The effect on poly (ethylene oxide) / poly (vinyl chloride) / polyaniline (PAni) films by ethylene dimethacrylate as surface modifier: electrical conductivity and characterization

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Abstract: In this paper, the electrical conductivity and the characterizations of poly (ethylene oxide) / poly (vinyl chloride) / polyaniline (PEO/PVC/PAni) films with and without the presence of Ethylene Dimethacrylate (EDMA) were investigated. The films were prepared using solution casting method using tetrahydrofuran as the solvent. The results indicated that the electrical conductivity of PEO/PVC/PAni films increased as the PAni loadings increased while PEO/PVC/PAni films with EDMA showed higher electrical conductivity than PEO/PVC/PAni films. PEO/PVC/PAni films with EDMA showed a value as high as 0.68 x 10⁻⁴ S/mm as it enhanced the interfacial adhesion between the matrix and the filler as proved by the SEM morphology. Meanwhile, the FTIR analysis confirmed there are no new chemical bonding occurred with the introduction of EDMA into the films.

1. Introduction

Intrinsically conducting polymers (ICPs) have caught many recognition due to their exclusive physicochemical properties and huge potential in applications [1-6]. Among numerous ICPs, polyaniline (PAni), polypyrrole (PPy) and polythiopene (PTh) are favorable to be applied in practical application as they acquire a combination of unique chemical and physical processes besides enough stability at normal processing conditions [1,2,7]. PAni itself has been extensively studied as it holds many advantages compared to many other ICPs such as ease of synthesis, high electrical conductivity, decent environmental stability, fast oxidation-reduction reactions and relatively cheap [8].

However, PAni still has some deficiencies that need to overcome which hindered their commercial potential. Poor mechanical properties and difficulties in processing are some of the drawbacks that require attention [9]. Various approaches have been reported to solve these shortcomings in the last three decades. One of the favorable way to counter these issues is by polymer blending [10]. Synthesis of PAni with poly (vinyl chloride) (PVC) for example, can be reflected as versatile and efficient method for exploiting PAni and reducing its shortcoming [11, 12]. Likewise, the potential of poly (vinyl chloride) (PVC) and poly (ethylene oxide) (PEO) as matrix will be analyzed in this study with PAni as a function of conductive filler. In addition, solution casting which offers simplicity in processing and also cost effective is chosen as the preferred fabrication method. Studies on PEO and PVC blend have been reported as the blend offers one important criteria in polymer blend, which is miscibility [13-16]. PVC is one of the major commercial polymer which provides low cost, chemical stability, application versatility and also biocompatible [17]. Furthermore, PVC has competent compatibility with many types of plasticizers besides easiness in processability.

On the other hand, PEO is one of the most frequently studied polymer in this field as PEO can dissolve huge capacity of inorganic salts homogeneously [18] and ether oxgens in PEO makes it able
to hold large dipole moment. These unique properties of PEO is very useful in helping PAni to transfer its electrical conductivity.

On the other hand, the integration of filler into matrix will typically resulting in deficiencies of matrix/filler interfacial adhesion. This phenomenon affected the properties of composites and common method to enhance the interfacial adhesion is by utilizing surface modifier or chemical treatment. These methods helps to modify the composites surface and consequently improve the transfer of electrical conductivity in the composites [19]. Ethylene dimethacrylate (EDMA) were used in this paper to represent the effect of surface modifier on the properties of PEO/PVC/PAni films. In short, the effect of PAni and EDMA were analyzed on PEO/PVC/PAni films according to the electrical conductivity properties, morphology and Fourier Transform Infrared (FTIR) study.

2. Materials
PAni in emeraldine salt form with 20 wt% of carbon black has the particle size of 21 µm was brought from HmBG Co. Inc. PEO with 100,000 g/mol molecular weight and PVC powder with molecular weight of 220,000 g/mol were applied in this study as the matrix were obtained from AR Alatan Sdn. Bhd., Kedah, Malaysia. The solvent used, tetrahydrofuran, with molecular weight of 72.11 g/mol was analytical grade from Sigma Aldrich. Diocyl terephthalate with molecular weight of 390 g/mol was used as a plasticizer was provided by AR Alatan Sdn. Bhd., Kedah, Malaysia. Ethylene dimethacrylate with the density of 1.05 g/mL and molecular weight of 198.22 g/mol was obtained from Fisher science.

