



Article Dielectric Properties of All-Organic Coatings: Comparison of PEDOT and PANI in Epoxy Matrices

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Abstract: The technological demands imposed on dielectrics and electrical insulation materials are being increasing with the transition from traditional to smart grids. Epoxy resin/conductive polymer (CP) blends with high dielectric permittivity have been prepared by means of a straightforward methodology. Poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI), doped with *p*-tosylate and ammonium peroxide sulfate (APS), respectively, were synthesized and blended with an epoxy matrix. The addition of 3 wt % of PEDOT and PANI results in permittivity values of 68.9 and 9.5, respectively at 0.1 Hz—1300 and 111 times higher than pure resin. Hence, PEDOT is more effective than PANI at improving the permittivity of the epoxy resin. Moreover, the material retains the electrical insulation of the resin and exhibits a slight increase in thermal conductivity.

Keywords: polyaniline (PANI); poly(3,4-ethylenedioxythiophene) (PEDOT); epoxy; dielectric permittivity; smart grid

1. Introduction

Growing environmental awareness and the progress on generators from renewable sources are transforming the electrical sector towards the implementation of smart grids [1,2]. This transition from passive and unidirectional systems to flexible and multi-participant grids increases the technological demands imposed on dielectrics and electrical insulation materials [1]. Hence, there is a growing interest in research to increase the dielectric permittivity of polymers to ensure the reliability of the grids, while also reducing costs.

A large body of research has focused on the addition of both ceramic and conducting fillers to improve the dielectric permittivity of polymers, particularly of cross-linked polyethylene and epoxy resins [3]. An alternative route is the development of all-organic dielectric systems using conductive polymers, which can be either in situ polymerized in the matrix or blended as a filler [4]. Conductive polymers (CPs) are conjugated systems, which possess alternate single and double bonds along the chains. This configuration provides them with a low band gap, environmental and thermal stability, and electrical conductivity that can be tuned with appropriate doping [5–7].

Among the different CPs, polyaniline (PANI) is the most widely used material, followed by poly(3,4-ethylenedioxythiophene) (PEDOT). The interest in these two CPs and their derivatives is owed to their combination of high stability, tunable conductivity, and low cost [8,9]. Mixing PANI with insulating thermoset polymers is an area of active research driven by the prospect of combining good electrical properties with the processability of resins; in particular, epoxies. Several studies have already shown the potential of PANI/epoxy blends as conductive adhesives [10–14], anticorrosion coatings [15,16], flame-retardant conductive composites [17,18], microwave absorbing materials [19,20],

and lightning damage suppressors in carbon-fiber reinforced composites [21,22]. A recent review by Perrin et al. [4] thoroughly summarizes the current state of PANI/epoxy blends. Meanwhile, PEDOT is considered the most stable conducting polymer currently available, and can be water-soluble when doped with poly(styrenesulfonate) (PSS) [7]. Due to its good optical transparency in visible light and good film-forming ability, PEDOT:PSS has mostly been studied in optoelectronic applications and flexible devices [23]; meanwhile, its potential in polymer blends has been limited to thermoplastic materials, such as PVA and PMMA [24,25], and as anti-corrosion paints [26].

Here, we analyze the potential application of PEDOT to increase the dielectric permittivity of an epoxy system and compare it to the already known system based on PANI. To that end, we selected anhydride-cured epoxy due to its use in the electrical industries as switchgear parts; pin insulators; and power, current, and voltage distribution transformers.

2. Experimental Section

2.1. Synthesis of the Conductive Polymers

Polyaniline (PANI) doped with ammonium peroxide sulfate (APS) (Scheme 1) and poly(3,4-ethylenedioxythiophene) (PEDOT) doped with *p*-tosylate (TOS) (Figure 1) were synthesized as follows.



Scheme 1. Structure of PANI and PEDOT doped with APS and TOS, respectively.

(a) PANI synthesis [27]: two 50 mL solutions were prepared, one of 0.2 M aniline hydrochloride (2.59 g, 20 mmol) and another of ammonium peroxide sulfate (5.71 g, 25 mmol). Both solutions were separately stirred for 1 h at room temperature. Subsequently, they were gently mixed and left for one day for polymerization to occur. The next day, the PANI precipitate was washed by filtration. Three washes were done with a solution of 0.2 M HCl (100 mL), and then one was with acetone. The powder obtained was dried in a vacuum oven at 60 °C.

