

Polyvinyl Alcohol Processed Templated Polyaniline Films: Preparation, Characterization and Assessment of Tensile Strength

J. Subbalakshmi, G. Dhruvasamhith, S. M. Hussain

Abstract—Polyaniline (PANI) is one of the most extensively studied material among the conducting polymers due to its simple synthesis by chemical and electrochemical routes. PANIs have advantages of chemical stability and high conductivity making their commercial applications quite attractive. However, to our knowledge, very little work has been reported on the tensile strength properties of templated PANIs processed with polyvinyl alcohol and also, detailed study has not been carried out. We have investigated the effect of small molecule and polymers as templates on PANI. Stable aqueous colloidal suspensions of trisodium citrate (TSC), poly(ethylenedioxythiophene)-polystyrene sulfonate (PEDOT-PSS), and polyethylene glycol (PEG) templated PANIs were prepared through chemical synthesis, processed with polyvinyl alcohol (PVA) and were fabricated into films by solution casting. Absorption and infra-red spectra were studied to gain insight into the possible molecular interactions. Surface morphology was studied through scanning electron microscope and optical microscope. Interestingly, tensile testing studies revealed least strain for pure PVA when compared to the blends of templated PANI. Furthermore, among the blends, TSC templated PANI possessed maximum elasticity. The ultimate tensile strength for PVA processed, PEG-templated PANI was found to be five times more than other blends considered in this study. We establish structure–property correlation with morphology, spectral characterization and tensile testing studies.

Keywords—Processed films, polyvinyl alcohol, spectroscopy, surface morphology, templated polyanilines, tensile test.

I. INTRODUCTION

PANI is a well-known and most enormously considered amid conducting polymers. It has always been attractive due to its synthesis, strength, low price and good environmental stability [1]–[4]. PANIs also possess unique optical characteristics and conductivity which lead them towards superior industrial applications. At a recent time, extent development has been made on the process of PANI [5]–[7]. With the focus on environmental safety and processing methodologies, aqueous solution processed PANIs, turned out to be attractively important. Composites/blends of PANIs have

excellent adhesion and anticorrosive properties [8]. By blending with other polymers [9]–[11] or by substitution and copolymerization, exploration has been made to enhance the poor mechanical properties and the processability of PANI [12]. Polyvinylidene fluoride, (PVDF)/PANI blends were synthesized using chemical polymerization of aniline and their thermal and mechanical properties were studied as a function of PANI doping levels. It was observed that presence of PANI led to the increase in the tensile strength and Young's modulus due to the reinforcement of PANI over PVDF matrix, thereby constraining the chain movements of PVDF [13]. Study on the effect of feeding ratio of aniline in PANI/PVA blend on the mechanical and electrical properties of the composites was reported by [14]. The tensile strength of the blend films has been attributed to the hydrogen bonding between PANI and PVA. Electromechanical response of the solution blended and HCl doped PANI/PVA blends subjected to static, dynamic and time-dependent strains was reported by [15]. Though recently, polyethylene terephthalate/PANI [16], polyurethane/PANI [17], PANI/polybenzimidazole [18] blends were characterized using IR and NMR spectra. The tensile strength was found to be diminished and permeability, diffusion, sorption capacities of all measured gases are observed to be decreased with increased content of PANI. Recently, enhancement of mechanical property by strategic inclusion of graphene oxide nano-filler in chitosan/gelatin polyelectrolyte complex [19] has been reported. However, we have limited our search on PANI/PVA blends only, relevant to the work presented in this paper.

We have prepared stable aqueous colloidal suspensions of templated PANIs, through modified procedure (along the similar lines reported in [20] and processed with PVA by solution casting into free standing films. We have characterized the films using various spectroscopy techniques and studied mechanical properties. For the TSC-templated PANI processed film, the ultimate tensile strength was found to be considerable, this could be due to the strong intermolecular interactions between the TSC-PANI and PVA, leading to the restricted orientations of TSC-PANI chains. Also, PVA being a good stabilizer leads to the rigidification of the polymer chains.