3. Methods

3.1 Samples Preparation
Two types of films were prepared, PEO/PVC/PAni films and PEO/PVC/PAni films with EDMA were fabricated using solution casting technique. The ratio of PEO/PVC was fixed at 40/60, and these materials were incorporated with PAni loading from 2.5 wt% to 10 wt%. First, PEO and PVC were dissolved in THF in a separate beaker. The fully dissolved PEO and PVC were then mixed and stirred at 400 rpm. Afterward, DOTP, EDMA and 2.5 wt% of PAni were poured into the PEO/PVC solvent and were continuously stirred for another 4 hours to reach homogenous solution. Lastly, the solvent were poured onto a mold and left to dry under controlled conditions. Similar procedures were used to fabricate another films with PAni loadings of 5 wt%, 7.5 wt% and 10 wt%. The formulations for PEO/PVC/PAni films and PEO/PVC/PAni/EDMA films are shown in Table 1.

| Conductive films code | PEO/PVC (wt%) | DOTP (wt%) | PAni (wt%) | EDMA (wt%) |
|------------------------|---------------|------------|------------|------------|
| PEO/PEO                | 85            | 15         |            |            |
| PEO/PVC/PAni -2.5      | 82.5          | 15         | 2.5        |            |
| PEO/PVC/PAni -5        | 80            | 15         | 5          |            |
| PEO/PVC/PAni -7.5      | 77.5          | 15         | 7.5        |            |
| PEO/PVC/PAni -10       | 75            | 15         | 10         |            |
| PEO/PVC/PAni /EDMA-2.5 | 76.5          | 15         | 2.5        | 6          |
| PEO/PVC/PAni /EDMA-5   | 74            | 15         | 5          | 6          |
| PEO/PVC/PAni /EDMA-7.5 | 71.5          | 15         | 7.5        | 6          |
| PEO/PVC/PAni/EDMA-10   | 69            | 15         | 10         | 6          |

3.2 Electrical Conductivity Test
4 point probe technique was performed via Keithley Model 4200 semiconductor characterization system to determine the electrical conductivity value. The value of the electrical conductivity were figured out via the relationship with resistivity such illustrated using Eq. (1) and Eq. (2):

$$\rho = R \left( \frac{w \times l}{t} \right)$$  \hspace{1cm} (1)

where $R = \text{resistance of the films}$, $w = \text{width}$, $t = \text{thickness}$, $l = \text{length between the metal probe contact}$, and the conductivity, $\sigma$, was calculated using the Eq. (2):

$$\sigma = \frac{1}{\rho}$$  \hspace{1cm} (2)

### 3.3 Scanning Electron Microscopy (SEM)

The morphology of the PEO/PVC/PAni films and PEO/PVC/PAni/EDMA films were carried out by using model JOEL JSM-6460LA. The samples undergo a thin palladium layer of 20 nm sputtering coating. The surface of the films were coated to inhibit electrostatic charges during the analysis. The morphology were examined at 400x magnification and 10 kV.

### 3.4 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra of the films were established with Perkin-Elmer Spectrum 400 Series equipment using attenuated total reflectance (ATR) technique. The spectra of % transmittance versus wavelength (cm\(^{-1}\)) were analyzed at room temperature with scanning range of 650 cm\(^{-1}\) to 4000 cm\(^{-1}\).

### 4. Results and Discussion

#### 4.1 Electrical Conductivity

Figure 1 displays the effect of PAni loadings on the electrical conductivity of PEO/PVC/PAni films and PEO/PVC/PAni/EDMA films. Increasing of PAni loading on the PEO/PVC matrix improved the films conductivity and lead to percolation threshold at 10 wt% of PAni loading. This could be explained by the ability of intrinsically conducting polymer, PAni, to transmit the electrical conductivity into the PEO/PVC matrix. Moreover, as the filler loading increase, the gap between PAni particles will become narrower which will subsequently create conductive paths. As a results, electrons will effortlessly transmitted in films and enhanced the electrical conductivity of PEO/PVC/PAni films and PEO/PVC/PAni/EDMA films. In a study reported by Merlini et al., the presence of PAni in PAni-coated coconut fibers exhibited significant rise in electrical conductivity as PAni provides the conductivity through its conjugated backbone [20].

