Preparation, Characterization and Spectroscopic Investigations of PEOX-PVOH Blend Films

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Abstract: A stable and free standing polymer blend films of poly (2-ethyl-2-oxazoline) [PEOX] and poly(vinyl alcohol) [PVOH] were prepared by solution casting technique at different weight percentages (70/30, 50/50, 30/70). The prepared blends were characterized by scanning electron microscopy (SEM), and ultraviolet-visible (UV-Vis) and Fourier transform infrared (FTIR) spectroscopy. Various optical properties such as absorption band edge, direct and indirect band gap, and optical activation energy were obtained by UV-Vis spectral analysis. FTIR analysis confirms the specific hydrogen bonding between –CH\textsubscript{3} groups of PEOX and –OH groups of PVOH, and also the hydrophilic nature of the blends.

Keywords: Polymer blend, Solution casting, Band edge, Band gap, Optical spectroscopy.

1. Introduction

The studies on water soluble polymers like poly(vinyl alcohol), poly(ethylene oxide), poly(acrylamide), poly(vinyl pyrrolidone), poly(2-ethyl-2-oxazoline) etc. has a considerable interest due to their bio-compatibility, which in turn find applications in field of bio-medical and pharmacy.

Poly(2-ethyl-2-oxazoline) [PEOX] is an amorphous, water soluble, non-ionic, and thermoplastic polymer. PEOX belongs to the group of polymers known as poly(oxazolines) and is called as tertiary amide polymer. Poly(oxazolines) are useful in a various applications, including biocompatible materials for drug delivery and steric stabilizers [1-3]. PEOX has good Newtonian characteristics, shear stability, melt flow and is a potential substitute for PVOH and poly(vinyl pyrrolidone), and has good thermal stability [4]. US Food and Drug Administration (FDA) have approved PEOX for use as an indirect food additive. Liposomes on which PEOX was grafted have been shown to circulate for a long time in the blood and to be associated with a reduction of the clearance rates in spleen and liver [5]. PEOX is readily soluble in water and softens at 110 to 120 °C with a thermal stability up to 380 °C, and hence it’s both solution and melt can be used in adhesive applications [6, 7]. It combines very well with many polymers to form polymer blend, and thus, can be used to improve the properties of polymer system [7-10]. PEOX is used as a compatibilizing agent in various personal care products and medical field due to its
water solubility, dispersant properties and biocompatibility [11-13]. This polymer also finds its application in photo resists inks and coatings [14, 15]. PEOX is a pH responsive polymer, in addition to being hydrophilic, which enables very specific control of drug delivery and release at the appropriate site through pH cues [16-18]. Polyvinyl alcohol [PVOH] is a water soluble, biocompatible, odorless, tasteless and non-toxic polymer. PVOH is not known to occur as a natural product. The physical properties and specific functions of PVOH depend on the degree of polymerization and the degree of hydrolysis. The key characteristics of PVOH are outstanding film forming, high binding strength, adhesive and emulsifying properties [19]. It has resistance to oils, grease and solvents, and also has high tensile strength and flexibility as well as high aroma and oxygen barrier properties. PVOH is ecological advantageous due to its bio-degradability and combustion does not generate any residues. It can react with many type of functional groups since it has number of hydroxyl groups. Polyvinyl alcohol with high molecular weight is useful for preparing gel which possesses both high strength and modulus, and, hence, it is used for the production of fibers, films and gels. It is a useful industrial, medical and biometric material [20]. PVOH finds application in textile, paper making, and variety of coatings. Physically and chemically modified PVOH is helpful in biomedical applications. Due to its water solubility and bio-degradable properties, PVOH is widely used as packing material for chemicals such as detergent, cleanser, disinfector, laundry powder, pesticide and dye stuff. It has broad industrial applications due to its chemical resistance and physical properties. PVOH is useful, as modifier and thickener, in water transfer printing process and hard contact lens solution as a lubricant, and for making protective chemical-resistant gloves.