(b) PEDOT synthesis: It was carried out by oxidative polymerization using methanol as the solvent [28]; 2.2 mL EDOT, 20.47 g oxidizing agent (iron (III) p-toluenesulfonate), 2.14 mL catalyst (imidazole), and 110 mL methanol were used. EDOT was dissolved in 55 mL of methanol (Solution 1), and the catalyst with the oxidizing agent were added in the other 55 mL of methanol (Solution 2).

Subsequently, Solution 2 was slowly added for 10 min in Solution 1 and stirred for 15 min. Thus, the total reaction time was 25 min. The solution was deposited in a crystallizer and left to dry at 50 °C for 4 h. The resultant precipitate was filtered and washed with methanol, and left to dry at room temperature overnight. The precipitate changed color from green to dark blue. The powder obtained was dried in a vacuum oven at 60 °C.

2.2. Sample Preparation

Epoxy resin based on diglycidyl ether of bisphenol A (DGEBA), Araldite[®] XB 5940, and an anhydride type hardener Aradur[®] HY 5914, were purchased from Huntsman (Huntsman Advanced Materials, Pamplona, Spain). The resin to hardener ratio was 100:80 in parts by weight, according to the supplier specifications. The CP powders were dispersed in the epoxy resin using a three-roll calender (EXAKT 80E, EXAKT Technologies, Inc., Oklahoma City, OK, USA), following a three-step protocol described in Table 1.

| Step | Gap 1 (µm) | Gap 2 (μm) | Speed (rpm) | Time (min) | | |
|--------|------------|------------|-------------|------------|--|--|
| Step 1 | 100 | 50 | 200 | 10 | | |
| Step 2 | 50 | 25 | 250 | 10 | | |
| Step 3 | 30 | 15 | 300 | 30 | | |

Table 1. Dispersion protocol.

The dispersion was then mixed with the hardener in a vacuum reactor, at 2400 rpm for 45 min at 60 °C, and subsequently, poured into preheated silicone molds. The samples were cured in an oven at 80 °C for 4 h, and then post-cured at 140 °C for 8 h. Two different loading fractions were studied, 1 and 3 wt %.

2.3. Characterization

Both CPs were characterized in a high-resolution scanning electron microscope (HRSEM, Hitachi SU-8000, Tokyo, Japan) operated in transmission mode at 30 kV. Cryo-fractured cross-sections of the cured blends were analyzed by scanning electron microscopy (SEM), Philips ESEM XL30, after sputter-coated with Au/Pd.

Thermogravimetric analysis (TGA) of the synthesized CPs was carried out in a TA Instrument Series Q500. Samples were heated from 40 to 700 °C at a heating rate of 10 °C/min under an air atmosphere (with a flow rate of 90 mL/min). The degradation temperature was determined from the curve of the weight loss as a function of temperature.

Impedance spectroscopy measurements were performed on an ALPHA high-resolution dielectric analyzer (Novocontrol Technologies GmbH & Co. KG, Montabaur, Germany). The bulk electrical conductivity of the CP was measured on vacuum-pressed disks, 13.0 ± 0.1 mm in diameter and 0.8 ± 0.2 mm thickness, which were placed between two gold-plated electrodes (the diameters of upper and lower electrodes were 10 and 20 mm, respectively) applying a voltage of 20 mV. The dielectric behavior of the cured epoxy/CP samples was measured in cylindrical samples (22 ± 0.2 mm in diameter and 1 ± 0.2 mm in thickness) mounted in the dielectric cell between two parallel gold-plated electrodes (the diameters of upper and lower electrodes were 20 and 30 mm, respectively). Isothermal frequency sweeps were measured over a frequency window of $10^{-1} < f/\text{Hz} < 10^7$ ($f = \omega/2\pi$ where f and ω are the frequency and angular frequency of the applied electric field) at room temperature. The amplitude of the applied ac electric signal was 1 V. The surfaces of the specimens were coated with silver paint. Eight specimens of each material were measured, and the experimental error was less than 10%.

Thermal conductivity was measured under stationary conditions using a heat flow meter, model FOX 50 (Lasercomp—TA Instruments, Wakefield, MA, USA), according to ASTM C518 and ISO 8301 standards on cylindrical specimens, 45 ± 0.1 mm diameter and 8 ± 0.1 mm thickness. At least three

measurements were carried out for each sample with an experimental error of less than 2% of the absolute value.

3. Results and Discussion

Inspection of the synthesized CPs reveals a clear difference between both polymers; PANI presents a larger and broader particle size dispersion, 300 nm to 1 μ m, than PEDOT—itself having a more homogeneous size range, between 70 and 120 nm (Figure 1).



Figure 1. TEM images of the synthesized conductive polymers (CPs): (a) PANI and (b) PEDOT.

