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Structural and Optical Characterization of Rice-Husk-Derived SiO_2 Crystals-Reinforced Polyvinyl Alcohol Composites

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Abstract**—**The objective of this study was to investigate the optical properties of polyvinyl alcohol (PVA) and its prospective applications by adding crystalline silica which is usually used as a reinforcing agent. To do this, we synthesized and evaluated PVA-based composites reinforced with silica crystals, namely cristobalite, derived from rice husk. The experimental procedure involved the production of SiO_2 particles using rice husk precursors, which were subsequently subjected to calcination at a rate of 10 °C/min for a duration of 3 hours. This process primarily resulted in the formation of SiO_2 crystals in the cristobalite phase, according to X-ray diffraction (XRD). Following this, the crystals were incorporated into PVA via a casting technique, resulting in the formation of composite sheets. The SiO_2 contents in the composites were 0%, 2.5%, 5.0%, and 10%. XRD and Fourier-transform infrared spectroscopy (FTIR) techniques provided confirmation of the composites' successful synthesis, i.e., it did not yield any indications of chemical bonding between PVA and silicon dioxide (SiO_2), indicating that the interaction was limited to interfacial reactions. The incorporation of SiO_2 crystals resulted in a notable enhancement in UV-vis light absorption and a decrease in the optical band gap. Addition of 2.5%, and 10% SiO_2, for example, decreases the direct optical band gap of the composites form 5.37 eV, 5.19 eV, and 5.02 eV respectively, while the indirect band gaps of the samples were 4.44 eV, 4.84 eV, and 4.48 eV, correspondingly. These findings emphasize the efficacy of rice husk-derived SiO_2 crystals as both reinforcement agents and modifiers of optical properties in the polymer composites, showcasing their significant potential to modify the composite's structural and optical characteristics.

Keywords**—**Rice husk, crystalline SiO_2, PVA-based composites, structural characteristics, optical properties.

I. Introduction

THE use of agricultural byproducts in sophisticated material applications has gained considerable attention in recent years due to their availability, cost-effectiveness, and ecological advantages. Rice husks, which are a significant byproduct of rice milling, have been recognized as a valuable source of silica (SiO_2) [1], [2]. Rice husk silica can be converted into different crystalline structures, such as cristobalite, using carefully regulated thermal methods. PVA, a synthetic polymer renowned for its exceptional ability to form films, emulsify substances, and adhere to surfaces, presents a favorable framework for incorporating silica to improve its mechanical and optical attributes [3]. By incorporating biogenic silica into PVA, it is possible to create novel composite materials that possess enhanced characteristics, making them well-suited for both environmental and industrial uses.

The process of creating and examining SiO_2-reinforced PVA composites requires a thorough understanding of the interactions between the polymer matrix and the silica particles, and how these interactions impact the properties of the composites. Prior research has demonstrated that the inclusion of silica in polymer matrices can modify their physical characteristics, such as thermal stability, mechanical strength, and optical clarity [4], [5]. Nevertheless, the precise impact of silica generated from rice husk on the optical characteristics of PVA has not been thoroughly investigated. Investigating this approach could yield valuable knowledge on the development of sophisticated composite materials with customized characteristics for specific uses, such as in photonics, electronics, and barrier materials.

This study presents an analysis of the structure and optical properties of composites made from SiO_2 crystals generated from rice husks and reinforced with PVA. We examine the impact of changing the SiO_2 content in the PVA matrix on the structure and optical properties of the composite. Specifically, we focus on how these inclusions affect the absorption of UV-vis light and the energy of the band gap. This study seeks to clarify the interfacial interactions between SiO_2 and PVA and evaluate the potential of these composites for diverse technological applications using XRD, FTIR, and UV-Vis spectroscopy.

II. Materials and Methods

Preparation of SiO_2

Silicon dioxide (SiO_2) was obtained from rice husks using the sol-gel method described in previous studies [6]. At first, a mixture of 25 grams of rice husks and 250 ml of a 7% KOH solution was prepared. The mixture was then heated to a temperature of 300 °C and stirred manually for 30 minutes. Following the application of heat, the mixture was allowed to undergo precipitation at ambient temperature for the duration of the night. Afterwards, it was subjected to filtration in order to obtain a solution containing silicate. Around 100 ml of this solution underwent titration with a 10% HCl solution while being stirred at 400 rpm until a pH of 7 was reached, resulting

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in the formation of a SiO_2 gel. The gel underwent six rounds of washing using 500 ml of distilled water, followed by filtration to obtain a white gel. Subsequently, it was dried at a temperature of 100 °C. The dehydrated gel was crushed and filtered using a 600 mesh screen to obtain a fine SiO_2 precursor powder. The precursor was subjected to calcination at a temperature of 900 °C for a duration of 3 hours, resulting in the formation of crystalline SiO_2.