Blending of polymers is an interesting way of making new materials with attractive properties. The properties of the blend can be tailored by varying the composition and processing conditions. To the best knowledge of authors, there are no reports on optical properties and the interaction study of PEOX-PVOH polymer blends. Therefore, in the present study, an attempt is made to prepare PEOX-PVOH polymer blends by solution casting method with an aim to make blends with enhanced properties. This investigation will be quite helpful for understanding compatibility and miscibility of the polymer blends.

2. Experimental

2.1. Preparation of PEOX-PVOH Polymer Blends

Poly (2-ethyl-2-oxazoline) [Mw: 500000] and poly(vinyl alcohol) [Mw: 85000-124000] were obtained from Sigma-Aldrich, India and used as received. The PEOX-PVOH polymer blend films were prepared by solution casting method in three different weight percentages (wt%) [70/30, 50/50, 30/70] using deionized water (DI water) as a solvent. PEOX and PVOH were first separately dissolved in the DI water, and then both polymer solutions were mixed homogeneously using a magnetic stirrer at about 60 °C. This homogeneous solution was poured into the petridishes and kept in vacuum oven (at 60 °C) for evaporation of solvent for 4 days. The fully dried films were peeled off from the petridishes, and heated in a vacuum oven at 100 °C for 3 h to remove residual water and to make cross linking reaction. For the purpose of comparison, pure PEOX and pure PVOH films were also prepared. Thickness of the obtained films was in the range of 120-180 µm.

2.2. Measurements

Surface morphology of the pure PEOX, PVOH, and blend films was studied by a scanning electron microscope (Tescan Vega3, Czech Republic). Ultraviolet-Visible (UV-Vis) absorption spectra of the samples were recorded in the wavelength range of 200-800 nm using UV-Vis spectrophotometer (Shimadzu 1800, Japan). Fourier transform infrared (FTIR) spectra of samples were obtained in the spectral range of 400-4000 cm⁻¹ using Bruker Alpha FTIR spectrometer. Thickness of these samples was measured using digital vernier (Aerospace, India) which has least count of 0.01 mm.

3. Results and Discussion

3.1. Morphological Characterization

Fig. 1a-e shows SEM images of pure PEOX, pure PVOH, and PEOX/PVOH blend films. SEM images show that the polymer surfaces (blend and pure) have heterogeneous type of morphology which may be due to the irregular shaped clusters formed by polymer chains. This may be attributed to the formation of hydrogen bonding between polymers chains.

3.2. UV-Vis Spectral Analysis

UV-Vis spectra of pure PEOX, pure PVOH, and PEOX/PVOH blend films are shown in Fig. 2a. It can be observed that, there is an increase in the absorbance, and absorption edges are slightly shifted toward lower wavelength with the increase of weight percentage of PVOH in the PEOX/PVOH blend system. However, absorption plays an important role in the optical properties of polymers. The relationship between absorption coefficient, \( \alpha \), and photon energy can be expressed as [21, 22]:

\[
\alpha h v = A(hv - E_g)^\beta, 
\]  

\( h \) is the Planck’s constant, \( v \) is the frequency of light, \( E_g \) is the band gap energy, and \( \beta \) is a function of \( \alpha \).
where $\alpha$ is the absorption coefficient, $A$ is the parameter that depends on the transition probability, $h$ is the Planck's constant, $\nu$ is the frequency of photon, $E_g$ is the optical energy gap of the substance, $r$ is the parameter that gives the type of electron transition. Two distinct linear relations can be found from equation (1), one for $r = 1/2$ (direct transition), and other for $r = 2$ (indirect transition) [23].

The position of the absorption edge, the direct band gap and indirect band gap were obtained from the plots of absorption coefficient ($\alpha$) versus photon energy ($h\nu$), ($\alpha h\nu$)$^2$ versus $h\nu$, and ($\alpha h\nu$)$^{1/2}$ versus $h\nu$, respectively, and are shown in Fig. 2 (b-d). The values of the absorption edge and the direct/indirect band gap were determined by extrapolating the linear portions of these curves to zero absorption in the large absorption region. The values of various optical parameters are shown in Table 1. The optical activation energy has been determined using the Urbach rule [24],

$$\alpha = B \exp(h\nu / E_a),$$  

where $B$ is the constant and $E_a$ is the activation energy which represents the width of the tail of localized states in forbidden band gap. The values of $E_a$ are calculated by taking the reciprocal of slopes obtained from the plot of $\ln\alpha$ versus photon energy ($h\nu$) as shown in Fig 2e, and are listed in Table 1.

