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Studies on Polyvinyl Pyrrolidone (PVP) and Tapioca-Based Polymer Nanocomposites for Solid Polymer Electrolyte Applications in Batteries

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ABSTRACT

Blending polymers has wide applications in batteries, since it possess different physical and chemical properties. In this study blending of PVP/tapioca and PVP/tapioca/polyamide have been prepared and characterized. The compatibility or miscibility of the polymers at the molecular level determines the new properties of the polymer blends. The synthesised polymer blends were characterized using Fourier Transform Infrared Spectroscopy (FTIR), Ultraviolet-Visible Spectroscopy (UV-Vis) and Atomic Force Microscopy (AFM). Acoustical and excess parameters were studied for blends of PVP/tapioca and PVP/tapioca/polyamide in organic solids. By measuring ultrasonic velocity and adiabatic compressibility, the excess parameters were used to determine the nature of polymer interactions in the solvent. The topographical images are shown small particles approximately 50 nm in size, medium particles 100 nm in size, and large particles 175 nm in size were all observed. All particles exhibited a lobed-type fine structure; for the 175 nm sized particles, the lobes were 50 nm – 175 nm in size and appeared evenly distributed around the center of the particles.

1. Introduction

Significant efforts have been made to improve current lithium-based rechargeable batteries and develop new materials with better properties for high-performance, safe, and economical energy storage solutions. Solid polymer electrolytes (SPEs) are combinations of polymers and lithium salts dissolved in a polymer matrix. They offer flexibility, low weight, and cost-effective processing methods [1, 2]. In the development of polymer electrolytes, those with a polymer host typically have very low ionic conductivity. To improve conductivity and stability, plasticizers and ceramic fillers can be added [3]. New polymer matrices, such as polymer blends, can offer interesting ion conduction properties [4]. Blending polymers allows for the combination of different physical and chemical properties from the individual polymers. The compatibility or miscibility of the polymers at the molecular level determines the new properties of the polymer blends. Some polymers are immiscible, so to obtain a good blend from immiscible polymers, a compatibilizer is often needed. Various techniques are available to study the miscibility of polymer blends, such as intrinsic viscosity [η], SEM, DSC, and ultrasonic velocity measurements, among others [5, 6].

Biopolymers have several advantages, including reduced environmental impact, lower energy consumption during production, and being renewable materials. These materials can be incorporated into solid polymer electrolytes (SPEs) to form a new type of ionic solid, which can be used in the development of batteries and other electrochemical devices [7]. Among various polymers, polyvinylpyrrolidone (PVP) is an amorphous polymer with high stability and ease of processing. However, PVP shows low conductivity due to the rigid pyrrole group, which gives it a very high glass transition temperature (Tg). The tertiary amide carbonyl group in PVP has Lewis base properties and can form bonds with various inorganic salts [8]. PVP is hygroscopic and soluble in both water and organic solvents. Because of its hygroscopic nature, the presence of solvent can cause PVP to behave differently when used as the polymer host in electrolytes. Tapioca starch consists of two major macromolecular components: amylose and amylopectin (Fig. 1) [9, 10]. Amylose makes up about 20% of the starch, while the major component is amylopectin.

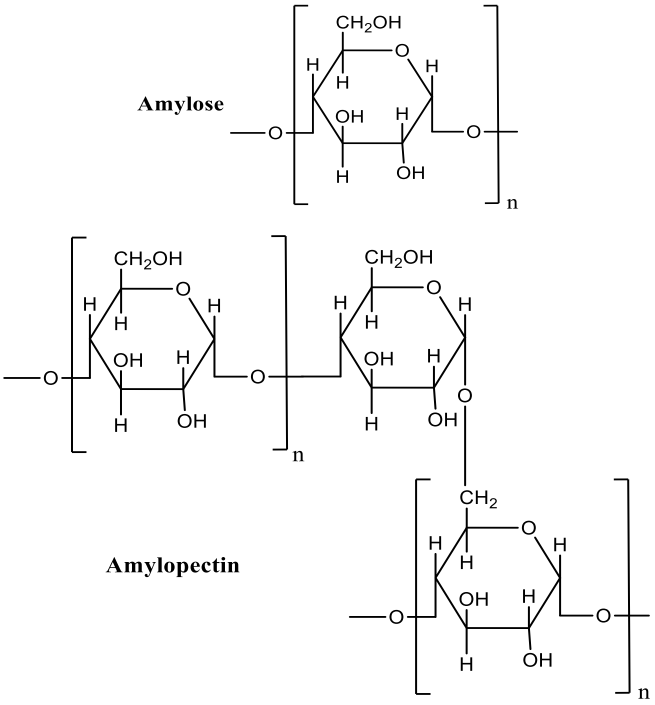

Fig. 1 Structures of amylose and amylopectin

This work presents a study of the miscibility between polyvinylpyrrolidone (PVP) and tapioca starch (cassava starch), which can be used to form polymer blends. These polymer blends can be applied in electrochemical applications.