II. MATERIALS AND METHODOLOGY

A. Synthesis

TSC, ammonium persulfate (AP) and HCl (12 N) were

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S. J. thanks financial support from the Department of Science and Technology, New Delhi, India, under FIST grant.

obtained from SD fine chemicals. Aniline (analytical grade), PEDOT-PSS and PEG were obtained from Sigma Aldrich. All colloidal suspensions were prepared in Milli-Q water. To a 0.84 mL (4.6 mmol) of aniline in round bottomed flask, 30 mL of 3M HCl was added slowly and the solution was kept for stirring for 15 min. 1.67 gm of PEG dissolved in 10 mL water was added to anilinium hydrochloride solution while stirring. 2.04 gm (4.4 mmol) of AP dissolved in 5 mL water was added dropwise for at least 30 mins. The solution was stirred for 2.5 hours more, to complete the polymerization (Fig. 1). Dark green colloidal solution was centrifuged and subjected to sonication. This solution was further processed into free standing films. 1 gm of PVA was dissolved in about 10 mL of water and left for about 3 days for dissolution. The templated PANIs and PVA solution were mixed in 1:1 volume ratios due to better film formation and subjected to solution casting. Similar methodology was followed for the preparation and fabrication of other templated PANI blends too.

B. Characterization

1. FT-IR and UV-Vis Spectroscopy

FT-IR spectra were recorded on Jasco FTIR-4200 spectrophotometer. Samples of blends in the form of KBr pellets were made from vacuum drying. Absorption spectra were recorded on the Jasco V-650 make of model Jasco-ISV-727.

2. Fabrication of Films

Glass plates were cleaned thoroughly with detergent, high purity water, acetone and were dried in hot air oven at 110 °C, prior to solution casting.

3. Differential Scanning Calorimetry

Shimadzu DSC-60 in the range of temperature 30-800 °C with heating and cooling rate of 10 °C min⁻¹ for the differential scanning calorimetry study (DSC). Data were obtained using alumina pan containing 4 mg of sample under nitrogen atmosphere and at the rate of 100 mL min⁻¹. Empty alumina pan was used as reference.

4. Scanning Electron Microscopy

Morphology of solution casted films was studied under Philips XL 30ESEM scanning electron microscope. Gold sputtering was provided before examination of the micro features. Micrographs presented are at the same magnification for the films coated on glass substrates. An acceleration voltage of 5-10 kV and an emission current of 10 µA was supplied. To confirm that the features observed are due to processed templated PANIs, EDXS was used.

5. Optical Microscopy

Optical microscope images were obtained from MEIJI, IM 7200 model with viewing head MA 816, stage size 150×200 mm, polarizing filter 20 mm diameter.

6. Tensile Testing

Tensile strength, of the materials (~35 mm × 11 mm × 1.7 mm) have been found by performing tensile tests on the

specimens as per ASTM standards on stable microsystems, TA.XT plus texture analyzer. In these tests, specimen was gripped between two supports and applied force by gradually increasing it. We measured elongation of specimen under these continually increased forces, calculated the stress developed in the specimens and measured the strain. The system was switched on and the polymer film was kept in between the grips. Tensile testing was conducted with strain rate as 1 mm/sec, till the time there was a failure in polymer film. The obtained data were later converted to stress vs strain.

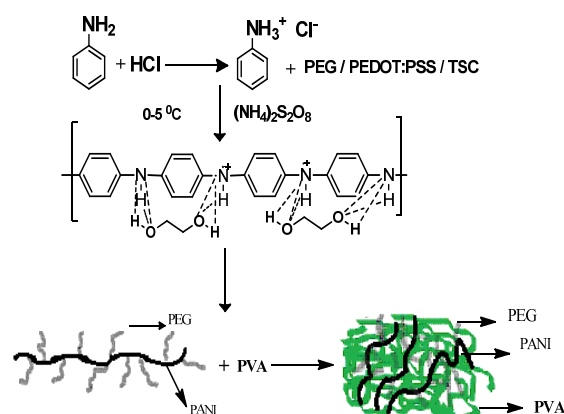


Fig. 1 Schematic representation of the plausible reaction and intermolecular interactions in (PANI-TSC/PVA) blend as an example

