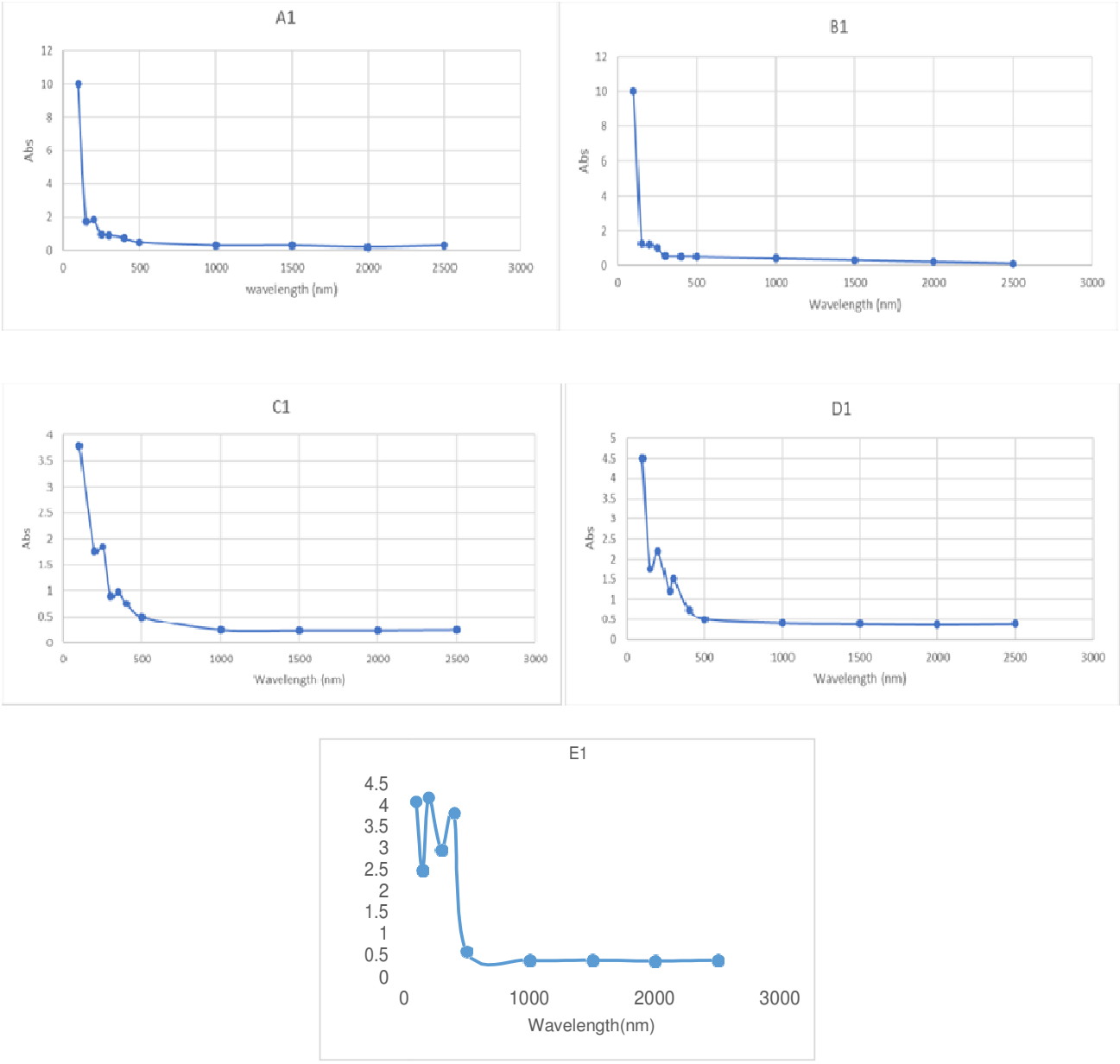

Figure 1: Absorbance spectra of iodine-doped film.

