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The Effect of Ethylene Dimethacrylate (EDMA) on Electrical Conductivity and Tensile Properties of Poly (Vinyl Chloride)/Poly (Ethylene Oxide)/Polyaniline (PAni) Conductive Films

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Abstract: *The effect of ethylene dimethacrylate (EDMA) as surface modifier and polyaniline (PAni) into poly (vinyl chloride) (PVC)/poly (ethylene oxide) (PEO) blends was studied. PVC/PEO conductive films with 2.5, 5, 7.5 and 10 wt % of PAni were prepared using solution casting technique. The addition of EDMA showed higher electrical properties, tensile strength and modulus of elasticity for all compositions of PVC/PEO conductive films. Scanning electron microscopy (SEM) results show that the addition of EDMA in conductive films gives good fillers dispersion in the PVC/PEO/PANI conductive films.*

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

1. INTRODUCTION

Intrinsically conducting polymers (ICPs) receive great attention worldwide thanks to their novel electronic and electrical properties. They offer very exciting electrical, magnetic and optical properties which can be used to develop scientific knowledge and technological applications. Despite these attractive potentials, poor mechanical properties and processing difficulties have hindered their commercial use.[1] Numerous techniques have been developed to overcome these limitations in the past three decades. One of the most successful methods is the coating of conducting polymers such as polyaniline (PAni) or polypyrrole (PPy) onto filler surfaces. ICP-coated fillers can be normally prepared through the in situ oxidative polymerisation of aniline or pyrrol in the existence of a suitable filler using an appropriate oxidant[2] or an electrochemical technique.[3]

Polymer blending is a great technique for designing materials with variety of properties. Compounding of conductive particles with nonconductive polymer is the most commonly used method for making conductive polymer composites. Normally, polymers are easily mixed with conductive fillers to form compounds with various properties and shapes. In this study, poly (vinyl chloride)/poly (ethylene oxide) (PVC/PEO) blends was incorporated with PAni. The PVC/PEO blend was prepared by solution casting technique which is low in cost and easy to process.

PAni shows good electrical, chemical and optical properties, which are associated with its conducting and insulating forms. However, two major limitations of polyaniline are its poor mechanical properties and the inability to process it by conventional methods. These drawbacks can be overcome by preparing polyaniline blends and composites which have the mechanical properties of the matrix and the electrical properties of the conducting polyaniline. Note that if the host is a polymer, the system is named a polyaniline blend (or composite), but if the host is a nonpolymer material (e.g. silica, metal oxides), it is invariably termed as a composite.[4] It has the potential applications in electromagnetic shielding, sensor materials, conducting glues and electricity dissipation.

The homogeneity of matrix/filler influenced the degradation of the mechanical properties of conductive polymer composites. Improved dispersion of fillers in the polymer matrix for conductive film can be accomplished by the modification of filler particles with chemical treatment and the addition of surface modifier. This leads to improve films surface to transmit conductivity in non-conductive polymer blends.[5] In this paper, the effect of ethylene dimethacrylate (EDMA) as surface modifier and PAni into PVC/PEO blends on the tensile properties and electrical conductivity were studied.

2. EXPERIMENTAL

2.1 Materials

PVC and PEO were used as matrixes in this study. The molecular weight of PVC powder used was 220,000 g/mol with the melting temperature of 100°C–260°C. PEO powders used consist of 100,000 g/mol of molecular weight and 65°C of melting temperature. PAni (emeraldine salt with 20 wt % of carbon black) used in this study is a commercial product with particle size of 21 μm, and melting point of 300°C. Tetrahydrofuran (72.11 g/mol of molecular weight and 66°C of boiling point) was used to dissolve PVC and PEO. It was obtained from AR Alatan Sdn. Bhd., Alor Setar, Kedah, Malaysia. Dioctyl terephthalate with molecular weight of 390 g/mol and melting point of –48°C was supplied by AR Alatan Sdn. Bhd. Ethylene dimethacrylate with density of 1.05 g/mL and molecular weight of 198.22 g/mol was purchased from Fisher science.

2.2 Conductive Films Preparation

The PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films were formed by using solution casting technique. First, PVC and PEO are dissolved individually in separate conical flask using THF solvent at room temperature. Afterwards, the dissolved PVC and PEO were mixed and stirred to achieve homogeneous solution. The amount of dioctyl terephthalate (DOTP) added into the mixture was fixed for all composition ratios. Then, PAni and EDMA were added into the solution after the DOTP were incorporated. The solution was allowed to stir for 4 h at 400 rpm at room temperature to achieve homogeneous solution and suitable viscosity for casting. The solutions were then casted onto a glass mold and were placed inside a fume cupboard at room temperature. The same method was used to prepare thin films for all different ratios of PAni loading as shown in Table 1.

