Utilization of Polyaniline (PAni) as Conductive Filler on Poly (Ethylene Oxide) / Poly (Vinyl Chloride) Films: Effects of Naphthalene as Surface Modifier on Electrical Conductivity

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Abstract: The aim of the study was to utilize polyaniline (PAni) as conductive filler in poly (ethylene oxide) / poly (vinyl chloride) (PEO/PVC) films. Naphthalene was used as surface modifier to increase the properties of PEO/PVC/PAni films. The electrical conductivity of PEO/PVC/PAni film improved with higher loading of PAni until it reached the percolation threshold at 10 wt%. Moreover, the conductivity of the films also improved with the addition of naphthalene compared to the films without naphthalene. These enhancements were due to the improved interfacial bonding between PEO/PVC blend and PAni, which were supported by scanning electron microscopy (SEM) analysis. In addition, no new chemical bonding was created with the incorporation of naphthalene as proved by the FTIR analysis.

1. Introduction

Polymers typically do not conduct electricity and are used universally as an insulator. However, since the discovery of polyacetylene by Shirakawa and his fellow researchers, intrinsically conducting polymers (ICPs) such as polyaniline, polypyrrole and polythiophene have change the conventional perspective on polymers. Among numerous intrinsically conducting polymers available, polyaniline (PAni) has gain a great reputation as one of the most promising intrinsically conducting polymers (ICPs) due to its manageable electrical conductivity through protonation/deprotonation method, easiness to synthesis, good environmental stability and relatively inexpensive reagents [1].

However, despite all that, PAni still possess several issues that need to be solves to fulfill its high potential. PAni blending with commercially available polymers are one of the frequently practiced methods to overcome the drawbacks of PAni such as the processing difficulties and relatively poor mechanical properties [2,3]. This methods is advantageous when it comes to designing polymer products with wide variety of characteristics. Research on the blending of PAni with conventional polymers have been reported and have been proved to balance the good mechanical properties of polymers with good electrical conductivity of PAni [4,5]. In this study, poly (ethylene oxide) (PEO) and poly (vinyl chloride) (PVC) blend were chosen as the matrix to compliment PAni as the filler. The PEO/PVC/PAni films were fabricated via solution casting as this method offers cheap, easy and efficient processing.

PVC is one of the most utilized thermoplastic thanks to its application versatility, biocompatibility and chemical stability. Interestingly, for several decades, researchers have been developing and studying the ways to improve electrical conductivity of PVC. Such reports suggest several methods including blending with intrinsically conducting polymers (ICPs), coating of conductive layers onto PVC surfaces, and also incorporating liquid anti-static agents or conductive
inorganic filler into PVC [6-9]. Otherwise, PEO which is also used as a matrix in this paper, have been repeatedly reported as a promising material in this field. PEO is well known for its ability to dissolve large amount of inorganic salts homogeneously [10] and the ether oxygen of PEO also made it useful to hold large dipole moment. These features made PEO stand out from the rest as it facilitated the transfer of conductivity from intrinsically conducting polymers (ICPs) to PEO with ease. One significant criteria to consider when designing a new polymer is miscibility. Researchers had analyzed the miscibility of PEO and PVC and they all came out with the same conclusion which confirmed that PEO and PVC formed a miscible blend [11,12].

In contrast, filler incorporation into matrix usually disrupted the interfacial adhesion between matrix and filler. In order to overcome this drawback, several techniques such as chemical treatment or surface modifier were applied. These practices altered the surface of the filler or establishing new bonds respectively which in turn improved the electrical conductivity of the composites [13]. Naphthalene were used as a surface modifier on the properties of PEO/PVC/PAni films. In this paper, the effect of PAni loading and naphthalene as the surface modifier were discussed according to the electrical conductivity properties, morphology and Fourier Transform Infrared (FTIR) study.