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2. Experimental Methods

2.1 Materials

Polyvinylpyrrolidone (PVP) with a molecular weight of 40,000 was purchased from Sisco Research Laboratories Pvt. Ltd (SRL), Mumbai, India. Tapioca starch (cassava starch) was purchased from Oxford Lab Fine Chem LLP, India. All the chemicals were used as received.

2.2 Preparation

PVP and tapioca starch in different compositions were mixed in dimethylformamide (DMF). The total weight of the PVP/tapioca mixture in the solution was always maintained at 2 g per 10 mL. The aqueous solutions were continuously stirred with a magnetic stirrer to obtain homogeneous mixtures. In the second system, PVP/tapioca/polyamide was also prepared, with polyamide as 12 wt./wt. and maintained in all compositions.

2.3 Measurement of Ultrasonic Velocity and Related Parameters

Ultrasonic velocities of the blend solutions were measured using the ultrasonic interferometric technique. The ultrasonic interferometer, supplied by Mittal Enterprises, New Delhi, with a 2 MHz single-frequency generator, was used. The temperature was maintained at 35 °C by circulating water from a thermostat. The density of the solutions was measured using 10 mL specific gravity bottle and a digital balance.

2.4 Characterization

The FT-IR spectra were recorded using a Thermo Fisher Nicolet iD3 instrument (wavenumber range of 400 cm^{-1}- 4000 cm^{-1}). UV-VIS DRS spectrum was carried outJascoV-650 spectrophotometer, JAPAN. Atomic force microscope (AFM) surface was examined by Nanosurf easy 2 scan, USA. The Nanosurf easy2scan BT02218 profiler, which has a sharp cantilever tip that interacts with the sample surface to sense local forces between the tip and the molecules, completed the atomic force microscopy.

3. Results and Discussion

3.1 UV-Visible Spectral Characterization

Starch is a mixture of two molecular components: the linear fraction is called as amylose and the branched fraction called as amylopectin. The maximum absorption was observed at wavelengths of 560 nm and 240 nm for tapioca starch and polyvinylpyrrolidone (PVP), respectively. The absorption maximum for the tapioca complex was reported at shorter wavelengths 410 nm and 260 nm. These differences could be due to variations in the purity of the materials or differences in starch types [11].

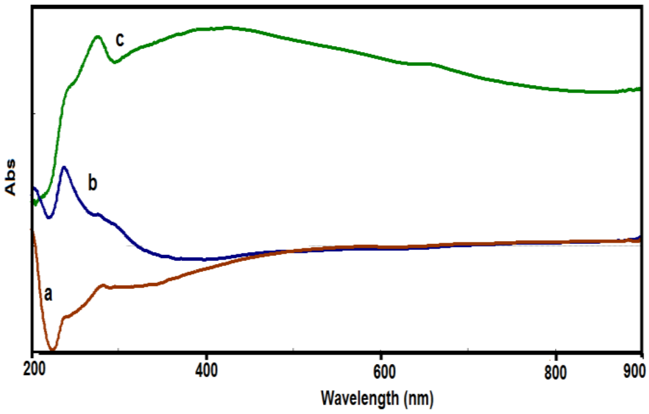

Fig. 2 UV-Vis spectra of a) Tapioca starch b)polyvinylpyrrolidone and c) polymer blends

Optical transitions are allowed if the transition matrix element of the dipole operator between the valence and conduction bands is non-zero from a symmetry point of view. If the transition matrix element is zero, the transition is optically forbidden. Since the absorption coefficient α(E) of crystalline semiconductors depends on the transition matrix element, optically allowed and forbidden bandgap transitions have different absorption profiles near the band edge. The Tauc plot method, originally developed to investigate the optical absorption edge of amorphous semiconductors, allows for the possibility of transitions between localized states. These transitions within the mobility gap help define the value of the optical gap. The band gap value is 3.68 eV for Tapioca starch, 3.332 eV for polyvinyl pyrrolidone and 2.457 eV for polymer blends. The matrix element for these inter band transitions is considered independent of photon energy [12].