Preparation of PVA /SiO_2 Composites

The PVA/SiO_2 composite has been produced with particular attention to the concentrations of SiO_2. A solution was prepared by combining PVA and SiO_2 in deionized water in a beaker. The weight of SiO_2 was 2.5%, 5%, and 10% of the weight of PVA. The chosen range of concentrations was intended to thoroughly investigate the attributes of the composite. The mass-to-solvent ratio was kept at 1:10 to produce reliable outcomes. The mixture was then heated to a temperature of 125 °C and agitated at a speed of 700 revolutions per minute for one hour until it achieved a uniform consistency. Subsequently, it was poured onto a petri dish with a diameter of 7.9 cm and left to solidify at room temperature, resulting in the formation of composite sheets. The samples were designated as PSC-2.5%, PSC-5%, and PSC-10% to indicate different SiO_2 concentrations, whereas P was used for the pure PVA sample, ensuring obvious identification and facilitating straightforward comparison.

Characterizations

The identification of functional groups in the composite was performed using FTIR at a wavenumber range of 400-4000 cm^{-1}. The crystal structures were analyzed using XRD with CuKα radiation through a 2θ range of 5° to 65°. The XRD instrument was operated at 40 kV and 30 mA. UV-Vis Spectroscopy was employed to undertake photon absorption measurements within the range of 200–1050 nm, encompassing UV and visible wavelengths.

III. Results and Discussion

Fig. 1 displays a diffractogram illustrating samples of SiO_2, pure PVA, and composites of PVA/SiO_2. Using the search-mach approach, it was determined that the SiO_2 precursor in the calcinated dough at a temperature of 900 °C creates the cristobalite phase as the main phase, along with the tridymite phase. The presence of two phases is identified by distinct peaks at certain angles. The first phase is marked by a sharp peak at an angle of 2θ 21.83° (PDF No. 96-900-8228), while the second phase is characterized by peaks at an angle of 2θ 20.84° (PDF No. 96-901-3492), with each peak being the primary feature of its respective phase. Meanwhile, PVA has a semi-crystalline structure that is defined by a peak with high intensity but wide width, located at an angle of 19.68°, as observed in earlier studies [7]. An analysis of a PVA/SiO_2 composite sample using a diffractogram revealed alterations in the diffraction pattern when the SiO_2 levels were raised. Specifically, the presence of cristobalite and tridymite phases rose in proportion to the SiO_2 content, but no new phase development was seen. This demonstrates that the matrix and the filler only interact physically through the interface.

The indication that there was no chemical bonding between PVA and SiO_2 molecules is further clarified by the analysis of functional groups as shown in Fig. 2. The FTIR spectrum of the SiO_2 sample revealed absorption peaks at wavenumbers ~1060, ~800, and ~451 cm^{-1}, respectively associated with Si–O–Si asymmetric stretching, Si–O symmetric stretching, and Si–O rocking [9]-[11]. Meanwhile, the absorption peak at ~630 cm^{-1} originates from Si–O–Si bending, a characteristic feature indicating the presence of the tridymite phase as reported in previous studies [9]. Observations on the PVA sample showed a strong absorption band at ~3265 cm^{-1} indicating the presence of –OH groups on the PVA surface, suggesting significant intermolecular and intramolecular hydrogen bonding [7], [12], [13]. Absorption peaks at wavenumbers ~2937 and ~2909 cm^{-1} both indicate C–H asymmetric stretching, while the peak at ~2860 cm^{-1} shows C–H symmetrical stretching. The presence of C–H groups in the pure PVA sample is reinforced by the peaks at ~1416, ~1327, and ~833 cm^{-1}, respectively related to C–H bending, C–H deformation, and C–H rocking. Peaks at ~1708 and ~1658 cm^{-1} both indicate C=O stretching [4], [7], while peaks at ~1142 and ~1087 cm^{-1} show C–O stretching vibrations [14], and the peak at ~916 cm^{-1} indicates C–C stretching [7].

