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Investigation of optical and electrical properties of Pyrrole-2-carboxyldehyde (PCL) in PVA polymer matrix

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ABSTRACT

In this work, we have investigated the optical and electrical properties of pyrrole-2-carboxyldehyde (PCL) dispersed in sodium dodecyl sulphate (SDS) micellar system and freezed in polyvinyl alcohol (PVA) polymer matrix. PVA polymer is chosen as hosting materials in the composite fabrication due to its vast applicability. The optical properties have been studied with the help of different spectroscopic techniques. The optical and electrical properties of trapped PCL were observed to be highly detectable even in solid form freezed in a polymer matrix. Our study shows that PCL in solid phase may be considered as the promising candidates for bio medical applications.

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1. Introduction

Pyrrole-2-carboxaldehyde (PCL) is a heterocyclic compound, which possesses broad biological and pharmacological activities [1,2]. It is also used for the enhancement of flavor [3] and serves as a medicine for curing many diseases [4]. The main problem associated with PCL is, its cytotoxic nature. Because of its cytotoxic nature we cannot directly introduce it in the human being body. To overcome this problem, normally we entrap the PCL in the micellar system above a “critical micellar concentration” (CMC). There are a number of micellar systems available for the encapsulation of ambiphilic and low solubility drugs [1,2]. Micelles are self-assembling colloidal nanosize particles a hydrophobic core and hydrophilic shell (Fig. 1). Their size is almost 10–100 nm. Different drugs in the micellar systems provide a number of advantages such as they improve the solubility of drugs and avoid its environmental degradation [5,6]. These micellar systems are used as a carrier for drugs so that it can be inserted into the human body without any harm. However, still a major disadvantage associated with micelles is their dynamic nature which causes instabilities at high temperature as well as lower concentrations [7]. Because of which there has been major interest mainly in the polymer micelles stabilisation.

The incorporation of organic molecules in different polymer films has a versatile importance in every field of research such as: biosensors, drug delivery, energy storage materials, gas sensors, and nonlinear optics [8]. Organic molecules freezed in a polymer matrix provide better optical, thermal, electrical, and mechanical properties than organic molecules in liquid or micellar phase.

The aim of the present study is to prepare PCL/SDS/PVA polymer films. The optical and electrical properties of polymer thin films in solid freezed is further studied. These optimized PCL/SDS/PVA polymer thin film may be utilized for drug delivery and evaluation of some technological applications.

2. Materials and methods

2.1. Materials

PCL, Tetrahydrofuran (THF), PVA were purchased from Sigma – Aldrich and used only after checking the purity fluorimetrically in the wavelength range of interest. Deionized water (Millipore) was used for solution preparation.

2.2. Apparatus

X-ray diffraction (XRD) patterns were recorded by “Bruker D8 Advance diffractometer with CuK α radiation source”. UV–Visible absorption spectra were recorded at 300 K by a “Perkin Elmer spectrophotometer (model Lambda-35) with a varying slit width in the

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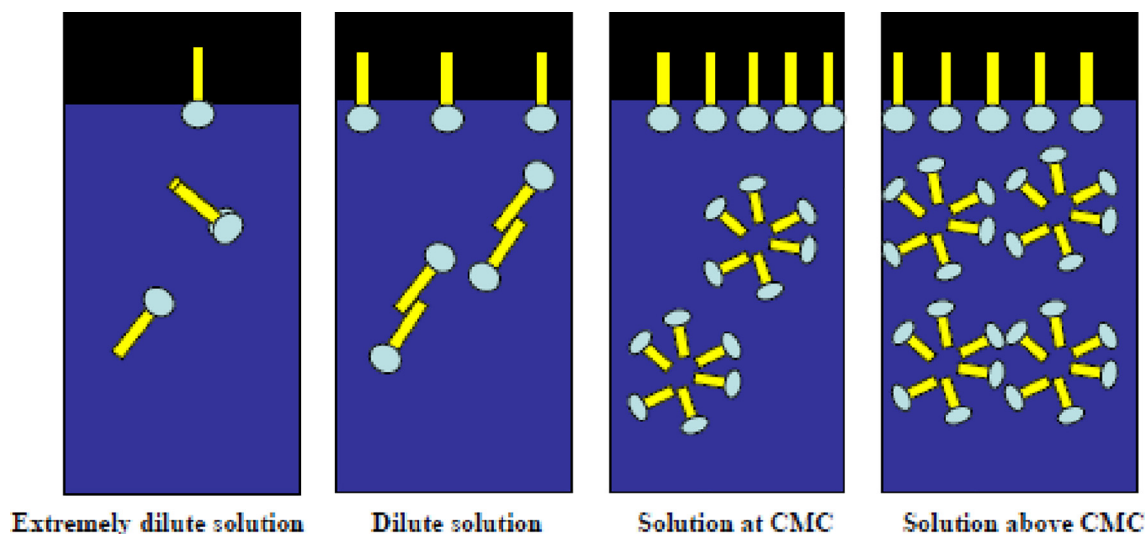


