

Enhancement of Electrical Conductivity and Tensile Properties of Conductive Poly(vinyl Chloride)/Poly(ethylene Oxide)/Polyaniline Conductive Composite Films: Effect of Polyaniline Loading and Ethylene Dimethacrylate

Mohammed Izzuddeen Mohd. Yazid,¹ Supri A. Ghani,² Azlin Fazlina Osman^{1*}
and Siti Hajar Mohd. Din¹

¹School of Materials Engineering, Universiti Malaysia Perlis (UniMAP),
Jejawi-2 School Complex, Taman Muhibbah, 02600 Jejawi,
Arau, Perlis, Malaysia

²Faculty of Engineering Technology, Universiti Malaysia Perlis (UniMAP),
Level 1, Blok S2, UniCITI Alam Campus, Sungai Chuchuh,
02100 Padang Besar, Perlis, Malaysia

*Corresponding author: azlin@unimap.edu.my

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ABSTRACT: *The effect of ethylene dimethacrylate (EDMA) as a surface modifier and polyaniline (PAni) loading on poly(vinyl chloride) (PVC)/poly(ethylene oxide) (PEO) matrix was investigated. PVC/PEO conductive composite films with different PAni loading were fabricated using solution casting technique. The inclusion of EDMA exhibited higher tensile strength, modulus of elasticity and electrical properties for all filler loadings of PVC/PEO/PAni conductive composite films. The scanning electron microscopy (SEM) morphology indicated that the inclusion of EDMA in conductive films provided decent fillers dispersion in the PVC/PEO phases. The structural modifications, if occurred, will be interpreted with the assistance of FTIR spectroscopy.*

Keywords: Poly(vinyl chloride), poly(ethylene oxide), polyaniline, ethylene dimethacrylate, PAni

1. INTRODUCTION

Intrinsically conducting polymers (ICPs) exhibit good electrical, magnetic and optical properties that could be utilised to catalyse scientific discoveries and develop technical applications. Despite these attractive potentials, low mechanical characteristics and drawbacks in fabricating have hindered their commercial capacities.¹ Numerous methods have been established to counter these drawbacks in the past three decades. A promising method to promote the processability of these polymers is by blending conventional polymers with conductive polymers.² Polymer blending is a great way to manipulate materials to produce various properties of polymers. Moreover, polymer blending is one of the leading modern-day methods to establish new polymeric materials and it is a beneficial method to produce polymers with various properties. In this study, poly(vinyl chloride) (PVC) and poly(ethylene oxide) (PEO) acted as the matrix which will be incorporated with polyaniline (PAni) as the filler. Solution casting technique will be used to fabricate the PVC/PEO/PAni conductive composite films and this method is known for its ease of processing and is cost efficient. On the contrary, a more popular method, i.e., melt mixing is apparently more expensive and requires a higher work load.

PVC as a significant commercial polymer has been studied and consumed widely in industrial fields for countless years. PVC is chosen as a polymer matrix as it is inexpensive, has vast applications, is biocompatible and exhibits high chemical stability.³ In addition, it holds the advantages of easy processability, decent compatibility with various plasticisers, and forms miscible blend with PEO. PEO, however, has been commonly applied as polymer matrix as PEO holds large dipole moment, owing to its ether oxygens. Furthermore, PEO is capable of dissolving a great volume of inorganic salts homogeneously and without the need of low molecular weight solvent.⁴ The blends of PVC/PEO have been extensively deployed as a matrix in polymer electrolytes system.

Nowadays, studies on the blending of polymer with conductive polymer are growing as the application has been substituting metals in many applications. The most frequently studied categories of conducting polymer were polyacetylene, polypyrrole, polythiophene and PAni.⁵ However, studies on the ability of natural fibres to conduct electric were still reported as reviewed by Al-Oqla et al.⁶ They reported that even the maximum conductivity of conductive polymer composites filled with natural fibres was lower compared to the intrinsically conducting polymers. The improvement in the conductivity of the natural fibres remains a problem to be figured out. In principle, the dielectric properties of natural fibre conductive composites are critically reliant on the nature and size of the fibres

whereas the chemical treatments of fibres cause the dielectric constant of the composites to drop.

