Electrostatic discharge properties of modified poly(3,4-ethylenedioxythiophene) /poly(4-styrenesulfonate) coated hydrophobic fabrics

C. J. Lee[a.b] I. S. Tsai[a]

[a]*Graduate Institute of Textile Engineering, Feng Chia University, Taichung,Taiwan (R.O.C)*
[b]*Dept. of Polymer Materials, Vanung University of Technology, Chungli, Taoyuan, Taiwan (R.O.C)*

Abstract

The conductivity of poly(3,4-ethylenedioxythiophene)(PEDOT) doped with poly(4-styrenesulfonate) (PSS) containing various organic solvents was measured. The solvents used were isopropanol (IPA), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), N,N-dimethyl acetamide(DMAC).It was found that an addition of organic solvent lowered the sheet resistance by two or three orders of magnitude. Conducting PEDOT/PSS solution mix with polymethyl methacrylate(PMMA) resin to coat hydrophobic fabrics, which can be used for the dissipation of electrostatic charge. We design different screen patterns (square, round, cross, triangle) and utilize it coating PET fabrics, witch are subjected to electric conductivity and electrostatic discharge. Attenuation of the electrostatic discharge (ESD) for various pattern shape be described. We adopt percolation theory to analyze different shape conductive films relate with electric conductivity, in order to find out the best pattern shape and prescription.

Key words：Poly(3,4-ethylenedioxythiophene)/Poly(4-styrenesulfonate); Organic solvents;Sheet resistance; Hydrophobic fabrics; Electrostatic discharge; Percolation theory

1. Introduction

Conducting polymers have been developed over the past 30 years, like polyanilines, polypyrroles, polythiophenes and so on, which have attracted the most attention 〔1,2〕. During the second half of the 1980s, scientists at the Bayer AG research laboratories in Germany developed a new polythiophene derivative, poly (3,4-ethylenedioxythiophene), often abbreviated as PEDT or PEDOT. Prepared using standard oxidative chemical or electrochemical polymerization methods, PEDOT was initially found to be an insoluble polymer, but exhibited some very interesting properties. In addition to a very high conductivity, PEDOT was found to be almost transparent in thin, oxidized film and showed a very high stability in the oxidized state 〔3,4〕. The solubility problem was subsequently overcome by using a water-soluble polyelectrolyte, poly (styrene-sulfonic acid) (PSS), as the charge-balancing dopant during polymerization to yield PEDOT/ PSS. This combination resulted in a water-soluble polyelectrolyte system with good film forming properties, high conductivity (10 s/cm), high visible light transmissively, and excellent stability 〔5,6〕. For more information about PEDOT, its synthesis, characterization, properties and application, see the review article by Groenendaal et al〔7〕. Films of PEDOT/ PSS can be heated in air at 1000℃ for over 1000h with only a minimal change in conductivity. With this new system, now known under its commercial name BAYTRON P, which are characterized by outstanding properties: high conductivity, high transparency, high stability and easy processing, have been able to develop several applications〔8,9〕. Specifically, it use as an antistatic coating on plastics, taking the coating of photographic film, and its use as an electrode in solid electrolyte capacitors and as a conducting layer in through-hole plating and so on〔10,11〕. We may utilize PEDOT/ PSS conducting polymer to coat hydrophobic fabric, which was restrained its poor electronic conductivity, in order to eliminated the static charge.

2. The Characterization of PEDOT/PSS

PEDOT is a conjugated polymer that is positively doped and neutralized with the PSS polyanion. An H^+ disassociates from the PSS and dopes the PEDOT polymer backbone. Oxidation (p – doping) of PEDOT/PSS results in more free charge carrier, i.e. bi-polarons, and the initial sky-blue coloured polymer turns to a more transparent and uncoloured state. PEDOT/PSS absorbs strongly in the red /orange wavelength region upon reduction, therefore, it appears as a dark blue colour in its reduced state. The reduced form of PEDOT/PSS shows very low electronic conductivity, while the pristine (semi-oxidized) form of PEDOT/PSS acts as one-dimensional synthetic metal with high electronic conductivity〔12〕.Figure 1.showed the chemical structure of PEDOT/PSS.