2.3 Tensile Test

Tensile tests were carried out according to ASTM D638 by using Instron 5569 with crosshead speed of 30 mm/min. An average of five rectangular shaped samples were used for each conductive films. The tensile strength and Young's modulus of each of the films were attained.

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

Conductive films code	PVC/PEO (60:40) (wt %)	DOTP (wt %)	PAni (wt %)	EDMA (wt %)
PVC/PEO	79	15	–	–
PVC/PEO/PAni-2.5	76.5	15	2.5	–
PVC/PEO/PAni-5	74	15	5	–
PVC/PEO/PAni-7.5	71.5	15	7.5	–
PVC/PEO/PAni-10	69	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

Notes: PVC = poly (vinyl chloride); PEO = poly (ethylene oxide); PAni = polyaniline; EDMA = ethylene dimethacrylate

2.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) observation was carried out by using scanning electron microscope (SEM) model JEOL JSM-6460LA. The PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films were extracted with toluene for 46 h at room temperature. Before the examination of SEM, the samples were mounted on aluminium stubs and allowed to undergo sputtering coating. A thin palladium layer was sputter coated on the samples surfaces to avoid electrostatic charged during examination.

2.5 Electrical Conductivity Test

The electrical conductivity test of PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive film was analysed using two-probe I-V measurement system. The electrical conductivity were measured using Keithley Model 4200 semiconductor characterisation system with voltage varied from 0 to 10 V. The conductivity was calculated using its relationship with resistivity. The resistivity can be calculated using the Equation 1:

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

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:

$$\sigma = \frac{1}{\rho} \tag{2}$$

3. RESULTS AND DISCUSSION

3.1 Tensile Properties

The tensile strength of PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films is shown in Figure 1. The PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films showed a decreasing trend when PAni loading increased. This was due to the incorporating of fillers into the blend and the inability of PAni to support the stress transfer from the matrix, PVC/PEO blend. Larger amount of filler leads to larger particle formation due to the inability of filler to properly disperse. These large PAni particles increased the stress-concentration points in the blend which caused tensile strength failure at lower strain. The PVC/PEO/PAni/EDMA conductive films show a higher tensile strength compared to PVC/PEO/PAni conductive films. The presence of EDMA in the conductive film improved the interfacial adhesion between PVC/PEO blends and PAni. Roy et al.[6] also found a similar trend in their research. The addition of ethylene glycol dimethacrylate showed further increase of tensile strength in the coir fibre-reinforced ethylene glycol dimethacrylate (EGDMA)-based composite.

The Young's modulus of PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films at different fibre loading is presented in Figure 2. The Young's modulus increased as filler loading increased. This could be attributed to the ability of PAni to provide greater stiffness to the conductive films. Ramesh et al.[7] investigated the mechanical properties of PVC/PEO based polymer electrolytes for lithium polymer cell. They found that the Young's modulus improved with the addition of silica. The polymer chains become rigid and stiffened, making the composite polymer electrolytes harder to stretch. In addition, the PVC/PEO/PAni/EDMA conductive films have a greater Young's modulus than the PVC/PEO/PAni conductive film. The improvement of filler dispersion due to the presence of EDMA increase the Young's modulus. At a similar report by Jagtap et al.,[8] around 67% improvement in the tensile modulus was found when half neutralised adipic acid (modifier), improve the dipersion of multiwall carbon nanotube (filler) in PEO (matrix).

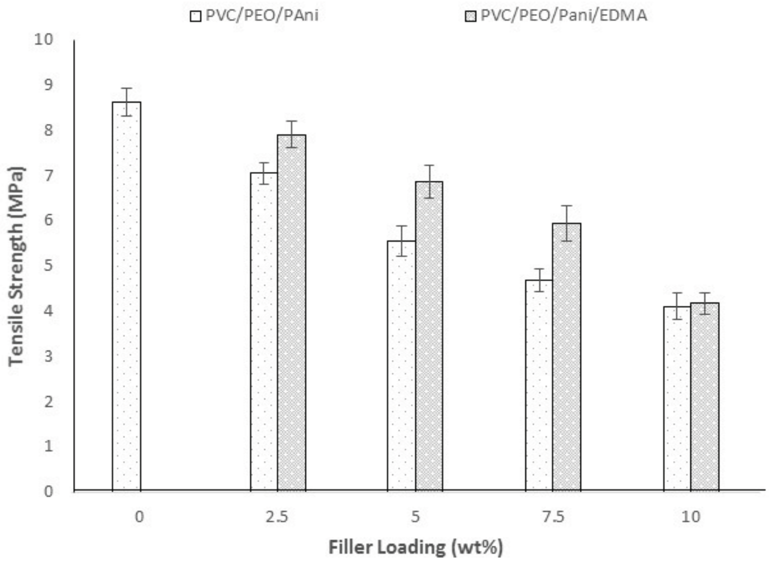


Figure 1: Tensile strength vs fibre loading of PVC/PEO/PAni conductive films and PVC/PEO/PAni/EDMA conductive films.