From the Table 1, it can be seen that, the values of absorption edge, direct and indirect band gap increases with increasing PVOH weight percentage in PEOX/PVOH blend, and they become maximum for 30/70 wt% PEOX/PVOH blend. The increase in the optical energy gap values is due the interaction between the polymer chains [25, 26] and the formation of some bonds [27]. This shows that as a result of blending, there is a change in the number of final states in the band gap [23, 28]. The increase in the number of defects which led to increase in the density of localized states in the band structure also led to increase of optical energy gap [29].

Table 1. Absorption edge, optical energy gap (direct and indirect), and activation energy values of pure PEOX, pure PVOH, and PEOX/PVOH blends.

<table>
<thead>
<tr>
<th>PEOX/PVOH blends</th>
<th>Absorption edge (eV)</th>
<th>Direct band gap (eV)</th>
<th>Indirect band gap (eV)</th>
<th>Activation energy $E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PEOX</td>
<td>5.02</td>
<td>5.09</td>
<td>4.92</td>
<td>0.69</td>
</tr>
<tr>
<td>70/30</td>
<td>4.92</td>
<td>4.97</td>
<td>4.81</td>
<td>0.53</td>
</tr>
<tr>
<td>50/50</td>
<td>4.95</td>
<td>5.01</td>
<td>4.84</td>
<td>0.59</td>
</tr>
<tr>
<td>30/70</td>
<td>4.97</td>
<td>5.03</td>
<td>4.87</td>
<td>0.67</td>
</tr>
<tr>
<td>Pure PVOH</td>
<td>5.27</td>
<td>5.41</td>
<td>5.05</td>
<td>0.55</td>
</tr>
</tbody>
</table>
3.3. FTIR Spectral Analysis

FTIR spectroscopic characterization is carried out to find out whether there will be a shift in the peaks in the spectra of blends due to the various interactions between polymers, e.g. hydrogen bonding. FTIR spectra of pure PEOX, pure PVOH, and PEOX/PVOH blends are shown in Fig. 3. Wave numbers for various spectral peaks and their assignments for all the prepared polymer blends are listed in Table 2 [30].

PEOX shows strong absorption band at 3436 cm\(^{-1}\) indicating \(-\text{OH}\) stretching vibrations. The peaks at 2929 and 1631 cm\(^{-1}\) are assigned to \(-\text{CH}_2\) asymmetric stretching and amide C=O stretching, respectively. The two peaks at 1442 and 1035 cm\(^{-1}\) are attributed due to the \(\text{CH}_3\) bending and C\(-\text{N}\) stretching, respectively. PVOH as two strong absorption peaks at 3510 and 2980 cm\(^{-1}\) which can be assigned to \(-\text{OH}\) stretching and \(-\text{CH}_2\) asymmetric stretching, respectively. The band corresponding to C=O symmetric stretching occurred at about 1738 cm\(^{-1}\). The bands at 1636, 1455 and 1377 cm\(^{-1}\) correspond to C=C stretching, C\(-\text{H}\) bending, and \(-\text{CH}_2\) bending, respectively.

FTIR spectra for PEOX-PVOH polymer blends clearly shows that, there is a clear shift of absorption bands indicating the formation of strong intermolecular bonding between \(-\text{CH}_3\) groups in PEOX and \(-\text{OH}\) groups in PVOH. The 30/70 wt % PEOX-PVOH blend has a maximum shift in the higher wave number side evidencing a formation of strong hydrogen bond. As the PVOH content in the blend increases, the peak intensity diminishes.