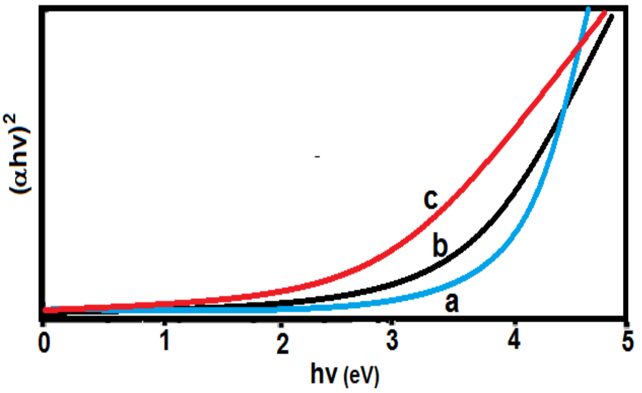

Fig. 3 Tauc plot of a) Tapioca starch b)polyvinylpyrrolidone and c) polymer blends

3.2 FTIR Studies

Fig. 4a given FT-IR behaviour of Tapioca starch; and three regions of the spectra have been studied: the OH stretching region 3650-3000 cm^{-1}, the CH stretching region 3000-2800 cm^{-1}, and the finger print region, below 1600 cm^{-1}; broad signal at 3350 cm^{-1} corresponds to O–H stretching from carboxyl groups superposed with the O–H stretching hydroxyl group, at 3080 cm^{-1} represents OH stretching of alcohol; band 2950 cm^{-1} obtained due to C–H vibration from CH_2 group, the bands 1670–1600 cm^{-1} assigned to C=O stretching due to the carboxylic group and C=O stretching from sample. The bands corresponding to O-H bending from hydroxyl group appear in the 1550–1500 cm^{-1} spectral range, partly overlapping with the aromatic –C=C stretching. Another prominent bands, such as 1400–1200 cm^{-1} correspond to –C–O stretching from carboxylic group, 940 cm^{-1} to O–H bending out of plane and 830 cm^{-1} to CH_2 adjacent hydrogens on an aromatic ring, para substitution.

Fig. 4b represents the FTIR spectrum of PVP where a vibrational band observed at 2900 cm^{-1} may be attributed to aliphatic CH_2 asymmetric stretching [13]. The bands around 1651 cm^{-1} and 1451 cm^{-1} are attributed to C=O stretching and CH_2 bending, respectively [14]. Other peaks include 1286 cm^{-1} due to CH_2 and C-N wagging), 3400 cm^{-1} due to OH group, 1017 cm^{-1} due to C-C and 1080 cm^{-1} corresponds to C-C bending. For pure propylene carbonate, peaks include 2950 cm^{-1} (asymmetric stretching), around 568 cm^{-1}(N-C=O bending), and 1425 cm^{-1}. For pure lithium carbonate, two strong peaks at 1490 and 1450 cm^{-1} are observed, along with weak peaks at 858 cm^{-1}.

FTIR spectra, Fig. 4c, of blends of polyvinylpyrrolidone and tapioca starch typically display peaks in two discrete regions, with wavenumbers greater than 2500 cm^{-1} and less than 1300 cm^{-1}. The former region corresponds to hydroxyl (–OH) stretching due to absorbed or molecular water. It was attributed blends of polyvinylpyrrolidone and tapioca starch adsorption. The latter region is observed due to different modes of blends of polyvinylpyrrolidone and tapioca starch and three prominent peaks were observed. The peak at 460 cm^{-1} was assigned to rocking motion of oxygen atoms. A broader peak at 660 cm^{-1} was assigned to CH_2 vibration mode of blends which was due to symmetric vibrations of atoms in a blend bond. A peak at 1105 cm^{-1} along with weak absorption at 960 cm^{-1} was the largest peak observed in a NH_2 spectrum and was assigned to NH stretching vibration.