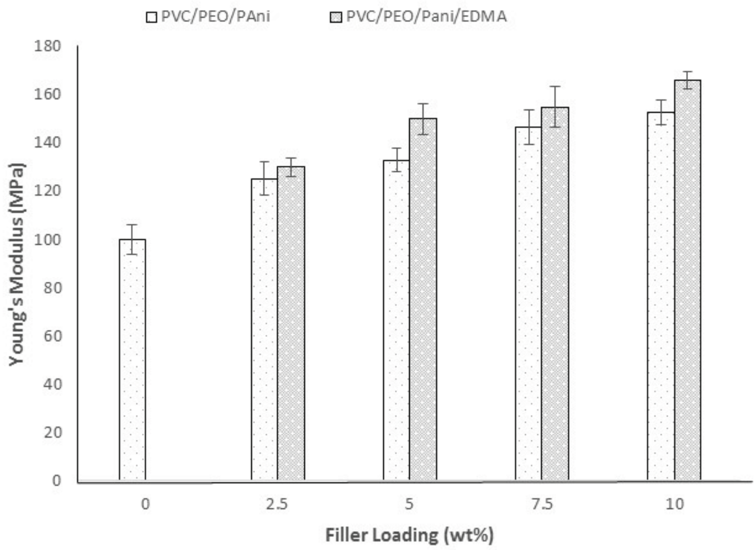
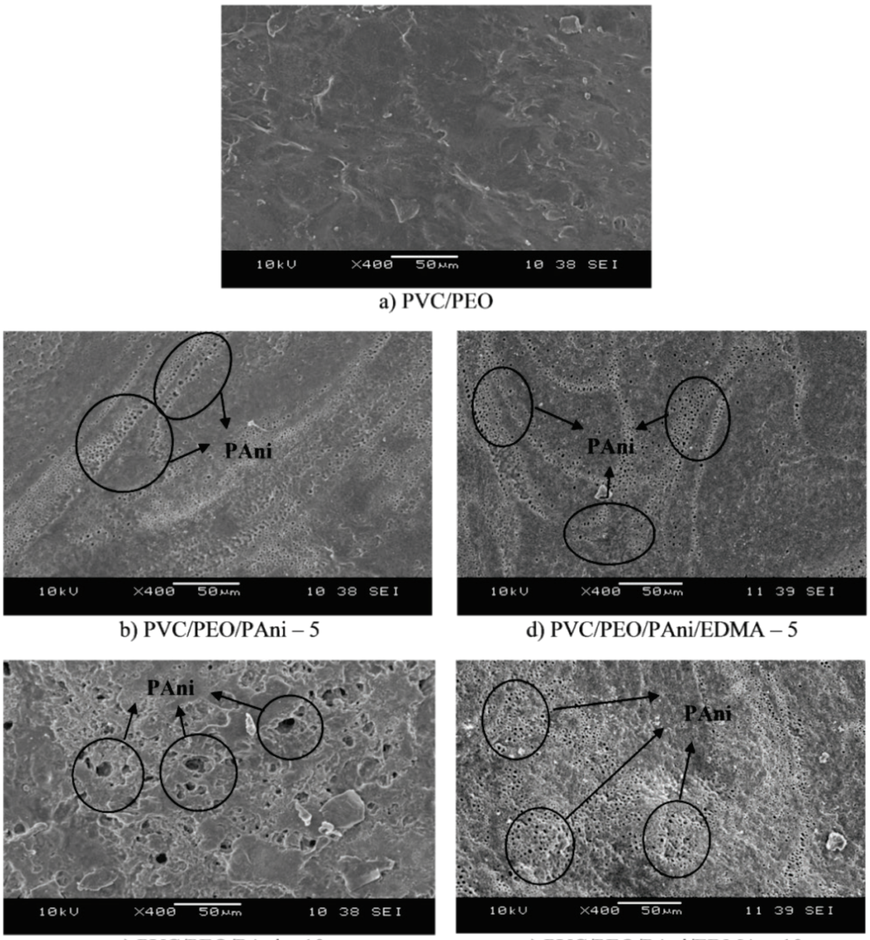


Figure 2: Young's modulus vs fibre loading of PVC/PEO/PAni conductive films and PVC/PEO/PAni/EDMA conductive films.