Fig. 1. Micelle formations above critical micellar concentration (CMC).

range 190–900 nm”. Luminescence measurement was made with a “Perkin Elmer spectrophotometer (Model Fluorescence-55) with a varying slit width (excitation slit = 10.0 nm and emission slit = 5 nm) ranging from 260 to 900 nm”. The Model “LS 55 Series uses a pulsed Xenon lamp as a source of excitation”. Deionized water (Millipore) was used for measuring absorption and emission spectra. To measure the spontaneous polarization properties of the polymer film, P-E loop Tracer (Marine India) was used. The dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of the PCL were measured in a wide frequency range (10 Hz–1 MHz) using LCR meter (Hioki 3522).

3. Synthesis of polymer film

For polymer film preparation, we have used deionised water as solvent. 1 gm of PVA polymer is mixed with 0.02 g of PCL and 0.02 g of SDS [9]. After mixing them properly, we have taken 30 ml of deionised water as a solvent and mixed the above mixture into it. Again mix it properly, and then keep the above solution at a temperature of 80 °C in oven for the time of 2 hrs. After that, stir the solution for 1 hr until the solution become completely transparent. Then remove the solution from the magnetic stirrer and pour it in the petadish and allow the solvent to evaporate completely and we can obtain the PVA/PCL/SDS polymer film (Fig. 2).

4. Result and discussion

4.1. X-Ray diffraction analysis

To determine the structure and size of the probe molecule or system X-Ray diffraction (XRD) analysis have been used. The XRD pattern of pure PCL, SDS and with PCL/SDS is shown in Fig. 3. We observe no change in the peak position or no new peak arises in the liquid phase when PCL and SDS were doped together (Fig. 3). The diffraction pattern of the pure PVA film shows a broad diffraction peak around $2\theta = 19.2^\circ$, which represent its semi crystalline nature (Fig. 4).

On adding SDS to the above polymer, film of PVA/PCL a shift was observed and no new peak arises. In PVA the peak was arising at 19.2° and on adding SDS and PCL, a red shift (19.5°) in peak position is observed (Fig. 4).

This shifting in peak shows that there is a chance that we can hold the micelle in the polymer film of PVA since it dissolved in

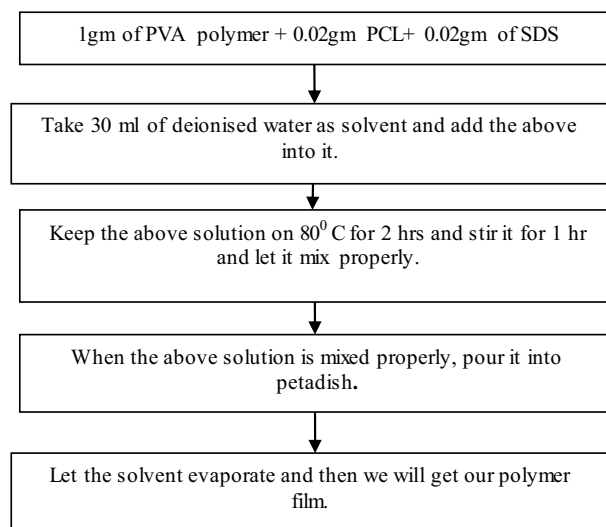


Fig. 2. Block diagram of synthesis of PCL/SDS/PVA polymer.

it properly. However to confirm this we have carried out different characterization as well.

4.2. UV-VIS absorption spectra

In order to check the suitability of PVA polymer to hold the micelle formation, we have performed UV-VIS Absorption within the range of 190 to 900 nm. Pure PVA film shows a single strong absorption with less intense peak at ~ 282 nm due to the presence of carboxylic $\geq C=O$ group (Fig. 5). On comparing PVA polymer film spectra with PVA polymer film with PCL, we observed no new peak arises. When we add SDS into it then the peak which was arising at 251 nm gets suppressed and the intensity of the peak at 282 nm gets enhanced on adding SDS into PCL.