Among the conducting polymers, PANi is emerging as the favoured choice for many applications. PANi shows decent electrical, chemical and optical characteristics, which are related to PANi's conducting and insulating forms. In spite of these exciting properties, PANi has two major limitations. First, this conducting polymer has poor mechanical properties and second, it is also difficult to process via conventional methods. However, these drawbacks can be reduced by forming PANi composites which incorporate the matrix's good mechanical properties with PANi's decent electrical properties. Note that a blend or composite is the preferred term used if polymer acts as the matrix. On the contrary, for non-polymer matrix such as metal, it is preferable to use the term composite.⁷ It has the potential applications in electromagnetic shielding, sensor materials, conducting glues and electricity dissipation.

The homogeneity of matrix/filler generally affects the properties of polymer composites. One way to enhance the filler dispersion is by using chemical treatment or surface modifier. This leads to the improvement of film surface which subsequently aids the transmission of electrical conductivity in polymer matrix.⁸ This study investigated the effect of PANi inclusion besides the effect of ethylene dimethacrylate (EDMA) into PVC/PEO blends. In particular, tensile test, scanning electron microscopy (SEM) analysis and electrical conductivity test were carried out.

2. EXPERIMENTAL

2.1 Materials

Two matrixes were used in this study, which is PVC and PEO. First, PVC powder with molecular weight of $220,000 \text{ g mol}^{-1}$ and PEO powder with $100,000 \text{ g mol}^{-1}$ molecular weight were used as the matrix. The conducting filler, PANi, encompassing emeraldine salt with 20 wt% of carbon black has the particle size of $21 \text{ }\mu\text{m}$. Tetrahydrofuran with molecular weight of 72.11 g mol^{-1} was chosen to dilute the PVC/PEO matrix. Dioctyl terephthalate with molecular weight of 390 g mol^{-1} was used as a plasticiser. Finally, ethylene dimethacrylate with the density of 1.05 g ml^{-1} and molecular weight of $198.22 \text{ g mol}^{-1}$ was acquired from Fisher Science.

2.2 Sample Preparation

The PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive composite films with 2.5 wt%, 5 wt%, 7.5 wt% and 10 wt% filler loading were fabricated via solution casting method. The matrixes, PVC and PEO were first dissolved in tetrahydrofuran (THF) solvents at ambient temperature. After both matrixes were completely dissolved, the solvent was mixed together and then stirred at 400 rpm to achieve a uniform mixture. Next, the solvent was mixed with dioctyl terephthalate (DOTP), PAni and EDMA. The solution was stirred using a magnetic stirrer for 4 h at 400 rpm at ambient temperature to reach the preferred viscosity with homogeneous solution. Finally, the solution was then poured onto a glass mold and let to dry in a fume hood. A similar method was used to prepare thin films for all different ratios of PAni loading as displayed in Table 1.

Table 1: Formulations of the PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive composite films with different polyaniline loading.

Conductive composite films	PVC/PEO (60:40) (wt%)	DOTP (wt%)	PAni (wt%)	EDMA (wt%)
PVC/PEO	85	15	–	–
PVC/PEO/PAni-2.5	82.5	15	2.5	–
PVC/PEO/PAni-5	80	15	5	–
PVC/PEO/PAni-7.5	77.5	15	7.5	–
PVC/PEO/PAni-10	75	15	10	–
PVC/PEO/PAni/EDMA-2.5	76.5	15	2.5	6
PVC/PEO/PAni/EDMA-5	74	15	5	6
PVC/PEO/PAni/EDMA-7.5	71.5	15	7.5	6
PVC/PEO/PAni/EDMA-10	69	15	10	6

2.3 Tensile Test

The mechanical properties of the conductive films with or without EDMA were determined via tensile test. ASTM D638 with the crosshead speed of 30 mm min⁻¹ were carried out using Instron 5569 machine. At least five rectangular shaped specimens were examined for every sample ratio.