At a similar composition, PEO/PVC/PAni/EDMA films exhibited higher electrical conductivity than PEO/PVC/PAni films. The improved conductivity of the films is credited to the enhanced distribution of PAni in the films as a results of EDMA incorporation. The results is in line with Castillo- Castro et al. as they reported that the addition of 5 wt % polyethylene-graft-maleic anhydride (PEGMA) as a coupling agent improve the conducting paths organization of PAni in low density polyethylene / n-dodecylbenzene sulfonate doped polyaniline films [21].
Figure 1. Electrical conductivity of PEO/PVC/PAni films and PEO/PVC/PAni/EDMA films at different filler loadings.

4.2 Morphology analysis
Figure 2 (a-e) explains the morphologies of PEO/PVC/PAni films with the effect of different loading of PAni and the effect of EDMA presence to the films. Figure 2a proves that the blend of PEO and PVC is miscible as the figure exhibits a smooth surface as expected. The finding is in line with other researchers such as Ramesh et al. that claimed PEO and PVC produced a miscible blend. Figure 2b and 2c present the effect of filler loading on the films with 5 wt% and 10 wt% PAni loading respectively [15]. PEO/PVC/PAni-5 wt% (Figure 2b) displays a better distribution of PAni and less visible PAni agglomeration compared to PEO/PVC/PAni-10 wt% (Figure 2c). PAni agglomeration at higher loadings is understandable as fillers have a tendency for filler-filler interaction rather than matrix-filler interaction [22]. Meanwhile, the addition of EDMA into the films (Figure 2d and Figure 2e) demonstrates lower filler agglomerations and better filler distribution at high PAni loading compared to the films without EDMA addition (Figure 2b and Figure 2c). EDMA improves the interfacial adhesion between the matrix and the filler and rearrange the conductive path in the films which explains the improvement on electrical conductivity of PEO/PVC/PAni/EDMA films.

![Figure 1](image1.png)

![Figure 2](image2.png)
a) PEO/PVC
b) PEO/PVC/PAni – 5

c) PEO/PVC/PAni – 10

d) PEO/PVC/PAni–5/EDMA

e) PEO/PVC/PAni–10/EDMA

Figure 2 (a-e). SEM morphology of PEO/PVC/PAni films and PEO/PVC/PAni/EDMA films at different filler loadings.

4.3 Spectroscopy Infrared Analysis

The FTIR spectra of PEO/PVC/PAni films and PEO/PVC/PAni/EDMA films are presented in Figure 3. The spectra shows no striking peak from 1750 to 2800 cm\(^{-1}\) but C-N stretching of secondary aromatic amine is detected at the medium intensity band of 1465 cm\(^{-1}\). On the other hand, a peak at 1278 cm\(^{-1}\) is spotted which signals to the PAni polaronic structure. The bands corresponding to the in-plane and out-of-plane C-H stretching appears at 962 cm\(^{-1}\) and 842 cm\(^{-1}\) while the band at 731 cm\(^{-1}\) are related to The C-Cl stretching. The FTIR spectra indicates that the presence of EDMA in films did not generate any new functional group. It shows that EDMA only enhanced the matrix-filler interfacial adhesion physically without creating any chemical interactions.
5. Conclusion
The addition of PAni and EDMA in PEO/PVC/PAni films significantly increased the electrical conductivity of the films. PEO/PVC/PAni films with EDMA exhibit better dispersion of PAni in the PEO/PVC matrixes compared to the films without EDMA, as evidenced by the morphological study using SEM. The FTIR spectra also confirms that there is no new functional group created with the addition of EDMA in the films.

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Figure 3. FTIR spectra of PEO/PVC/PAni films and PEO/PVC/PAni/EDMA films.
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