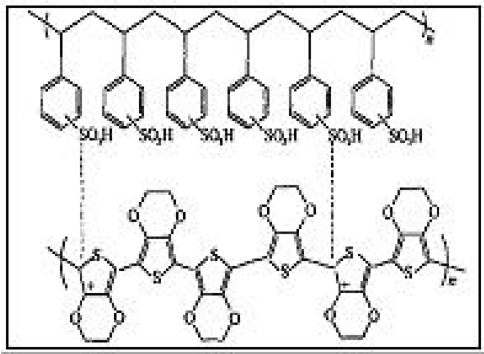


Figure 1. The chemical structure of PEDOT/PSS.

3. Experimental

The PEDOT/ PSS used in this study was BAYTRON P, a dark blue aqueous of Bayer AG (Germany).The characteristic properties and physical data is showed table1. IPA , NMP , DMSO , DMAC were used as organic solvents and added into the PEDOT/ PSS in different blend ratios. Each dispersion was filtered and stirred strongly.The mixed time of IPA, NMP , DMSO , DMAC with PEDOT/ PSS was 24 hr at RT. For each experiment, every types of PEDOT/PSS films were prepared. In order to find the higher electric conductivity of PEDOT/ PSS solution mixed with different solvent. Then, pick up the best prescription mixed solution to add into 200cc PMMA resin in different concentrations of 20, 30, 40 and 50 cc, and formed a gel. After stirring of 2 hours, which was coated onto the hydrophobic fabrics in different pattern screens (square, round, cross and triangle). Finally, the thin film and coated fabrics were dried in a vacuum oven 24 hr at a temperature of 80 ℃. The thickness of the free-standing films was 20~40 μm. The film were further measured by FTIR and TGA for investigating their chemical structure and thermal degradation. Both ESD and conductivity of the coated fabrics were measured by electrostatic charge decay meter and four probe tester. It is important to minimize the influence of environmental parameters on test results. Therefore, testing should be done at room temperature, relative humidity set at 40%, and atmospheric pressure from 86kPa (860mbar) to 106kPa (1060mbar). The discharged electrode of the ESD generator is held in contact with the sample, and the discharge is actuated by a spark to the target plane〔13〕. In this paper, the source voltage are used for each test method is ±5kv, and polarity of output voltage is positive and negative (switchable). The diagram of the static decay meter is given in Figure 2.

Figure 2. the static decay meter

Table 1.PEDOT/PSS characteristic properties and physical data (Baytron P)

Form	liquid
Colour	dark blue
Boiling Temperature	approx. 100℃
Density	approx. 1g/cm^3 at 20℃
Vapour pressure	23 mbar at 20℃
Viscosity	83 m Pa. s
PH-value	1.9 at 20℃
Solid content	1.29% by weight
Particle size	＞95% smaller than 200nm in swollen form

4. Results and Discussion

4.1 Conductivity of PEDOT/ PSS film with various solvents

The conductivity was measured using the four-point probe technique at 5 different locations on each film and an average of the measured values were taken. Table 2. showed thes electric conductivities of PEDOT/ PSS films mixed with 25%(volume ratio) IPA,NMP,DMSOand DMAC . It revealed that a highest electric conductivity was obtained when the mixed time was 24 h and the PEDOT-PSS-IPA film has the higher conductivity. The treatment of organic solvents result in a descendant of energy barrier for change hopping among the PEDOT/ PSS film, the similar results of other solvents found in some documents. MacDiarmid et al. explained that organic solvent is thought to improve the morphology of the film, expanding the coiled polymer chain, which increases π-conjugation length, makes the polarons more delocalized and changes the charge transport properties〔14〕. In comparison of treatment of IPA and without treatment, both electric conductivity was differed from ca. 100 times. There is no significant alternation of electric conductivity after mixed time over 24 hours.