2.4 SEM

The morphology of PVC/PEO/PAni conductive composite films with or without EDMA were executed using JEOL JSM-6460LA SEM. First, all samples were immersed in toluene for 46 h at ambient temperature. The extracted samples were

then dried to remove any moisture. Next, the samples were mounted on a standard specimen stubs before being subjected to sputtering coating to prevent electrostatic charging during testing.

2.5 Electrical Conductivity Test

Electrical conductivity test was carried out via Keithley Model 4200 semiconductor characterisation system with the voltage set from 0 V to 10 V. The electrical conductivity of the conductive films was determined using its relationship with resistivity such demonstrated using the Equations 1 and 2:

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

where R = resistance of the films, w = width, t = thickness, l = length between the metal probe contact, and the conductivity, σ , was calculated using the Equation 2:

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

3. RESULTS AND DISCUSSION

3.1 Tensile Properties

The tensile strength values versus PANi loading of PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive composite films were represented in Figure 1. Both types of conductive films show a decreasing trend when PANi loading increased. This can be explained by the incorporation of PANi into the conductive films which PANi then failed to support the stress transfer from the PVC/PEO phase. Greater amount of filler led to large particle formation caused by the filler's lack of ability to properly disperse. The PANi agglomeration taking place increased the stress-concentration points in the conductive films which resulted in tensile failure at lower strain. The same finding was reported by Chipara et al. who studied the tensile behaviour of PANi and low-density polyethylene (LDPE) blend.⁹ On the other hand, better tensile strength was noticeable with the presence of EDMA on the PVC/PEO/PAni conductive composite films. It is understandable that the integration of EDMA in the conductive composite films upgraded the filler-matrix interfacial adhesion as agreed by Roy et al. who found a similar trend in their research.¹⁰ The addition of ethylene glycol dimethacrylate showed further increase of tensile strength in the coir fibre-reinforced ethylene glycol dimethacrylate (EGDMA)-based composite.

Figure 2 compares the Young's modulus of PVC/PEO/PAni with PVC/PEO/PAni/EDMA conductive composite films at various filler loadings. The graph indicates that the values of Young's modulus escalate with the increment of filler. The increasing trend of Young's modulus was facilitated by the transferring of PAni's stiffness into the conductive films. Ramesh et al. investigated the mechanical behaviour of PVC/PEO-based electrolytes for lithium polymer cell and they found that the addition of silica improved the Young's modulus of the composites.¹¹ Silica interrupted the polymer chains, turning the composites to be more rigid and higher in stiffness, making the PVC/PEO based electrolytes harder to stretch. In addition, the EDMA added conductive films exhibited a greater Young's modulus than the PVC/PEO/PAni conductive composite films. The improvement of filler dispersion is resulted by the presence of EDMA which subsequently increased the Young's modulus. This finding was supported by fellow researchers such as Jagtap et al. where they reported an approximately 67% rise in the tensile modulus when half neutralised adipic acid (modifier) developed better dispersion of fillers in PEO matrix.¹²

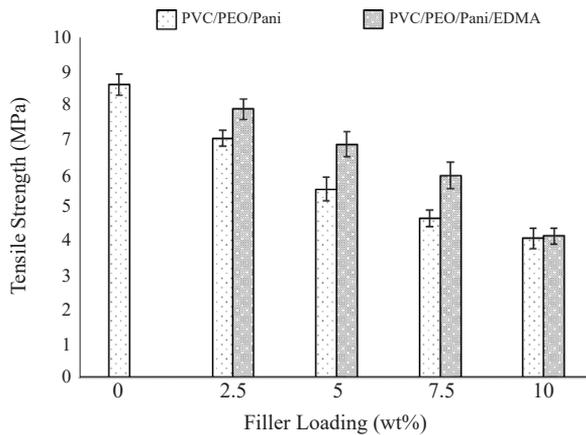


Figure 1: Tensile strength vs. filler loading of PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films.