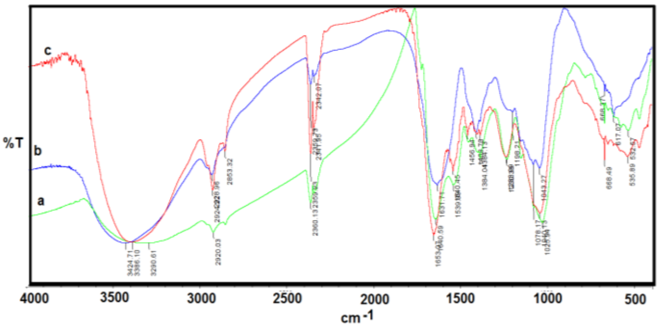

Fig. 4 FTIR behaviour ofa) Tapioca starch b)polyvinylpyrrolidone and c) polymer blends

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3.3 AFM Studies

The 3D AFM topography images, as shown in Fig. 5, indicate the role of PVP and Tapioca starch in changing the viscosity, where the plates seem to be smoother after the Tapioca starch addition. This decrease in the roughness of surfaces increases the friction between these, which was extracted from Fig. 5 which reveals the blends of PVP and Tapioca starch effects with all roughness parameters presented. After Tapioca starch addition, all amplitude parameters were affected significantly: the roughness average parameter (Sa)increased by 78.52%, the root mean square (Sq) increased by 89%, the peak-to-peak (Sy) increased by 83.6% and the ten-point height (Sz) increased by 90.9%. The hydride parameters increased also whereas the root mean square slop (Sq) by 96.67%. The particle size and surface morphology of the microspheres of the different formulations were compared via AFM. Although a statistically significant number of particles were not analyzed. AFM could be used as an indicator for both particle size and morphology. Fig. 5 shows that there are no striking differences regarding particle size and morphology when comparing the three model formulations. Particles are nanorod, tube, with a smooth, intact surface and an estimated diameter approximately between 30 nm and 70 nm. The 3D data emphasize that these images are acquired from the apex of immobilized nanotube. The 2D representation following the background subtraction of the image curvature reveals surface structure in details. AFM imaging of the three samples showed identifiable differences between the appearance and organization of the formulations. AFM provided spatial information on the distribution of different compounds at the surface at nanoscale resolution. Taken together these techniques provide insights into differences in distribution. In addition to influencing the particle formation process, changing the ratio of the components might result in different mixed phases each displaying different solubility.

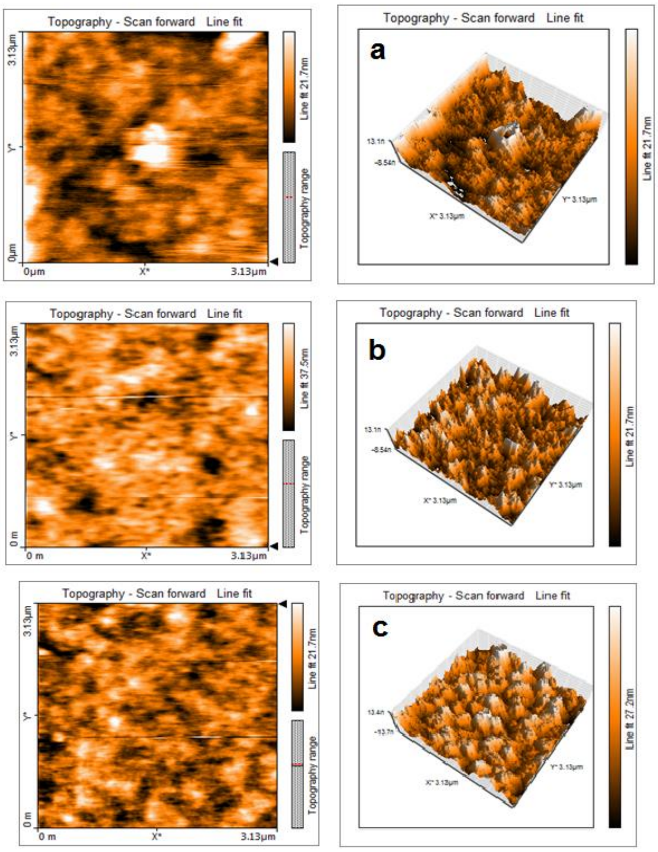

Fig. 5 AFM behaviour ofa) Tapioca starch b)polyvinylpyrrolidone and c) polymer blends

Weak physical forces, such as electrostatic and van der Waals forces, hold nanoparticles to the substrate. Therefore, intermittent contact mode is an appropriate imaging mode where a small piezoelectric device positioned in the AFM tip holder drives the cantilever to oscillate up and down at its resonance frequency. This oscillation's amplitude is more than 10 nm, usually between 100 and 200 nm. AFM image can be easily obtained by NanoScope. The particle distribution in three samples is estimated with the software. Topological features appear in the presence of nanocluster with size of particles 50 nm for Tapioca starch. The size of the polyvinyl pyrrolidone is form 100 nm to 150 nm and polymer blends is upto 175 nm.