2. Materials
PAni with the particle size of 21 µm was obtained in the form of emeraldine salt with 20 wt% of carbon black from HmBG Co. Inc. PEO (Mₐ of 100,000) and PVC (Mₐ of 220,000) used in this study were acquired from AR Alatan Sdn. Bhd., Kedah, Malaysia. The analytical grade of tetrahydrofuran (Mₑ of 72.11) was available through Sigma Aldrich. Dioctyl terephthalate (Mₑ of 390) used in this study as a plasticizer and were obtained via AR Alatan Sdn. Bhd. Naphthalene was acquired from a local shop in Kangar, Perlis, Malaysia.

3. Methods
3.1 Samples Preparation
To prepare the PEO/PVC/PAni films, required amount of PEO and PVC were dissolved individually in THF. The solution were stirred at ambient temperature until it became homogeneous. Later, DOTP and PAni and were integrated into the solution and were stirred with magnetic stirrer at 400 rpm for 4 hours. Noted for PEO/PVC/PAni/Naphthalene films, naphthalene were added together with DOTP and PAni at this stage. Lastly, the solution were left to evaporate at room temperature in fume cupboard for the film to form. The same procedures was repeated to prepare other films with different filler loading as displayed in Table 1.

Table 1: Formulations of the PEO/PVC/PAni films and PEO/PVC/PAni/Naphthalene films with different PAni loading.

| Conductive films code | PEO/PVC (40:60) (wt%) | DOTP (wt%) | PAni (wt%) | Naphthalene (wt%) |
|-----------------------|-----------------------|------------|------------|-------------------|
| PEO/PVO              | 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/Naphthalene-2.5 | 76.5 | 15     | 2.5      | 6              |
| PEO/PVC/PAni/Naphthalene-5 | 74       | 15     | 5        | 6       |
| PEO/PVC/PAni/Naphthalene-7.5 | 71.5       | 15     | 7.5      | 6          |
| PEO/PVC/PAni/Naphthalene-10 | 69       | 15     | 10       | 6          |

3.2 Electrical Conductivity Test
For the electrical conductivity measurement, 4 point probe technique was executed via Keithley Model 4200 semiconductor characterization system. The value were determined via the relationship with resistivity as displayed in Eq. (1) and Eq. (2):

\[ \rho = R \left( \frac{w \times t}{l} \right) \]  

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

\[ \sigma = \frac{1}{\rho} \]  

3.3 Scanning Electron Microscopy (SEM)
The morphology of the conductive films were analyzed via JEOL JSM-6460LA. The films were cut into square shaped sample to fit the dimension of the SEM aluminium stubs to determine the samples morphology. The samples must be coated first before the examinations can be carried out. The samples were coated with thin palladium layer to prevent 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 examined using attenuated total reflectance (ATR) technique via Perkin-Elmer Spectrum 400 Series equipment. The testing were operated from 650 cm\(^{-1}\) to 4000 cm\(^{-1}\) at room temperature.

4. Results and Discussion

4.1 Electrical Conductivity
Fig. 1 showed the electrical conductivity versus PAni loading of PEO/PVC/PAni films without and with naphthalene. The electrical conductivity was found to increase with the addition of PAni from 2.5 wt% to 10 wt%. The increment of PAni loading were related to the conducting path that occurred as PAni particles attracted to each other. This phenomenon resulted in improved efficiency of the electrons to flow in the films thus increased the conductivity. Merlini et al. also explained that PAni introduction in PAni-coated coconut fibers lead to increased electrical conductivity due to higher conducting pathway formed in the composites [14].