Table 2. The conductivity of PEDOT/PSS film with various solvents after stirring 24 hours

PEDOT/PSS-solvent	Conductivity(S/cm)
PEDOT/PSS(pristine)	0.7
PEDOT/PSS-NMP	15
PEDOT/PSS-DMAC	35
PEDOT/PSS-DMSO	78
PEDOT/PSS-IPA	83

4.2 Chemical structure of PEDOT/PSS film measured by FTIR.

Figure 3. and Figure 4. showed a FTIR spectrum both of the modified PEDOT/ PSS film in different IPA concentration between 10%~30% respectively, and the modified PEDOT/ PSS film in the same concentration of IPA,DMSO,DMAC and NMP. Apparently, there was no obvious difference between the curves, that is, the chemical structure was not altered after the each solvent treatment. It was proved that the treatment of organic solvents impacted only on electric conductivity and transparency.

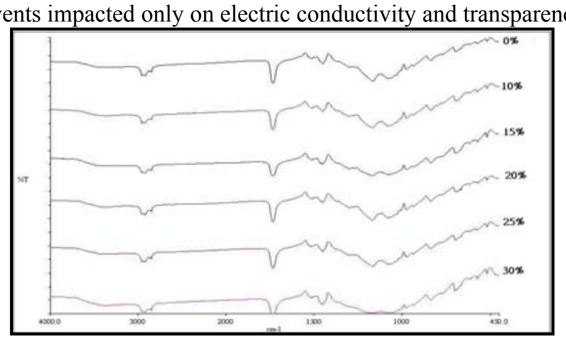


Fig.3. FTIR spectrum both of the modifiedPEDOT/ PSS film in different IPA concentration between 0%~30%

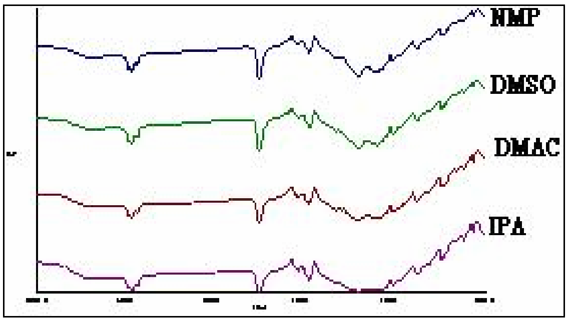


Fig.4. the modified PEDOT/ PSS film in the same Concentration(25%) of NMP,DMSO,DMAC and IPA

4.3 Thermal properties of PEDOT/PSS film

The thermal degradation of PEDOT/ PSS film with and without treatment of IPA were analysed , as it stated in Fig. 5 and fig. 6. It was found that the thermal degradation of PEDOT/ PSS film with IPA treatment was higher than that of without IPA treatment in 30℃. Because through IPA organic solvent treatment, the morphology was arranged . Polar solvents with higher dielectric constant induce the stronger screening effect between counter ions and charge carriers, which reduces the Coulomb interaction between positively charged PEDOT and negatively charged PSS dopants.This advantage can be applied for enhancing the thermal stability, especially in hydrophobic textiles.