The measured values ultrasonic velocity, density, adiabatic compressibility and excess values for PVP/ Tapioca and PVP/Tapioca/ polyamide in DMF at 35 °C are presented in Table 1 and Table 2 respectively. From the results of ultrasonic velocity, it is evident that the variation is non-linear. This nonlinear variation for the system studied showing multiphase nature in the blend [15]. The values of the measured and derived acoustical parameters of the PVP/Tapioca blend system for different compositions show non-linear behaviour. In general the parameters show a linear behaviour with compositions.

The behaviour of u and β with blend composition is linear for miscible blends [12]. Researchers have also attributed the non-linear variation of ultrasonic velocity shows the immiscible nature of blends. It shows that the compatibility of PVP with tapioca is very less. When a polymer film are formed of the blends containing PVP/ tapioca exist as two phase [16].

The excess parameters exhibit a nonlinear variation with compositions. The excess ultrasonic velocity (u^E) are both negative and positive. The negative values indicate decreasing strength of interaction between the component molecules. When the concentration increases the excess velocity values are positive shows tightly packed. The positive excess adiabatic compressibility βE suggests loosely packed molecules in the mixture due to the difference in size and shape of the molecules

Table 1 Values of U, ρ, β and excess values of PVP/Tapioca in DMS

PVP%	Ultrasonic velocity m/s	Density Kgm^{-3}	Adiabatic Compressibility 10^{10}m ^{2} /N	Excess Ultrasonic velocity m/s 10^{-1}	Excess Adiabatic Compressibility 10^{11}m ^{2} /N
0	1523.20	793.6	5.43	0.00	0.00
46.66667	1545.00	794.0	5.28	-3.03	0.03
60.65574	1536.00	793.6	5.34	11.60	-0.07
69.86301	1542.80	793.3	5.30	8.51	-0.05
74.13793	1538.20	793.2	5.33	14.83	-0.10
100	1563.43	792.6	5.16	0.00	0.00

Table 2 Values of U, ρ, β and excess values of PVP/Tapioca/polyamide

PVP %	Ultrasonic velocity m/s	Density Kgm^{-3}	Adiabatic Compressibility 10^{10}m ^{2} /N	Excess Ultrasonic velocity m/s 10^{-1}	Excess Adiabatic Compressibility 10^{11}m ^{2} /N
0	1420	809.47	6.13	0.00	-0.70
37	1440	801.94	6.01	32.91	-0.68
69	1428	817.41	6.00	90.67	-0.76
74	1470	809.17	5.72	55.82	-0.49
88	1550	801.13	5.20	-4.16	-0.01
100	1563	816.38	5.01	0.00	0.15

The variation in ultrasonic velocity of PVP/Tapioca/polyamide polymer blend solutions in DMS with different compositions is shown in Table 2. The ultrasonic velocity increases, while adiabatic compressibility decreases. This increase in ultrasonic velocity and decrease in adiabatic compressibility indicate the solvation/hydration behavior of the solute in the solvent. The results suggest that adding polyamide increases the interaction between the polymers. This indicates that the composite behaves as a single phase. Polyamide acts as a compatibilizer between PVP and Tapioca.

4. Conclusion

The ultrasonic velocity, acoustical parameters, and excess parameters were studied for the synthesised blends of PVP/Tapioca/polyamide polymer. The results indicate that the PVP/tapioca blends are immiscible in nature, which is further supported by the excess values. When polyamide is added to the system, the acoustical parameters show an almost linear variation. With the addition of polyamide, the polymers change from immiscible to miscible where polyamide acts as a compatibilizer. The topographical images are shown small particles approximately 50 nm in size, medium particles 100 nm in size, and large particles 175 nm in size were all observed. All particles exhibited a lobed-type fine structure; for the 175 nm sized particles, the lobes were 50 nm – 175 nm in size and appeared evenly distributed around the center of the particles.

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