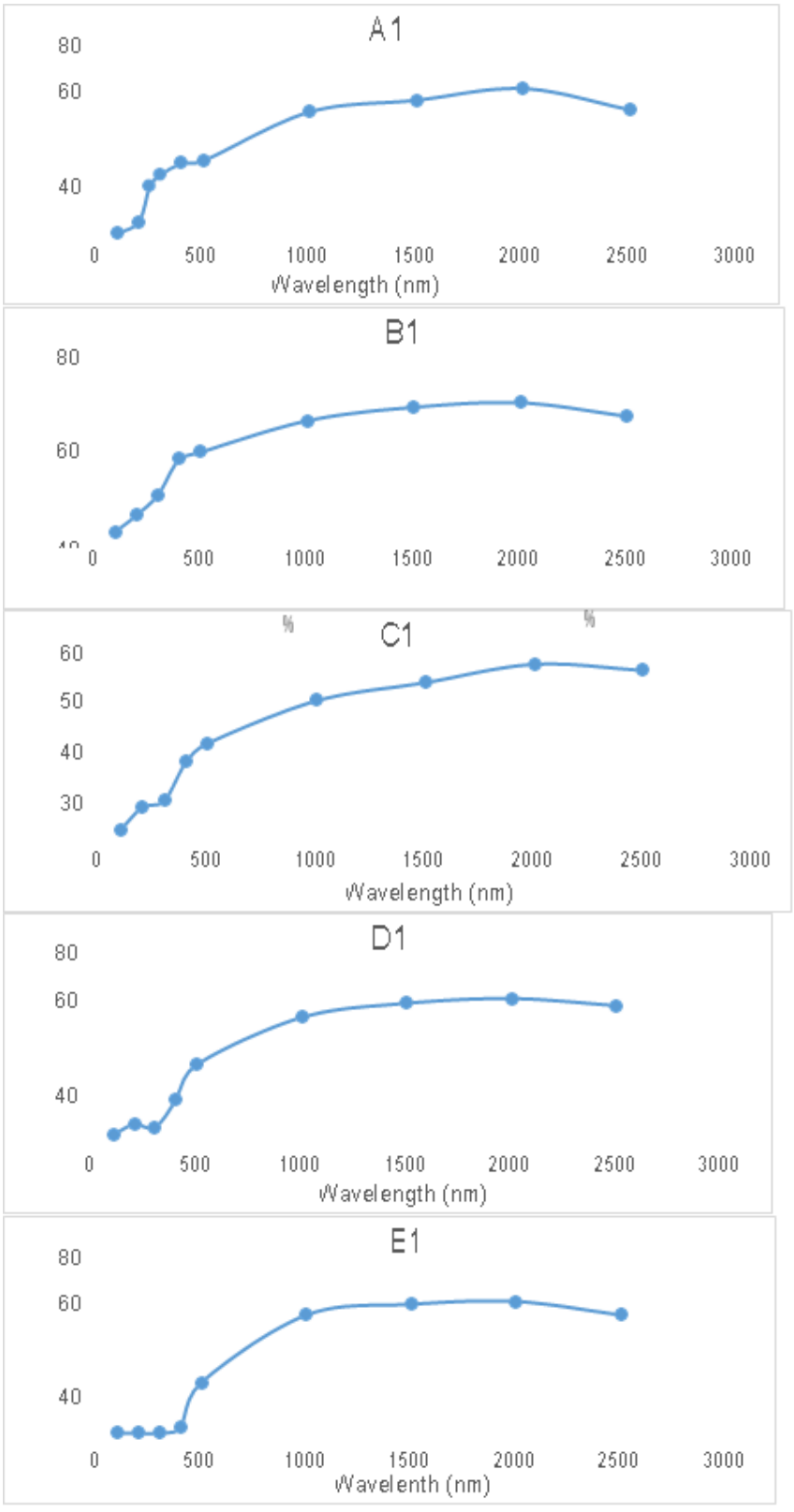

Figure 2: Transmittance spectra of iodine-doped films.