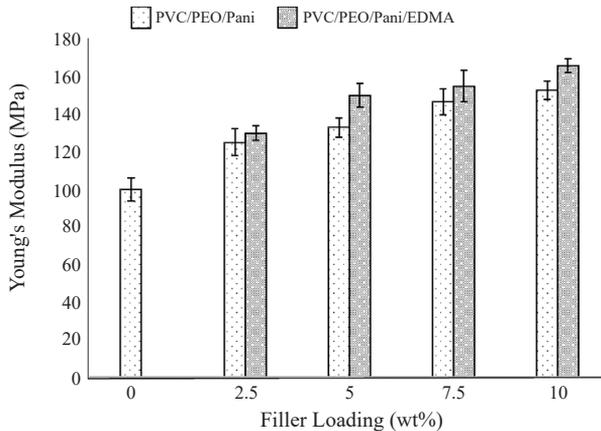


Figure 2: Young's modulus vs. filler loading of PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films.

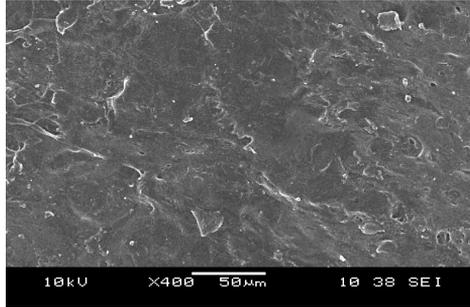
3.2 Morphology Analysis

The morphologies of PVC/PEO holding different filler loading of PANi with or without EDMA were shown in Figure 3. From the figure, it can be seen that the soaked conductive films filled with PANi created holes due to the extraction of PANi using toluene. The PVC/PEO blend shows smooth surface morphology, confirming that PVC and PEO are miscible blends. This result corroborates findings by Silva et al. which discovered that the blends of PEO and PVC are miscible.¹³ Figures 3(b) and 3(c) show the morphologies of PVC/PEO/PAni 5 wt% and 10 wt% while Figures 3(d) and 3(e) show the morphologies of PVC/PEO/PAni/EDMA conductive composite films. At 5 wt%, both types of conductive film exhibit good distribution of fillers and establish smooth surfaces on the films. However, at 10 wt% loading, filler agglomeration is visible as the result of matrix-matrix interaction. Supri et al. explained that PANi agglomeration at higher loadings tended to happen due to the tendency for filler-filler interaction rather than matrix-filler interaction.¹⁴ On the other hand, the presence of surface modifier on the composite films, as illustrated in Figures 3(d) and 3(e), shows improved distribution and dispersion, suggesting low formation of agglomerations at high PANi loading.

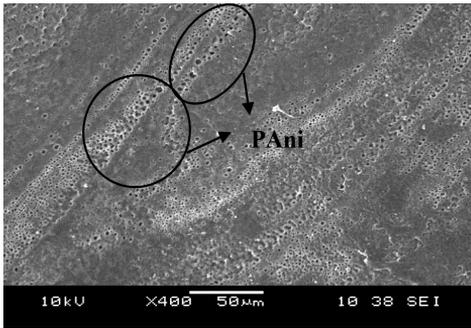
3.3 Electrical Conductivity

Figure 4 shows the electrical conductivity patterns of PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive composite films. It indicates that both sets of conductive film show positive improvement of conductivity as the filler loading escalates. This is caused by the conductive path occurrence as the space between

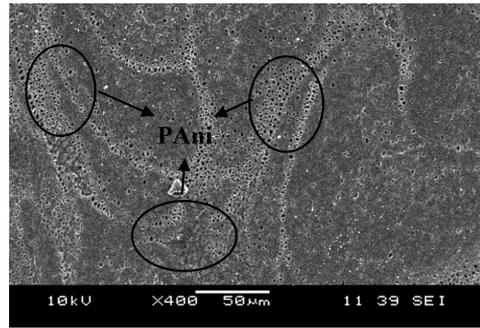
the conducting filler becomes narrower. This helps the electrons to easily flow through the films thus giving rise to the electrical conductivity of the conductive films. Merlini et al. stated that the incorporation of PAni-coated coconut fibres as the conductive fillers enhances significantly the electrical conductivity owing to the establishment of conducting pathways.¹⁵