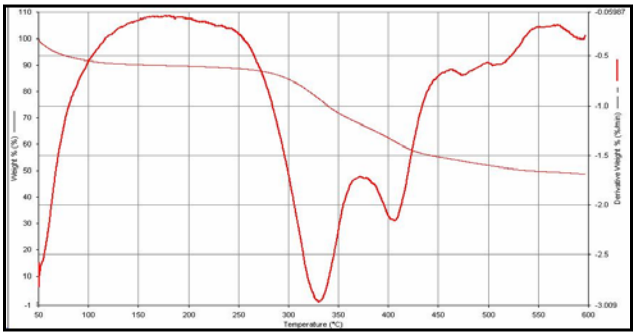


Fig.5. The thermal degradation of PEDOT/ PSS film without treatment of IPA

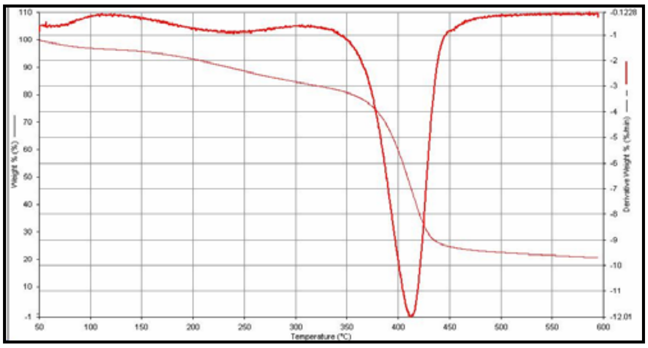


Fig.6. The thermal degradation of PEDOT/ PSS film with treatment of IPA

4.4 ESD effect of PET fabrics coated with PEDOT/ PSS film in different patterns

A better ESD effect was found when compared the PET fabrics coated with PEDOT/ PSS with those without coating, as shown in table 3. Furthermore, the pattern of separated square had the highest ESD effect among the patterns, while the pattern of triangle possessed the lowest ESD effect in average. For the most cases of patterns with connected shape, it revealed a satisfactory result of ESD behavior. The PEDOT/ PSS film with high concentration also resulted in a better ESD behavior. The ESD behavior was also related to a percolation area, it was proofed that a ESD effect of pattern with covered area (connected pattern) was higher that that of less covered area (separated pattern).

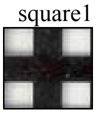
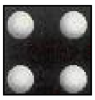
5. Conclution

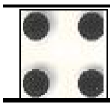
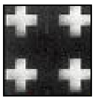
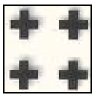
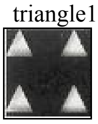
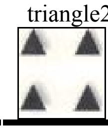
We observe the highest electric conductivity was obtained when the mixed time was 24h and the PEDOT-PSS-IPA film has the higher conductivity. In comparison of treatment of IPA and without treatment, both electric conductivity was differed from ca. 100 times. From FTIR spectrum, there was no obvious difference between the curves, that is, the chemical structure was not altered after the each solvent treatment. It was proved that the treatment of organic solvents impacted only on electric conductivity and transparency. From experiment, we found that the thermal degradation of PEDOT/ PSS film with IPA treatment was higher than that of without IPA treatment in 30℃. From static decay time test was found that the shape of connected patterns had the higher ESD effect than the shape of separated patterns. The ESD behavior was also related to a percolation area, it was proofed that a ESD value of pattern with covered area (connected pattern) was higher than that of less covered area (separated pattern).

Acknowledgements

This work was supported by the National Science Council of Taiwan, R.O.C., through reaserch grant NSC 95-2622-E-238-008-CC3. Thanks Are also due to the Taiwan Textile Reserch Institute, Taiwan, for providing a static decay meter to evaluate the ESD effect.

Table 3. Static charge decay time(second) of PET fabrics coated with PEDOT/ PSS film in different patterns

Concentration		PEDOT/PSS 10%		PEDOT/PSS 15%		PEDOT/PSS 20%		PEDOT/PSS 25%	
ESD effect	Patterns	Positive charge	Negative charge	Positive charge	Negative charge	Positive charge	Negative charge	Positive charge	Negative charge
	square1 	0.05	0.06	0.02	0.02	0.05	0.06	0.01	0.01
		0.02	0.06	0.02	0.02	0.01	0.06	0.01	0.01
		0.06	0.06	0.03	0.03	0.05	0.06	0.01	0.01
	square2 	7.36	6.87	18.36	11.51	11.36	7.71	3.65	3.47
		7.36	6.91	12.86	10.91	8.88	9.71	3.55	3.17
		7.38	7.1	11.58	10.01	8.68	8.41	4.8	4.07
	circle1 	0.03	0.04	0.03	0.03	0.02	0.02	0.01	0.01
Decay time(sec)		0.04	0.04	0.03	0.03	0.02	0.02	0.01	0.01
		0.03	0.04	0.03	0.03	0.02	0.02	0.01	0.01
	circle2	16.26	15.11	13.8	10.57	16.59	10.97	9.28	8.27