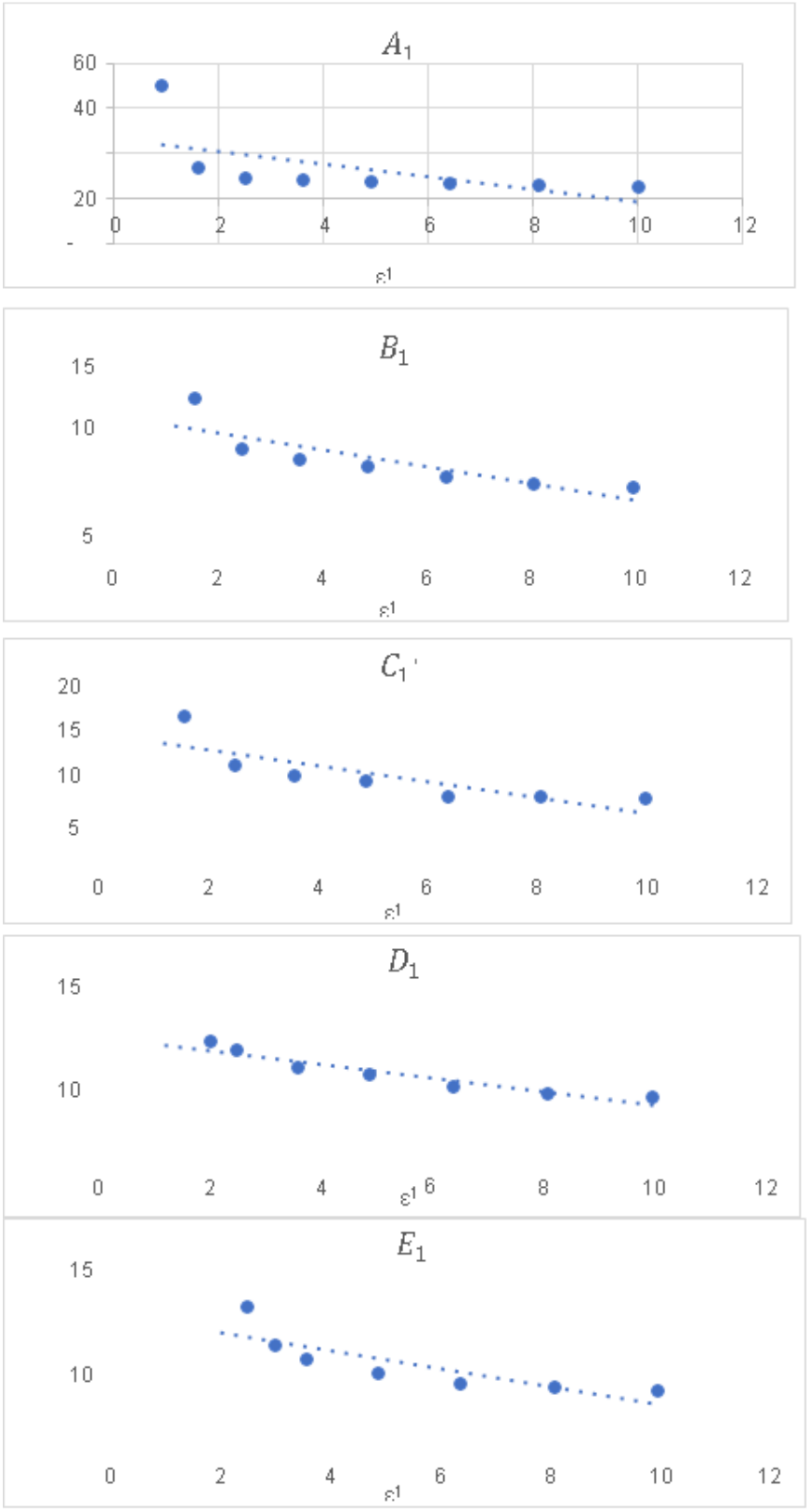

Figure 3: Variation of ε' versus $\lambda^2 \times 10$.

5. Discussions

The calculated value of $(n_0B)^{-1}$ is nonlinear. A similar observation was made in his $G_{20}Te_{80-x}Se_x$ thin films reported by Shokr et. al [26] and by Deshmukh et. al [25] was considered. A plot of permittivity $\in'$ versus λ^2 is shown in Figure 3 is linearity according to Equation 3 (effective mass carrier concentration) is shown in Table 1. Refractive index (n_0) and dielectric constant ($\in'$) values are nonlinear for all samples.

Such nonlinear behavior is observed in amorphous materials [25, 26]. The refractive index and optical permittivity are calculated over the wavelength range of 400 nm to 1000 nm. The refractive index values are nearly identical over the entire wavelength range (400 mm to 1000 nm). Therefore, the average value n_0 is given over this wavelength range.

The ratio of charge carrier concentration to the effective mass N/m* was calculated from the slope of the curve $\in'$ versus λ^2. Figure 3 is consistent with values reported by other workers [25-28].

6. Conclusions

It can be concluded that the evaluated optical parameters of doped polymer blends (PVC / PMMA doped with iodine) such as optical energy gap (E_{opt}), absorption edge optical dielectric constant, refractive index, constant B. $(n_0B)^{-1}$ and N/m* are found to be compositional dependent. The refractive index (n_0) (Calculated in the range 400 to 1000 nm) is found to be nonlinear with increasing content of iodine. The ratio of carrier concentration to the effective mass (N/m*) is found to be of the order of 10^{21} cm^{-1}.

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