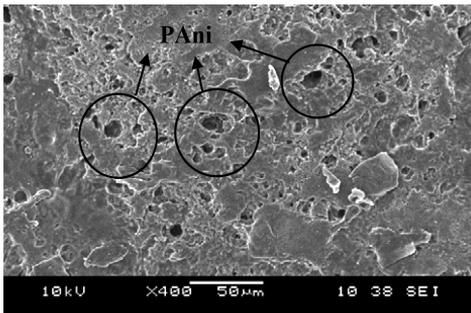
a) PVC/PEO



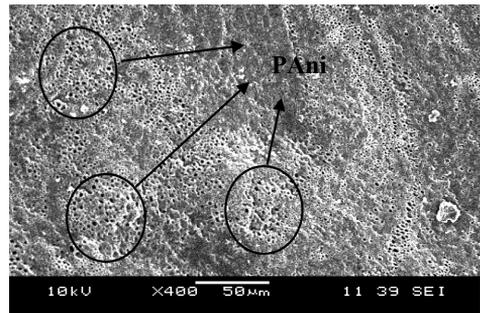
b) PVC/PEO/PAni – 5



d) PVC/PEO/PAni/EDMA – 5



c) PVC/PEO/PAni – 10



e) PVC/PEO/PAni/EDMA – 10

Figure 3: SEM morphology of extracted surface of PVC/PEO, PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films at different filler loadings.

On the other hand, the improved electrical conductivity of PVC/PEO/PAni/EDMA conductive composite films in Figure 4 can be associated to better distribution of PAni as a result of EDMA. Castillo-Castro et al. stated in their study that the coupling agent performed a significant part in the conducting paths' organisation.¹⁶ The electrical conductivity of low-density polyethylene/n-dodecylbenzene sulfonate doped PAni films significantly improved with 5 wt% polyethylene-graft-maleic anhydride (PEgMA), presenting an adequate improvement for greater filler contents.

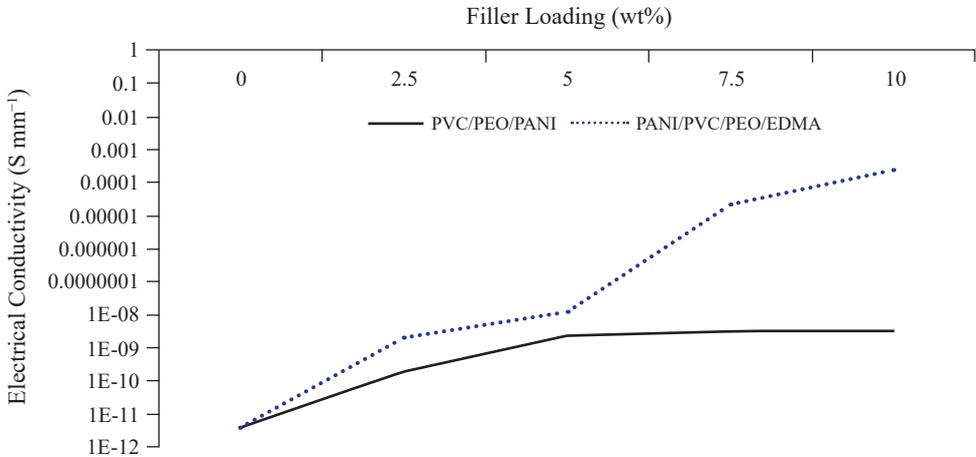


Figure 4: Electrical conductivity of PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films at different filler loadings.

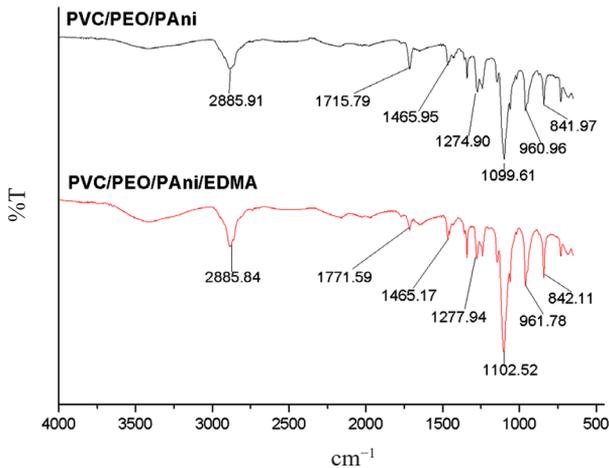


Figure 5: Infrared spectroscopy spectra of PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films.