![Fig. 2. Plot of (a) absorbance versus wavelength (\(\lambda\)), (b) absorption coefficient versus photon energy, (c) \((\alpha h \nu)^2\) versus photon energy, (d) \((\alpha h \nu)^{1/2}\) versus photon energy, and (e) ln\(\alpha\) versus photon energy.](image1)

![Fig. 3. FTIR spectra of pure PVOH, pure PVA, 70/30, 50/50 and 30/70 blends.](image2)
confirms that, increased bond strength is due to the compatible with enhanced properties. FTIR spectra PEox/PVOH with 30/70 wt% is most suitable and study it can be concluded that, the blend of the optical energy gap of the blends. Hence, from this PVOH, which is reflected in the form of increase in variation decreases with increasing concentration of structural variation occurred in blend system. This interaction between PEox and PVOH, and hence, a casting method. UV-Vis spectra studies confirm the blends have been prepared successfully by solution 2015-2016/GRD-470.

Acknowledgements

One of the authors (SRM) is thankful to the Vision Group on Science and Technology (VGST), Department of Information Technology, Biotechnology and Science & Technology, Government of Karnataka for providing the financial support under project no. KSTePS/VGST/03/CISEE/2015-2016/GRD-470.

3. Conclusions

The results shows that PEox-PVOH polymer blends have been prepared successfully by solution casting method. UV-Vis spectra studies confirm the interaction between PEox and PVOH, and hence, a structural variation occurred in blend system. This variation decreases with increasing concentration of PVOH, which is reflected in the form of increase in the optical energy gap of the blends. Hence, from this study it can be concluded that, the blend of PEox/PVOH with 30/70 wt% is most suitable and compatible with enhanced properties. FTIR spectra confirms that, increased bond strength is due to the intermolecular bonding interactions between \( \text{CH}_2 \) groups of PEox and \(-\text{OH}\) groups of PVOH and the interaction is maximum for 30/70 wt% blend.

Table 2. Assignments of the FTIR characterization of bands of the pure PEox, pure PVOH and PEox-PVOH blends.

<table>
<thead>
<tr>
<th>Wave no. (cm(^{-1}))</th>
<th>Peak Assignment (PEox)</th>
<th>Wave no. (cm(^{-1}))</th>
<th>Peak Assignment (PVOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3436</td>
<td>(-\text{OH}) stretching</td>
<td>3421</td>
<td>(-\text{OH}) stretching</td>
</tr>
<tr>
<td>2929</td>
<td>(-\text{CH}_2) asymmetric stretching</td>
<td>2922</td>
<td>(-\text{CH}_2) asymmetric stretching</td>
</tr>
<tr>
<td>1631</td>
<td>Amide C=O stretching</td>
<td>1738</td>
<td>C=O symmetric stretching</td>
</tr>
<tr>
<td>1442</td>
<td>(\text{CH}_3) bending</td>
<td>1653</td>
<td>(\text{C}=\text{C}) stretching</td>
</tr>
<tr>
<td>1035</td>
<td>C=N stretching</td>
<td>1437</td>
<td>C=H bending</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>1383</td>
<td>(-\text{CH}_2) bending</td>
</tr>
</tbody>
</table>

References


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**NANOSENSORS: Materials and Technologies**

Nada F. Alta, Ed.

**Nanosensors: Materials and Technologies** aims to provide the readers with some of the most recent development of new and advanced materials such as carbon nanotubes, graphene, sol-gel films, self-assembly layers in presence of surface active agents, nano-particles, and conducting polymers in the surface structuring for sensing applications. The emphasis of the presentations is devoted to the difference in properties and its relation to the mechanism of detection and specificity. Miniaturization on the other hand, is of unique importance for sensors applications. The chapters of this book present the usage of robust, small, sensitive and reliable sensors that take advantage of the growing interest in nano-structures. Different chemical species are taken as good example of the determination of different chemical substances industrially, medically and environmentally. A separate chapter in this book will be devoted to molecular recognition using surface templating.

The present book will find a large audience of specialists and scientists or engineers working in the area of sensors and its technological applications. The *Nanosensors: Materials and Technologies* will also be useful for researchers working in the field of electrochemical and biosensors since it presents a collection of achievements in different areas of sensors applications.