4.3. Photo luminescence analysis

PCL shows intramolecular proton transfer in excited state [10]. In the hydrocarbon medium, the molecule is free to move as if it is in a gaseous medium. In the hydroxyl medium there may be influence of external hydrogen bonding [11]. In the solid phase when

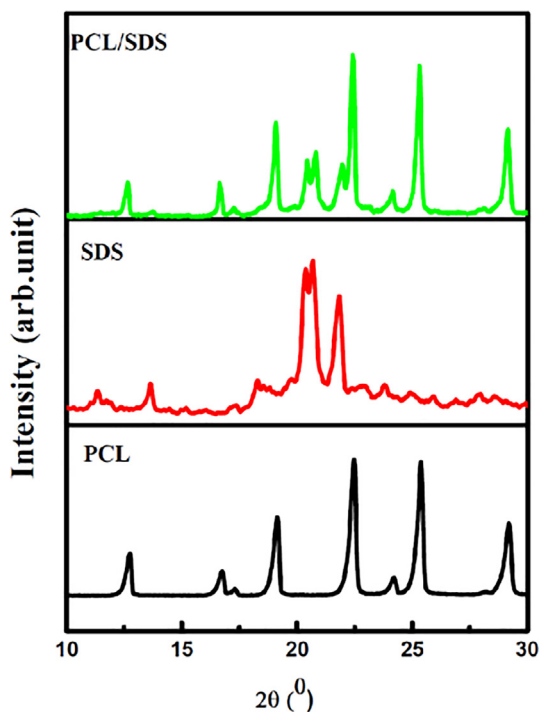


Fig. 3. X-ray diffraction graph of PCL, SDS, PCL/SDS in solid form.

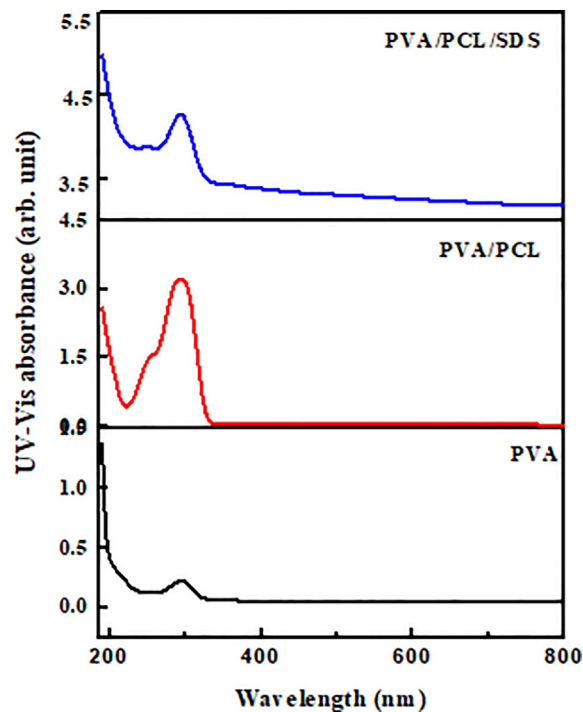


Fig. 5. UV-VIS absorbance graph of PVA, PVA/PCL and PVA/PCL/SDS.

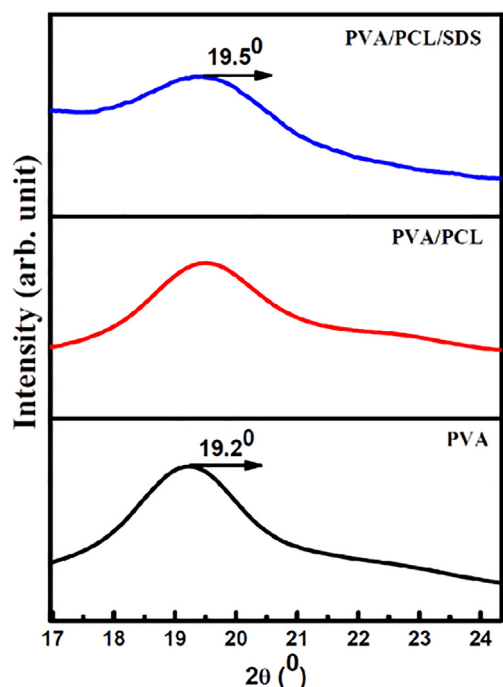


Fig. 4. X-ray diffraction graph of PVA, PVA/PCL, PCL/SDS/PVA polymer film.

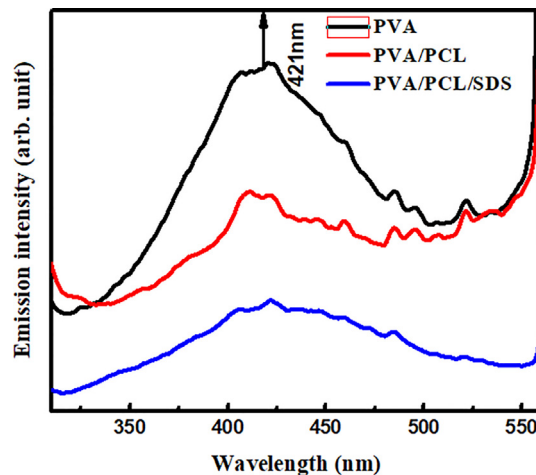


Fig. 6. Photoluminescence emission intensity vs. wavelength graph of PVA, PVA/PCL and PVA/PCL/SDS.