Figure 2 shows the typical degradation of CPs in air, presenting three degradation steps [29,30]. Both CPs present an initial weight loss around 100 °C, due to adsorbed water molecules. The second degradation step corresponds to the dopant phases, at around 250 °C and 300 °C for PANI and PEDOT, respectively. Finally, the decomposition of both polymers takes place above 300 °C, completely decomposing at around 600 °C for PANI and around 500 °C for PEDOT.



Figure 2. Weight loss as function of temperature of the synthesized CPs.

The electrical conductivity was calculated from the complex impedance and the sample geometry (Figure 3). Both polymers present the typical behavior of conducting systems with an independent value of the electrical conductivity from the frequency, reaching values of 0.1 S/cm for PANI and 2×10^{-3} S/cm for PEDOT. The differences in their electrical conductivity are related to their different dopant natures and polymer chains [31].



Figure 3. Electrical conductivity as a function of the frequency of both CPs.

Prior to the study of the dielectric properties of the all-organic dielectric composites, the dispersions of the CPs were analyzed by scanning electron microscopy. The cryo-fractured cross-sections of the samples show clear differences between both CPs (Figures 4 and 5). PEDOT particles present a uniform dispersion throughout the epoxy matrix and form interconnected paths, clearly visible as the concentration increases to 3 wt % (Figure 4). Meanwhile, PANI particles, or small clusters of them, appear to remain isolated and do not connect with each other (Figure 5). Hence, the dispersion of PEDOT particles is more homogeneous than that of PANI. No previous studies have been found on the dispersion state of PEDOT, which we ascribe to the smaller particle size and possible interaction with the matrix. Meanwhile, similar results have been described on the dispersion state of PANI particles, where the formation of interconnected networks of PANI particles have been reported at concentrations higher than 5 wt % [32].



Figure 4. SEM micrographs of PEDOT/epoxy samples with (a) and (b) 1 wt %, and (c) and (d) 3 wt %.



Figure 5. SEM micrographs of PANI/epoxy samples (a) and (b) 1 wt %, and (c) and (d) 3 wt %.

The dielectric behavior of the samples is clearly affected by the addition of the CP particles (Figure 6). Both CP contents clearly increase the dielectric constant of the epoxy matrix, PEDOT being more efficient than PANI. This behavior is ascribed to the observed morphological differences between the two systems, since the conductivity of PEDOT is two orders of magnitude lower than that of PANI. The better dispersion state and clear interconnection between PEDOT particles raise the dielectric constant to almost 70 at 0.1 Hz with 3 wt %; compared to 9.5 of PANI (Table 2). Those values represent improvements of 1300% and 111% compared to the pure epoxy resin. However, PEDOT also modifies the permittivity behavior, presenting a dependency on the frequency, which is not observed with PANI particles. The clear decrease of the permittivity with frequency of PEDOT samples is indicative of the presence of localized movement of charges; i.e., interfacial polarization or Maxwell–Wagner–Sillars polarization [33]. Additionally, the presence of PEDOT particles modifies the dielectric loss tangent, suggesting additional loss mechanisms, which could explain the slight increase of the thermal conductivity values (Table 2). In any case, PEDOT samples retain the non-conducting character of the epoxy resin, as demonstrated by the linear dependence of the conductivity with the frequency.

| Material | ٤' | σ' (S/cm) | tan(δ) | λ (W/mK) |
|--------------------|------|-----------------------|--------|----------|
| Ероху | 4.5 | 8.0×10^{-16} | 0.003 | 0.12 |
| 1 wt % PEDOT/epoxy | 10.3 | 4.2×10^{-14} | 0.072 | 0.13 |
| 3 wt % PEDOT/epoxy | 68.9 | 1.7×10^{-12} | 0.450 | 0.16 |
| 1 wt % PANI/epoxy | 7.5 | 5.3×10^{-15} | 0.013 | 0.12 |
| 3 wt % PANI/epoxy | 9.5 | 1.7×10^{-14} | 0.033 | 0.12 |

Table 2. Summary of the dielectric at 0.1 Hz and thermal conductivity properties of the CP/epoxy blends.



Figure 6. Permittivity (**left**), loss tangent (**middle**), and AC electrical conductivity (**right**) for PEDOT (**up**) and PANI (**down**) filled epoxy blends.

4. Conclusions

All-organic dielectric coatings with high dielectric permittivity were developed by blending two synthesized conductive polymers with an epoxy resin. While epoxy blended with PANI had already been shown to provide permittivity improvements, here we demonstrated that PEDOT is more effective, with an increase of 1300 times with respect to the pure resin, compared to 111 times for PANI. This efficiency was ascribed to the better dispersion state and clear interconnection between the PEDOT particles, since PANI had a higher electrical conductivity.