	12.86	16.71	13.26	12.11	14.66	11.37	8.05	7.41
	12.48	12.91	11.66	12.17	13.58	12.11	9.36	7.51
cross1	0.02	0.03	0.03	0.04	0.02	0.02	0.01	0.01
	0.03	0.03	0.01	0.04	0.02	0.02	0.01	0.01
	0.03	0.04	0.02	0.04	0.02	0.02	0.01	0.01
cross2	25.68	18.71	16.53	11.71	15.86	9.71	6.38	4.27
	26	17.07	16.36	12.11	15.08	10.71	5.58	4.91
	24.88	17.11	15.28	12.11	14	11.11	5.38	4.1
triangle1	0.05	0.04	0.01	0.01	0.01	0.01	0.01	0.01
	0.03	0.04	0.01	0.02	0.01	0.01	0.01	0.01
	0.03	0.04	0.01	0.02	0.01	0.01	0.01	0.01
triangle2	27.2	1831	23.69	16.11	17.27	12.34	10.21	8.17
	26.58	18.77	23.88	16.41	18.28	13.29	10	7.31
	26.48	18.57	23.86	17.11	18.29	13.31	9.66	8.31

Note：The static charge decay time of PET fabrics: positive charge is over 60 sec and negative charge is ca. 23sec.
1 represent connected pattern of PEDOT/PSS film
2 represent seperated pattern of PEDOT/PSS film

References

(1). L.B.Groenendaal,F.Jonas,D.Freitag,H.Pielartzik,J.R.Reynolds,Adv.Mater.12(2000)481.
(2). G.Heywang,F.Jonas,Adv.Mater.4(1992)116.
(3). A.N.Aleshin,R.Kiebooms,A.J.Heeger,Synth.Met.101(1999)369.
(4). A.N.Aleshin,R.Kiebooms,R.Menon,A.J.Heeger,Synth.Met.90(1997)61.
(5). K.Z.Xing,M.Fahlman,X.W.Chen,O.Inganal,W.R.Salaneck, Synth.Met.89(1997)161.
(6). S.K.M.Jonsson, J.Birgerson, X.Crispin, G.Greczynski, W.Osikowicz, Synth. Met.10361（2003）1-10.
(7). Eva Hakansson, Akif Kaynak, Tong Lin, Saeid Nahavandi, Trevor Jones, Eric Hu, Synth. Met.144（2004）21-28.
(8). C.Carlberg,X,Chen,O.Inganas,Solid State Ionics85(1996)73.
(9). R.B.Stinchcombe,“The branching model for percolation theory and electrical conductivity”,J.Phys. C:Solid State Phys.,Vol.6,L1-L5(1973).
(10). .J.Y.Kim,J.H.Jung,D.E.Lee,J.Joo, Synth. Met.126（2002）311.
(11). .R.S.Kohlman,J.Joo,Y.G.Min,A.G.MacDiarmid,A.J.Epstein,Phys,Rev.Lett.77(1996)2766.
(12). V.N.Prigodin,A.J.Epstein, Synth. Met.125（2001）43..
(13). . K.B.Cheng, T.H.Ueng, G.Dixon,“Electrostatic Discharge Properties of Stainless Steel/Polyester Woven Fabrics”,Textile Res.J,71(8),732-738（2001）.
(14). A.G.MacDiarmid,A.J.Epstein, Synth. Met.65（1994）103.