SDS broadening and decrement in the emission peak is observed. The above photo luminescence analysis clearly demonstrate the interaction of PCL with the SDS micellar system Figs. 7 and 8.

4.4. Dielectric analysis at room temperature

We have also done the dielectric analysis of composition PVA/PCL/SDS and calculate the frequency dependent dielectric constant (ϵ) and loss tangent ($\tan\delta$) in room temperature and varying frequency (10 Hz-1 MHz). It is observed that pure PVA, PVA/PCL, PVA/PCL/SDS shows a decreasing tendency in ϵ value with increasing frequency and reaches a constant value beyond a certain frequency [12]. However a certain increment is observed in the $\tan\delta$ value at higher frequency. PVA polymer shows a good value of dielectric constant. However, on the addition of PCL and SDS into

we added PCL and SDS in PVA polymer films certain changes were observed in the position and intensity value of the luminescence peaks. Photoluminescence spectra of pure PVA, PVA/PCL, PVA/PCL/SDS films are shown in Fig. 6. In case of pure PVA, we have observed a single strong and high intense luminescence peak at ~ 421 nm due to the presence of carboxylic ($\geq C=O$) group (Fig. 6). In the presence of PCL, PVA/PCL polymer film shows no new emission, but the decrement of existing emission intensity with a little broadening in emission (Fig. 6). With the addition of

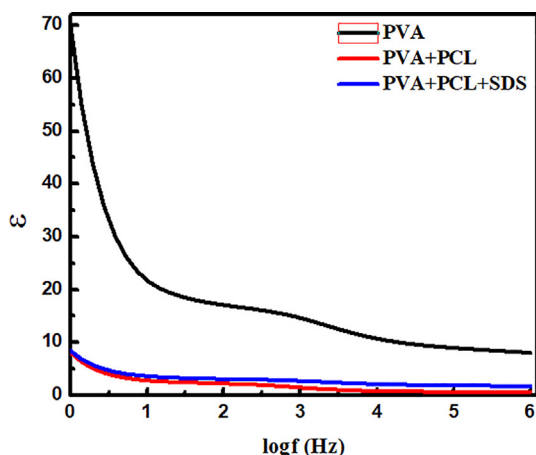


Fig. 7. Variation of dielectric constant with Log (frequency) of PVA, PVA/PCL and PVA/PCL/SDS polymer film.

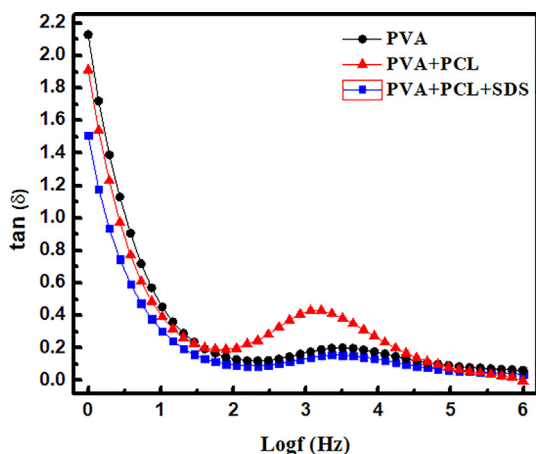


Fig. 8. Variation of dielectric Loss with Log (frequency) of PVA, PVA/PCL and PVA/PCL/SDS polymer film.

the PVA, the value of dielectric constant was reduced at lower frequencies.

Increase of ϵ and $\tan\delta$ in low frequency region with low resistivity and decrease of ϵ and $\tan\delta$ in high frequency region with high resistivity makes PCL a desirable candidate in the field of micro-electronics as energy storage devices [11].

5. Conclusion

Micelles possess an outstanding ability to solubilize poorly water-soluble drugs and increase their bioavailability. In this paper, PCL is a poorly soluble anti-cancer drug demonstrated with SDS micelle systems. Besides this, micelles, due to their small size show a very efficient spontaneous accumulation. Micelle specific targeting drug delivery to the required areas can be also achieved by attaching specific targeting ligand to the micelle surface. As the optical and structural properties of trapped PCL/SDS were highly detectable even in solid form freezed in a polymer matrix and since detectable photostability were also observed in matrix form, PCL/SDS in solid form may be considered as the most promising candidates for applications for biomedical industry.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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