High dielectric polymers are been demanded for a wide variety of applications, such as the ongoing transition towards smart grids, and different modern electronics. Here, we have presented a straightforward methodology that maintains the good processability and low density of thermosets.

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References

- Catterson, V.M.; Castellon, J.; Pilgrim, J.A.; Saha, T.K.; Ma, H.; Vakilian, M.; Moradnouri, A.; Gholami, M.; Sparling, B.D. The impact of smart grid technology on dielectrics and electrical insulation. *IEEE Trans. Dielect. Electr. Insul.* 2015, 22, 3505–3512. [CrossRef]
- 2. Markard, J. The next phase of the energy transition and its implications for research and policy. *Nature Energy* **2018**, *3*, 628–633. [CrossRef]
- 3. Pleşa, I.; Noţingher, V.P.; Schlögl, S.; Sumereder, C.; Muhr, M. Properties of Polymer Composites Used in High-Voltage Applications. *Polymers* **2016**, *8*, 173. [CrossRef] [PubMed]
- Perrin, F.X.; Oueiny, C. Polyaniline thermoset blends and composites. *React. Funct. Polym.* 2017, 114, 86–103. [CrossRef]
- Meer, S.; Kausar, A.; Iqbal, T. Trends in Conducting Polymer and Hybrids of Conducting Polymer/Carbon Nanotube: A Review. *Polym. Plast. Technol. Eng.* 2016, 55, 1416–1440. [CrossRef]
- Kumar, R.; Singh, S.; Yadav, B. Conducting polymers: Synthesis, properties and applications. *Int. Adv. Res. J. Sci. Eng. Technol.* 2015, 2, 110–124.