The incorporation of naphthalene, on the other hand, enhanced the electrical conductivity of PEO/PVC/PAni/Naphthalene films. The observations suggest that naphthalene improved the dispersion of PAni which subsequently enhanced the formation of conductive pathway in the films. Report by Kim and Jo, [15] analyzed the effect of naphthalene on electrical conductivity and their study concluded that a compatibilizer consisting naphthalene enhanced the dispersion of filler in the matrix. Moreover, the benzene ring in naphthalene structure also aided the interaction between PEO/PVC phase and and PAni which also helped to increase the electrical properties of the films.
4.2 Morphology analysis

The morphologies of the PEO/PVC/PAni films without and with naphthalene were recorded in SEM micrographs displayed in Fig. 2a-e. First, the morphology of PEO/PVC blend presented a smooth surface which pointed out that PEO and PVC formed a miscible blends. Moreover, from this micrograph, it can be understood that at 5 wt% of PAni loading, PAni were properly dispersed (Fig. 2b and d) while at higher filler loading (10 wt%), the SEM micrographs showed large agglomerates of PAni in the PEO/PVC blend (Fig. 2c and e). In short, at higher filler loading, PAni have a habit to agglomerate as it became harder to disperse in congested spaces.

On the other hand, the SEM micrographs of PEO/PVC/PAni/Naphthalene films (Fig. 2d and e) revealed better surface morphology than PEO/PVC/PAni films (Fig. 2b and c). The SEM micrographs presented good adhesion and fine dispersion between PEO/PVC blend and PAni filler which were verified by rough surface and less occupancy of the filler on the matrix surfaces. Furthermore, naphthalene developed strong chemical linkage between PEO/PVC phases and PAni to boost the interaction of matrix and filler which in turned formed good interfacial adhesion.
Figure 2. (a-e) SEM morphology of PEO/PVC/PAni films and PEO/PVC/PAni/Naphthalene films at different filler loadings.

4.3 Spectroscopy Infrared Analysis
Fig. 3 represented the FTIR spectra of PEO/PVC/PAni films without and with naphthalene. The peaks at 2885.91 cm\(^{-1}\) and 2886.33 cm\(^{-1}\) were assigned to CH\(_2\) asymmetric stretching which derived from PEO and PVC matrix. The band at 1715.79 cm\(^{-1}\) and 1771.13 cm\(^{-1}\) corresponded to the C=O stretching of PEO. The peaks at 1466.98 cm\(^{-1}\) and 1465.95 cm\(^{-1}\) were indicated to CH\(_2\) deformation while the absorption peak at 1342.28 cm\(^{-1}\) were attributed to CH\(_2\) vibration. Strong vibration of C-O structure was observed at 1278.77 cm\(^{-1}\) and 1274.90 cm\(^{-1}\). In addition to the above peaks, the spectrum recorded the C-O-C stretch at 1147.90 cm\(^{-1}\), 1103.54 cm\(^{-1}\), 1099.61 cm\(^{-1}\) and 1061.38 cm\(^{-1}\) and also the characteristics peaks of gauche conformation of [-CH\(_2\)-CH\(_2\)-] group from PEO at 962.69 cm\(^{-1}\), 960.96 cm\(^{-1}\) and 842.82 cm\(^{-1}\) and 842.82 cm\(^{-1}\). The peak at 732.59 cm\(^{-1}\) was attributed to the C-Cl stretching of PVC. In short, the FTIR spectra validated that the addition of naphthalene in
PEO/PVC/PAni/Naphthalene did not establish new functional group as naphthalene only created physical interaction between PEO/PVC blend with PAni. Fig. 4 displayed the proposed mechanism between matrix and filler with the presence of naphthalene.

Figure 3.: FTIR spectra of PEO/PVC/PAni films and PEO/PVC/PAni/Naphthalene films.
5. Conclusion
We executed the current research to relate the addition of PANi loading and naphthalene into the PEO/PVC blend by using electrical conductivity, SEM morphology and FTIR spectra. Electrical conductivity test revealed that the incorporation and PANi and naphthalene into the films increased the electrical conductivity values. PEO/PVC/PAni/EDMA films showed superior dispersion of filler in matrix compared to PEO/PVC/PAni films, as demonstrated by the SEM micrographs. The interaction of naphthalene between the PEO/PVC matrix and PANi filler did not formed any new functional group as sanctioned by the FTIR spectra.

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