III. RESULTS AND DISCUSSION

Fig. 2 shows the FT-IR spectra of blends considered in our study. Pure PVA possess broad band at 3400-3100 cm⁻¹ due to O-H and C-H stretching vibrations [21]. Absorption at 1573, 1452, 2911 and 2838 cm⁻¹ for PANI-PEG; 1541, 1406, 3047 and 2932 cm⁻¹ for PANI-PEDOTPSS and 1543, 1473, 2853 and 2911 cm⁻¹ observed for PANI-TSC correspond to C=C stretch of quinonoid and benzenoid rings and to the asymmetric and symmetric aliphatic C-H stretches respectively. The backbone of emeraldine salt has positive charges. Our investigations [22] on PANI-PEDOTPSS and PANI-TSC revealed that these form stable colloidal suspensions through electrostatic interactions as PEDOTPSS and TSC are ionic, while PEG behaves more like a surfactant and stabilizer. All samples exhibit absorption of O-H (H-bonded) stretching frequency with strong and broad feature; which also overlap with N-H and aromatic C-H stretch, extending from 3000-3600 cm⁻¹. Characteristic peaks of S=O, S-O and S-C at 1050, 668 and 595 cm⁻¹ were observed in PANI-PEDOTPSS. N-H stretch (2352-2368 cm⁻¹) [23] was observed in all samples. Imine and secondary amine peaks were observed at 1300 and 1225 cm⁻¹. These typical vibrational frequencies show that templates have strong interaction with PANI and PVA. In the wavelength region of 400 to 1400 nm, PVA is almost found to be transparent [21]. The UV-Vis spectra (Fig. 3) showed polaronic band at 840 nm in addition to the hump at ~420 nm, a characteristic for the emeraldine salt. This feature is found to be more prominent in PANI-PEG/PVA and PANI-TSC/PVA. Broader polaronic

band feature is likely to be due to the exciton transitions of the quinonoid rings [24].

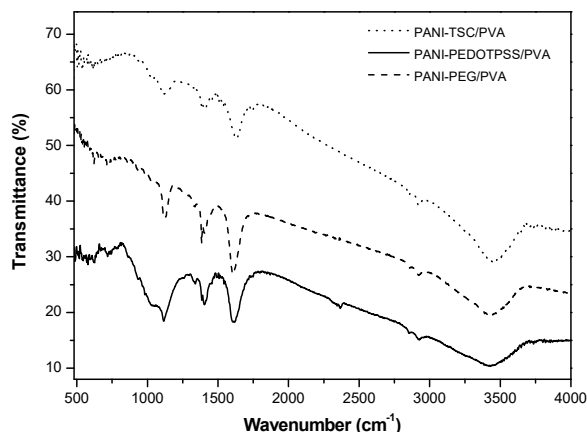


Fig. 2 FT-IR spectra of (....., PANI-TSC/PVA), (—, PANI-PEDOTPSS/PVA) and (- - -, PANI-PEG, PVA)

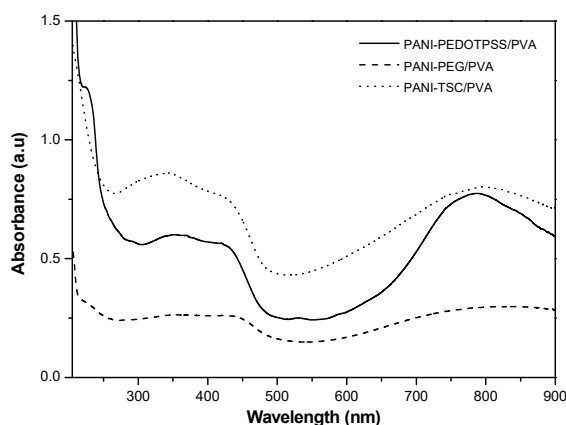


Fig. 3 UV-Vis spectra of (....., PANI-TSC/PVA), (—, PANI-PEDOTPSS/PVA) and (- - -, PANI-PEG, PVA)

The disappearance of 620 nm peak in all the blends indicates that imine nitrogen is protonated. Also, a broad band at 380 nm to 420 nm reveals the interactions in the components through hydrogen bonding [25]. PVA possess many hydroxyl groups that can strongly interact with templated PANI amine groups, this forces molecules to align along with it, also evident by the presence of a band elongated in the near infra-red region extending up to 1000 cm^{-1} .

The glass transition temperature (T_g) of PVA appears around 70-80 °C. The T_g of blends was observed to be higher than homo polymers, probably due to various intermolecular interactions. T_g of PANI-PEG/PVA and PANI-TSC/PVA was observed at ~100-106 °C (Fig. 4), broad exothermic peak ~230 °C in PANI-PEG/PVA corresponds to the crystallization of polymer. T_g of PANI-PEDOTPSS/PVA was found at 126 °C, small and broad exothermic peaks (Fig. 4) at 220 and 270 °C were also observed due to partial crystallization. T_g of PANI-PEDOTPSS/PVA was found to be higher than PANI-PEG/PVA, indicating some crosslinking and a complex

molecular structure. PANI-TSC/PVA showed a single sharp exothermic peak leading to the only phenomenon of crystallization. However, endothermic peaks were not noticed.