- 7. Elschner, A.; Kirchmeyer, S.; Lovenich, W.; Merker, U.; Reuter, K. *PEDOT: Principles and Applications of an Intrinsically Conductive Polymer*; CRC Press: Boca Raton, FL, USA, 2010.
- 8. Liao, G.; Li, Q.; Xu, Z. The chemical modification of polyaniline with enhanced properties: A review. *Prog. Org. Coat.* **2019**, *126*, 35–43. [CrossRef]
- 9. Stejskal, J. Conducting polymers are not just conducting: A perspective for emerging technology. *Polym. Intern.* **2019**. [CrossRef]
- Massoumi, B.; Farjadbeh, F.; Mohammadi, R.; Entezami, A.A. Synthesis of conductive adhesives based on epoxy resin/nanopolyaniline and chloroprene rubber/nanopolyaniline: Characterization of thermal, mechanical and electrical properties. *J. Compos. Mater.* 2013, 47, 1185–1195. [CrossRef]
- 11. Yang, Q.; Wei, S.; Cheng, G. Preparation of conductive polyaniline/epoxy composite. *Polym. Compos.* **2006**, 27, 201–204. [CrossRef]
- 12. Mir, I.A.; Kumar, D. Development of Polyaniline/Epoxy Composite as a Prospective Solder Replacement Material. *Int. J. Polymer. Mater.* **2010**, *59*, 994–1007. [CrossRef]
- Mir, I.A.; Kumar, D. Nanocomposites of Polyaniline as Conductive Adhesives. J. Adhes. Sci. Technol. 2012, 25, 2731–2744. [CrossRef]
- 14. Desvergne, S.; Gasse, A.; Pron, A. Electrical characterization of polyaniline-based adhesive blends. *J. Appl. Polym. Sci.* **2011**, *120*, 1965–1973. [CrossRef]
- Adhikari, A.; Karpoormath, R.; Radha, S.; Singh, S.K.; Mutthukannan, R.; Bharate, G.; Vijayan, M. Corrosion resistant hydrophobic coating using modified conducting polyaniline. *High Performance Polym.* 2018, 30, 181–191. [CrossRef]
- 16. Kausar, A. Performance of corrosion protective epoxy blend-based nanocomposite coatings: A review. *Polym. Plastics Technol. Mater.* **2019**. [CrossRef]
- 17. Zhang, X.; He, Q.; Gu, H.; Colorado, H.A.; Wei, S.; Guo, Z. Flame-retardant electrical conductive nanopolymers based on bisphenol F epoxy resin reinforced with nano polyanilines. *ACS Appl. Mater. Interfaces* **2013**, *5*, 898–910. [CrossRef]
- Zhan, Z.; Zhang, Y.; Zhang, Y. Improving the flame retardancy and electrical conductivity of epoxy resin composites by multifunctional phosphorus-containing polyaniline. *Mater. Lett.* 2020, 261, 127092. [CrossRef]
- Calheiros, L.F.; Soares, B.G.; Barra, G.M.O. DBSA-CTAB mixture as the surfactant system for the one step inverse emulsion polymerization of aniline: Characterization and blend with epoxy resin. *Synth. Met.* 2017, 226, 139–147. [CrossRef]
- Oyharçabal, M.; Olinga, T.; Foulc, M.-P.; Lacomme, S.; Gontier, E.; Vigneras, V. Influence of the morphology of polyaniline on the microwave absorption properties of epoxy polyaniline composites. *Compos. Sci. Technol.* 2013, 74, 107–112. [CrossRef]
- Yokozeki, T.; Goto, T.; Takahashi, T.; Qian, D.; Itou, S.; Hirano, Y.; Ishida, Y.; Ishibashi, M.; Ogasawara, T. Development and characterization of CFRP using a polyaniline-based conductive thermoset matrix. *Compos. Sci. Technol.* 2015, *117*, 277–281. [CrossRef]
- 22. Kumar, V.; Yokozeki, T.; Okada, T.; Hirano, Y.; Goto, T.; Takahashi, T.; Hassen, A.A.; Ogasawara, T. Polyaniline-based all-polymeric adhesive layer: An effective lightning strike protection technology for high residual mechanical strength of CFRPs. *Compos. Sci. Technol.* **2019**, *172*, 49–57. [CrossRef]
- 23. Gueye, M.N.; Carella, A.; Faure-Vincent, J.; Demadrille, R.; Simonato, J.-P. Progress in understanding structure and transport properties of PEDOT-based materials: A critical review. *Prog. Mater Sci.* 2020, *108*, 100616. [CrossRef]
- 24. Chen, C.-H.; Kine, A.; Nelson, R.D.; LaRue, J.C. Impedance spectroscopy study of conducting polymer blends of PEDOT: PSS and PVA. *Synth. Met.* **2015**, *206*, 106–114. [CrossRef]
- 25. Sanchis, M.J.; Redondo-Foj, B.; Carsí, M.; Ortiz-Serna, P.; Culebras, M.; Gómez, C.M.; Cantarero, A.; Muñoz-Espí, R. Controlling dielectrical properties of polymer blends through defined PEDOT nanostructures. *RSC Adv.* **2016**, *6*, 62024–62030. [CrossRef]
- Liesa, F.; Ocampo, C.; Alemán, C.; Armelin, E.; Oliver, R.; Estrany, F. Application of electrochemically produced and oxidized poly(3,4- ethylenedioxythiophene) as anticorrosive additive for paints: Influence of the doping level. J. Appl. Polym. Sci. 2006, 102, 1592–1599. [CrossRef]
- 27. Stejskal, J.; Gilbert, R.G. Polyaniline. Preparation of a conducting polymer(IUPAC Technical Report). *Pure Appl. Chem.* **2002**, *74*, 857. [CrossRef]

- 28. Kim, T.Y.; Kim, J.E.; Suh, K.S. Effects of alcoholic solvents on the conductivity of tosylate-doped poly (3, 4-ethylenedioxythiophene)(PEDOT-OTs). *Polym. Int.* **2006**, *55*, 80–86. [CrossRef]
- Mazzeu, M.A.C.; Faria, L.K.; Cardoso, A.d.M.; Gama, A.M.; Baldan, M.R.; Gonçalves, E.S. Structural and Morphological Characteristics of Polyaniline Synthesized in Pilot Scale. *J. Aerospace Technol. Manag.* 2017, *9*, 39–47. [CrossRef]
- 30. He, J.; Su, J.; Wang, J.; Zhang, L. Synthesis of water-free PEDOT with polyvinylpyrrolidone stabilizer in organic dispersant system. *Org. Electron.* **2018**, *53*, 117–126. [CrossRef]
- 31. Meng, Q.; Cai, K.; Chen, Y.; Chen, L. Synthesis of water-free PEDOT with polyvinylpyrrolidone stabilizer in organic dispersant system. *Nano Energy* **2017**, *36*, 268–285. [CrossRef]
- 32. Jia, Q.M.; Li, J.B.; Wang, L.; Zhu, J.W.; Zheng, M. Electrically conductive epoxy resin composites containing polyaniline with different morphologies. *Mater. Sci. Eng. A* **2007**, *448*, 356–360. [CrossRef]
- 33. Hedvig, P. Dielectric Spectroscopy of Polymers; Adam Hilger Ltd.: Bristol, UK, 1977.



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