3.2 Morphology Analysis

Figure 3 shows the SEM micrograph of extracted surface of PVC/PEO, PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films with different filler loading. Figure 3(a) displays the surface morphology of the soaked PVC/PEO blends at ×400 magnification. Soaked conductive films filled with PAni create 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. Figures 3(b) and 3(c) show the micrograph of PVC/PEO/PAni without EDMA while Figures 3(d) and 3(e) show the micrograph of PVC/PEO/PAni conductive films containing EDMA.



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 (a–e): SEM morphology of extracted surface of PVC/PEO/PAni conductive films and PVC/PEO/PAni/EDMA conductive films at different fibre loadings.

Figures 3(b) and 3(d) indicate that PVC/PEO/PAni and PVC/PEO/PAni/EDMA conductive films at 5 wt % have good distribution of fillers and the formation of smooth surfaces on the extracted surface. At high filler loading, filler agglomeration is easily occurred due to the formation of matrix-matrix interaction. The agglomeration of PAni can be clearly seen in Figures 3(c) and 3(e). The extracted surface of PVC/PEO/PAni conductive films with addition of EDMA (Figures 3[d] and 3[e]) showed improved distribution and dispersion compared to PVC/PEO/PAni conductive films. The addition of EDMA on PVC/PEO/PAni conductive films reduces the formation of agglomerations on the surface of the film at high filler loading.

3.3 Electrical conductivity

Figure 4 displays the electrical conductivity of PVC/PEO/PAni and PVC/PEO/Pani/EDMA conductive films with different filler loading. The electrical conductivity of PVC/PEO/Pani and PVC/PEO/PAni/EDMA conductive films increased as the filler loading increased. This is due to the increase of conductive path occurred as the distance between the conducting particles, PAni, becomes narrower. This rises the conductivity of the films as the electrons are easily flow through filler and matrix. Merlini et al.[9] have reported that addition of PAni-coated coconut fibres as the conductive fillers enhances significantly the electrical conductivity because of the formation of a conducting pathway through the matrix.

The electrical conductivity of PVC/PEO/PAni conductive films improve with the addition of EDMA. The presence of EDMA stimulates better distribution of PAni on the surface of PVC/PEO/PAni/EDMA conductive films compared to PVC/PEO/PAni conductive films. Castillo-Castro et al.[10] stated in their study that the coupling agent played a significant role in the arrangement of conducting paths in the composite. The electrical conductivity of low density polyethylene/n-dodecylbenzene sulfonate doped polyaniline films drastically increased with 5 wt % polyethylene-graft-maleic anhydride (PEgMA), showing a moderate improvement for higher concentrations.

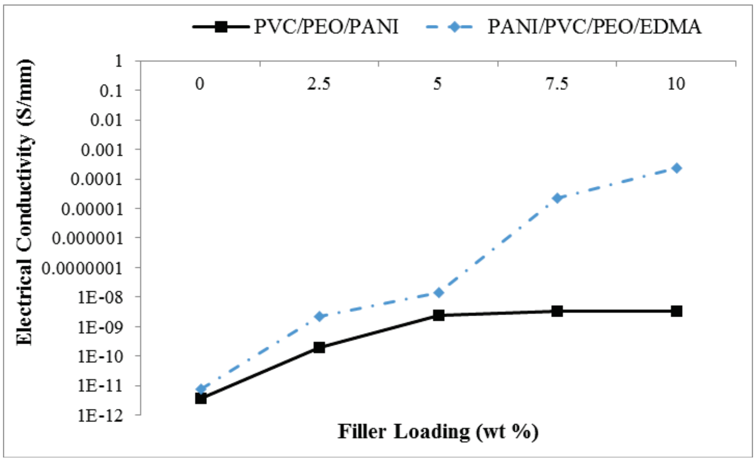


Figure 4: Electrical conductivity of PVC/PEO/PAni conductive films and PVC/PEO/PAni/EDMA conductive films at different fibre loadings.

4. CONCLUSION

The tensile strength and the Young's modulus of PVC/PEO/PAni/EDMA conductive films show higher value than the PVC/PEO/PAni conductive films. The SEM morphology supports the data by showing improves filler distribution on the surface of PVC/PEO/PAni conductive films with the addition of EDMA. The electrical conductivity increased gradually with the addition of EDMA in PVC/PEO/PAni/EDMA conductive films compared to PVC/PEO/PAni conductive films.

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