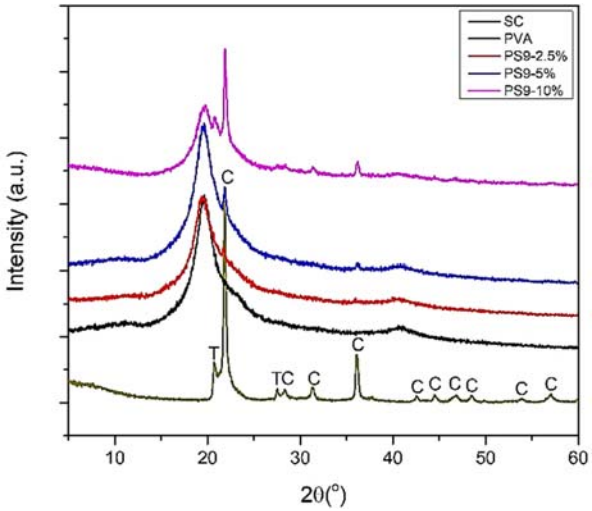

Fig. 1 XRD patterns of crystalline SiO_2, pure PVA, and PVA/SiO_2 composite, where T = tridymite, C = cristobalite

All detected functional groups are part of the PVA backbone structure. Observations of the FTIR spectrum on the PVA/SiO_2 composite sample showed no new absorption peaks. All peaks in the composite sample are derived from molecular vibrations present in both SiO_2 and PVA, confirming that only interfacial interactions occur between the functional groups on the surfaces of SiO_2 and PVA. Qualitative changes in the sample composition result in the weakening of absorption peaks related to hydroxyl groups, a consequence of the reduced concentration of hydroxyl-rich PVA. This phenomenon indirectly explains that more interactions occur between the hydroxyl groups on the PVA surface and the molecular groups in SiO_2 [13].

Fig. 3 shows the optical absorption spectra of pure PVA and the PVA/SiO_2 composites. The increase in SiO_2 concentration within the sample contributes to its absorption level. Absorption peaks observed in both pure PVA and the PVA/SiO^2 composites at wavelengths of 200-300 nm and 300-400 nm respectively indicate the occurrence of $\pi - \pi^*$ and $n - \pi^*$ electronic transitions. The increase in absorption values reflects enhanced interactions between photons and the composite sample due to the presence of SiO_2 particles incorporated into the PVA. The absorption spectrum also displays a sharp peak around the 200 nm wavelength, which is associated with the band gap energy of PVA [15]. Meanwhile, absorption in the visible light region (> 400 nm) tends to remain constant. The increase in absorbance in the composite sample is confirmed in the transmittance spectrum as shown in Fig. 4. According to this spectrum, photons at approximately 200 nm wavelength are nearly completely absorbed, and the extent of absorption increases with the concentration of SiO_2. The percentage of transmittance from the $\pi - \pi^*$ and $n - \pi^*$ electronic transitions of each sample is shown in Table I.

TABLE I
PERCENTAGE TRANSMITTANCE AT THE ELECTRONIC TRANSITION PEAKS $\pi - \pi^*$ AND $n - \pi^*$

Transition	P	PSC-2.5%	PSC-5%	PSC-10%
$\pi - \pi^*$	5.33%	2.53%	1.69%	1.29%
$n - \pi^*$	5.05%	2.85%	1.96%	1.59%

From the absorbance spectra as shown in Fig. 3, the direct bandgap energy, indirect bandgap energy, and Urbach energy were estimated using the absorption spectrum fitting (ASF) method and the values are presented in Table II.