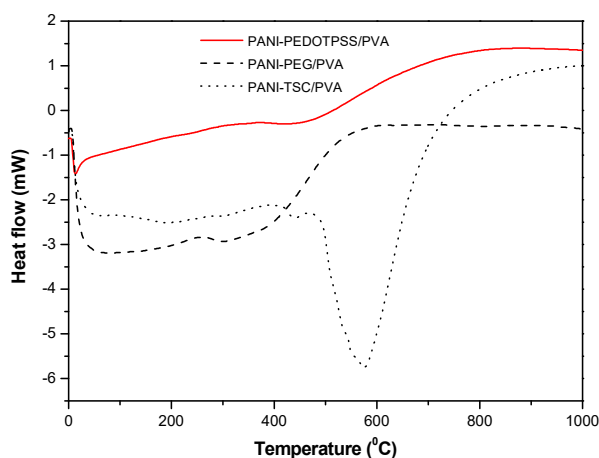


Fig. 4 DSC plots of the blends (....., PANI-TSC/PVA), (—, PANI-PEDOTPSS/PVA) and (- - -, PANI-PEG, PVA)

In our earlier investigations, SEM images on powders of templated PANI's [22] interestingly, revealed block like features with different particle sizes. Poly(4-styrenesulfonic acid sodium salt, NaPSS) when templated with small molecule such as TTF in different compositions, the SEM images [26] have shown flake and crystalline morphologies exhibiting various packing density. Carboxymethyl cellulose templated PANI film revealed uniform fibers of diameter 100-120 nm under scanning electron microscopy and showed semiconducting behavior [27]. Nevertheless, PSS templated PANI-carboxymethyl cellulose blend formed stable aqueous colloidal suspensions and their spin coated films prepared from different concentrations of colloidal suspensions under atomic force microscopy showed regular network-like structures for the films prepared at dilute/lower concentrations, indicating the efficacy of dilution as a new design element for network structures [28]. With such interesting morphological features observed in our previous PANI's, we extended our study on PVA processed template PANI's presented in this work.

SEM images (Figs. 5 (a)-(c)) showed that the blends were homogeneous without any holes or cracks. Aggregates or agglomerates like features in PANI-PEG/PVA, porous honeycomb network in PANI-TSC/PVA and homogeneity with spherical features in PANI-PEDOTPSS/PVA were observed. However, uniformity and good dispersion in the prepared blends leads to the significant retain in the mechanical property. As the strength of the blends is found to be less than PVA, probably, templated PANI could be acting as plasticizers. Optical microscope study (Figs. 5 (d)-(f)) also, exhibit the formation of homogenous blends. PVA is likely to be involved in some interactions at the surface level due to very little quantity considered.

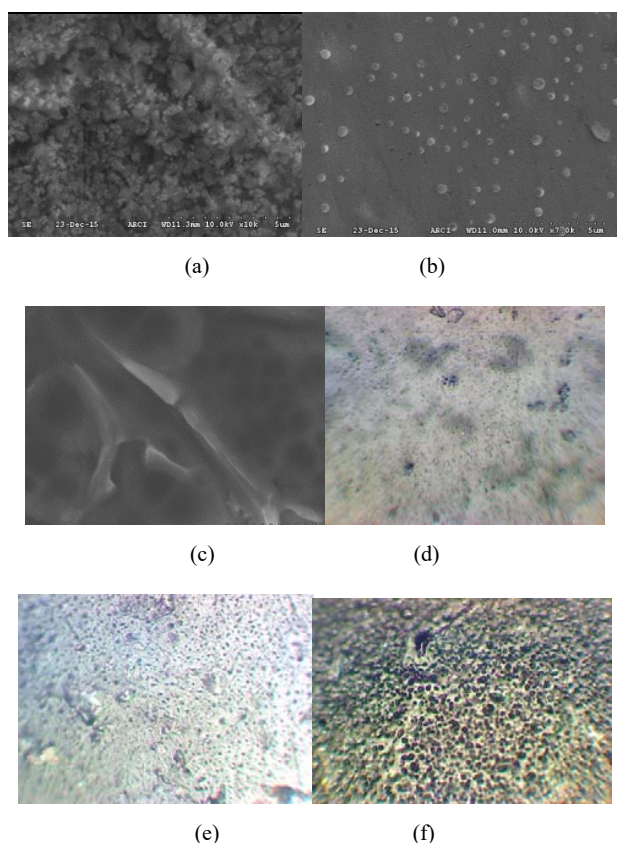


Fig. 5 Scanning electron microscopy images of (a) PANI-PEG/PVA (b) PANI-PEDOTPSS/PVA (c) PANI-TSC/PVA; Optical microscopy images of (d) PANI-PEG/PVA (e) PANI-PEDOTPSS/PVA and (f) PANI-TSC/PV