3.4 Spectroscopy Infrared Analysis

Figure 5 signifies the FTIR spectra of PVC/PEO/PAni/EDMA conductive composite films. No striking peaks are witnessed around 1750 cm^{-1} to 2800 cm^{-1} . The medium intensity band appearing at 1465 cm^{-1} corresponds to the C-N stretching of secondary aromatic amine. The band at 1278 cm^{-1} is assigned to the PAni polaronic structure. The bands at 962 cm^{-1} and peak at 842 cm^{-1} correspond to the in-plane and out-of-plane C-H stretching. The C-Cl stretching has been confirmed through the absorption band at 731 cm^{-1} .¹⁷ In brief, the PVC/PEO/PAni/EDMA conductive composite films spectra fail to prove any establishment of new functional groups. The analysis confirms that EDMA only made physical interaction of filler-matrix. The illustrated mechanism of EDMA and PAni with PVC/PEO matrix is shown in Figure 6.

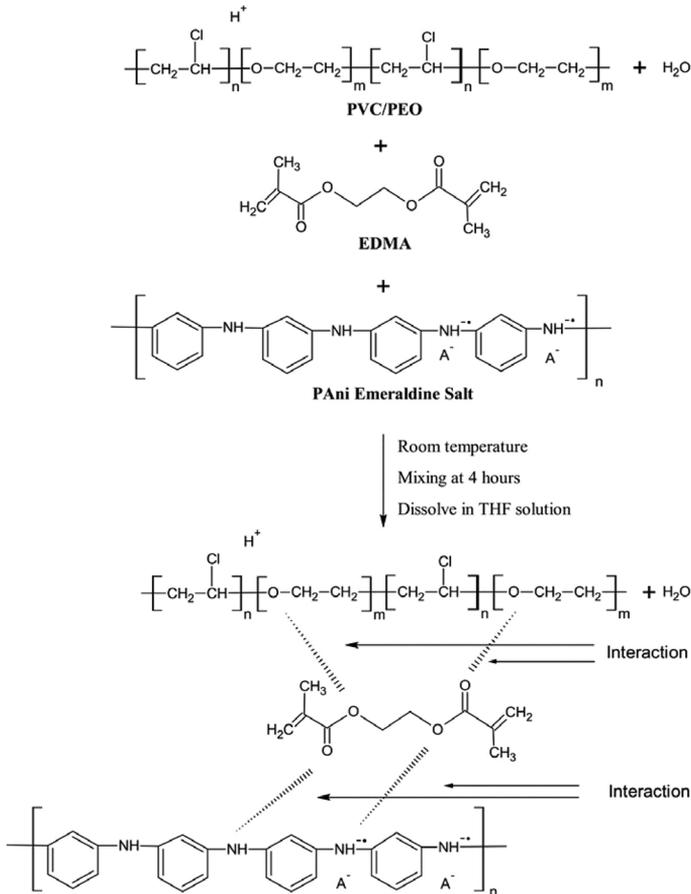


Figure 6: Illustrated mechanism of EDMA and PAni with PVC/PEO matrix.

4. CONCLUSION

The introduction of EDMA in PVC/PEO/PAni conductive composite films improves its tensile properties by an average of 16.16%. SEM supports the data by showing improved filler distribution of PVC/PEO/PAni/EDMA conductive composite films. The surface modifier also gives rise to the PVC/PEO/PAni/EDMA conductive composite films electrical conductivity which reach as high as $0.68 \times 10^{-4} \text{ S mm}^{-1}$. The FTIR test reveals no new functional group developed with the addition of EDMA into the conductive films.

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