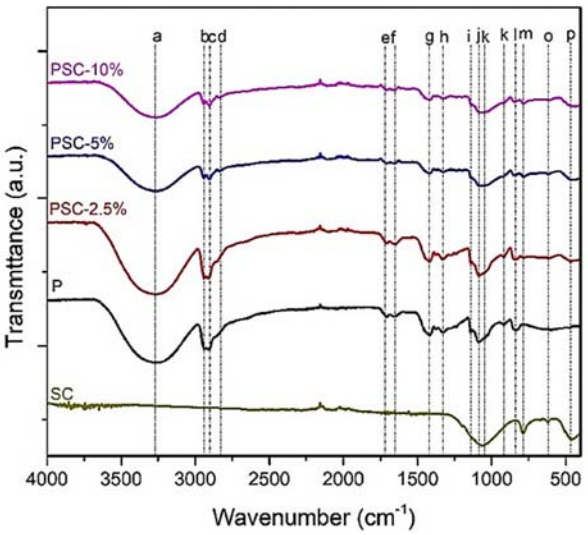

Fig. 2 FTIR spectrum of crystalline SiO_2, pure PVA, and PVA/SiO_2 composites

It is observed that the values of $E_{g(d)}$ and $E_{g(i)}$ representing the direct and indirect bandgap energies, respectively, slightly decrease as the concentration of SiO_2 increases. This reduction in bandgap energy can be associated with the formation of localized states within the bandgap and changes in the level of disorder within the PVA matrix due to interfacial interactions between SiO_2 particles and the -OH groups of the PVA matrix [13]. The change in the level of disorder is confirmed by investigating Urbach energy, which shows an increase in value. Higher Urbach energy indicates an increase in structural disorder within the composite. Urbach energy describes the width of the optical absorption tail located just below the forbidden bandgap and is related to localized states caused by irregularities and defects in the crystal structure. Therefore, a higher Urbach energy value indicates an increase in structural chaos or an increase in the number of defects within the material, which can affect its optical properties.

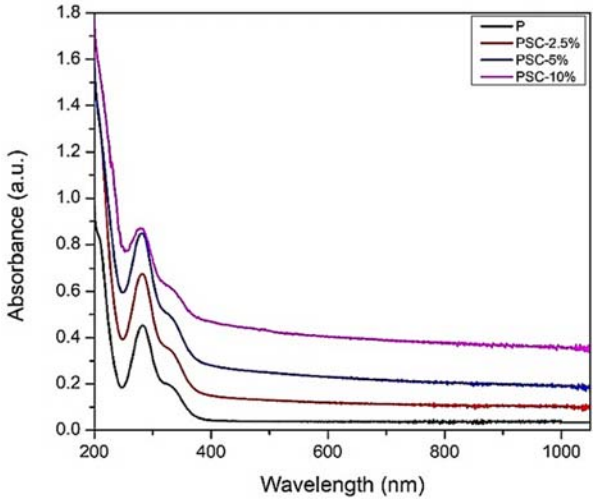

Fig. 3 Absorbance spectra of pure PVA and PVA/SiO_2 composites

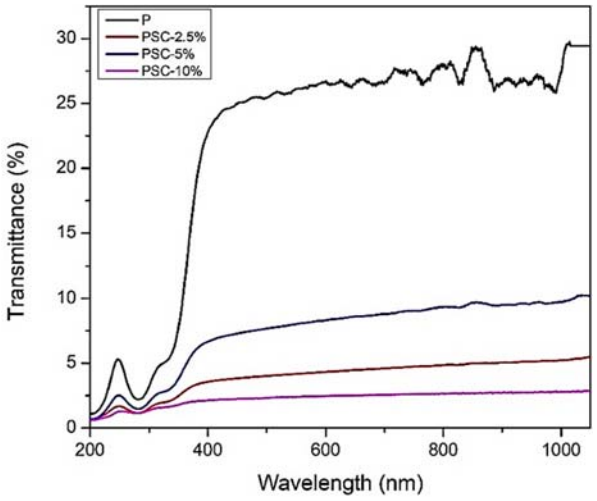

Fig. 4 Transmittance spectra of pure PVA and PVA/SiO_2 composites

TABLE II
DIRECT BAND GAP $E_{g(d)}$, INDIRECT BAND GAP $E_{g(i)}$, AND URBACH ENERGY E_u OF PURE PVA AND PVA/SiO_2 COMPOSITES

Sample	$E_{g(d)}$ (eV)	$E_{g(i)}$ (eV)	E_u (eV)
P	5.42	4.65	0.52
PSC-2.5%	5.37	4.44	0.65
PSC-5%	5.19	3.84	1.02
PSC-10%	5.02	3.48	1.36

IV. Conclusion

The present study thoroughly investigated the improvements in the structure and optical properties of PVA composites when they were strengthened with crystalline silica (SiO_2) obtained from rice husks. The results of our study reveal that the addition of SiO_2, specifically in the cristobalite form, greatly improves the ability of PVA composites to absorb UV-visible light. This is demonstrated by a noticeable decrease in both direct and indirect optical band gaps as the concentration of SiO_2 increases. The results highlight the effectiveness of SiO_2 produced from rice husk as a reinforcing agent and its crucial role in altering the optical characteristics of polymer composites. The interaction between SiO_2 particles and the PVA matrix was found to be solely physical, since no new chemical bonds were revealed in the FTIR spectra. This indicates that the observed changes in optical properties are a result of physical modifications rather than chemical ones. This attribute is crucial for applications that necessitate chemical stability. The improved optical characteristics, including decreased band gap energies and better absorption, enable the utilization of these composites in various applications such as photovoltaic devices and UV protective coatings

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