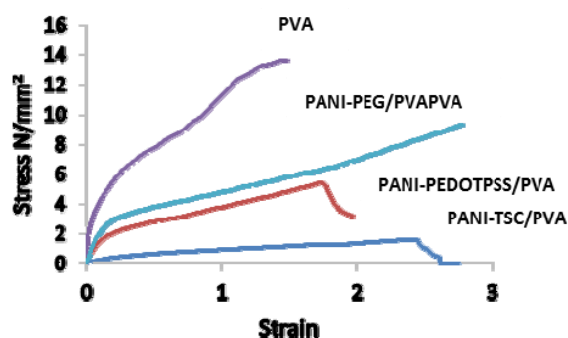


Fig. 6 Stress- strain curves of the studied polymer blends

PVA can form itself, very good quality films with appreciable strength and elongation. When it is blended with PANI templates, interesting mechanical properties were observed. In this paper, we try to investigate the strength of different polymer compositions and their combinations. The material when subjected to high-strain, it deforms permanently (plastic deformation) and at last fracture the specimen. At low stresses and strains, the polymeric material behaves as an elastic material. The point where the behavior starts to be non-linear is called the proportional limit. The local maximum in

the stress-strain linear curve is called the yield point and indicates the starting of permanent deformation. Beyond the yield point the material stretches considerably and beyond this region is called the plastic region. Further elongation leads to strain hardening and rupture of the material at the end. At the rupture point the corresponding stress and strain are called the ultimate strength and the maximum strain at break. The stress-strain behavior of a polymeric material depends on combination and composition of the polymer. Stress-strain studies (Fig. 6) were performed on all the polymer blends prepared. PANI-PEG/PVA possess highest strain, PANI-TSC/PVA also has high strain and good elasticity. All the blends studied are very good elastic materials. However, strength is less than 10 N/mm^2 .

PVA has highest mechanical strength 13.5 N/mm^2 , with moderate elasticity of 1.5 strain. PANI-PEG/PVA has highest strain of 2.8 but strength of 9.5 N/mm^2 . PANI-TSC/PVA has high strain of 2.5 with good elasticity, but its strength was very less only 1.8 N/mm^2 . The strength and strain of PANI-PEDOTPSS/PVA was found to be 5.2 N/mm^2 and 1.75. Strength of PVA could be due to extensive hydrogen bonding within the molecules. However, when it is blended with templated PANIs, PANI-PEG/PVA is found to have more strength when compared to PANI-PEDOTPSS/PVA and PANI-TSC/PVA. PEG being a stabilizer, when PANI is templated with PEG, we observed good uniform blend, moreover, when this is further blended with PVA, could lead to more stabilization due to several intermolecular interactions such as hydrogen bonding, weak Van der Waals interactions etc. Though, PANI-TSC/PVA has good elasticity, TSC being small molecule unlike PEG or PEDOT-PSS may not promote more extended polymer chains, thus decreasing the strength. However, the large strain exhibited by PANI-TSC/PVA could be due to several surface lever interactions. From our earlier reported work [22] we observed that PANI-PEDOTPSS and PANI-TSC form stable colloidal suspensions through electrostatic interactions as PEDOT-PSS and TSC are ionic. On the other hand, PEG behaves is more like a surfactant. Hence, PANI-PEG could more probably form via steric repulsions.

The synthesis and fabrication protocol we have developed allows the preparation of stable aqueous colloidal suspension of PANI in an environmentally friendly aqueous route and also the extension of this in the development of free standing elastic polymeric materials with appreciable strength and strain. FT-IR and UV-Vis spectra reveal possible intermolecular interactions between the templated PANI and PVA, which is correlated to their strength and strain. Effect of small molecule (TSC) and polymer (PEDOT-PSS and PEG) as templates on PANI and blend with PVA has been investigated. DSC suggests crystalline transformation in PANI-PEDOTPSS and PANI-PEG. SEM and optical microscopy reveals uniform features. Detailed characterization and tensile tests of all samples suggests organization and mutual interactions between templated polymers and PVA leading to an improved polymer blend leading for the fabrication of elastic materials. Presence of templated PANI's in the film helps in retaining

the tensile strength. Such blends might find their applications as optical, semiconducting materials and as organic vapor sensors.

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