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Highly processable method for the construction of miniature conducting polymer moisture sensors

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ABSTRACT

A polymer blend incorporating polyaniline (PAn) was used as a sensing medium in the construction of a resistance based humidity sensor. Aniline monomer was polymerised to PAn emeraldine salt (ES) in the presence of poly (butyl acrylate-co-vinyl acetate) and the processable blend was developed by redissolving 1-2 w/w% of the resulting sensing polymer residue in dichloromethane (DCM). Some of this residue was washed in ammonia solution to de-dope the PAn to emeraldine base (EB) to act as a protective layer on the surface of the sensing polymer. This residue was then washed with distilled water until a neutral pH was realised with the waste water, dried and redissolved in DCM at 1-2 w/w% to create a processable blend barrier polymer solution. The final sensor design utilised 125 μ m polyester insulated platinum wire as conducting electrodes that were dip coated in the PAn ES blend solution and dried in a desiccator. A protective coating was then applied by dip coating in the EB blend solution. The sensors had an overall final thickness of less than 200 μ m and showed high sensitivity to humidity, low resistance, and good reversibility without hysteresis. The EB protective layer was shown to give more stable and predictable responses to the sensors when placed inside curing epoxies. Polymer based thin film humidity sensors have the advantage that the high processability of the material allows for simple fabrication of a range of geometries including smaller sensor designs. Such sensors may find uses in detecting water content in a number of areas including composite materials, electronic textiles, food/ electronics packaging and corrosion detection.

Keywords: Polyaniline, Humidity, Sensor, Conducting Polymer

1. INTRODUCTION

The ingress of water has been well documented to change the mechanical properties of many polymers and polymer composites. In some composite systems the presence of water can lead to fibre/matrix interfacial breakdown and matrix degradation^[1-4] whereas in other systems water ingress has been shown to even enhance the energy absorption characteristics of epoxy composites^[5]. In either case, the ability to monitor the extent that water ingresses into an epoxy composite can be a useful tool to determine the strength and condition of the material at any point in time.

Various studies have been conducted into novel materials that can be used to detect humidity. Some studies have concentrated upon ceramic materials where the change in impedance or dielectric properties of the system were used to detect the ingress of water^[6-8]. Other systems incorporate humidity sensing polymers^[9-14] where either dielectric, capacitive or resistance based parameters have been found to change with water ingress. Each system in its own right measures the change in humidity (with consideration taken to hysteresis, linearity and reproducibility) but problems with overall size and processability of the sensing material can restrict applications in certain areas.

Ceramic humidity sensors based on ZnO, TiO₂ and SiO₂ films have been developed that show highly sensitive, reversible, linear responses^[6-8]. Processability of such designs however can be somewhat tedious requiring high temperatures and a multi layered construction to the sensor substrate. The use of sol-gels has improved this

processability^[15-19] but most designs still require a glass or quartz crystal substrate which can restrict the degree of miniaturisation.

Much work has also been undertaken into the humidity sensing properties of conducting polymers. It is known that water increases the electrical conductivity of polyaniline through an increase in the interchain electron transfer^[20-23] and / or by increasing the mobility of dopant ions^[24]. Conductivity increases of several orders of magnitude in the presence of water have been recorded with linear and reversible responses^[23-25].

Polymer based thin film humidity sensors have the advantage that the high processability of the material allows for simple fabrication of a range of geometries including smaller sensor designs. The ease of processing gives a low cost sensor, whilst the small size and good mechanical properties give a robust flexible sensor that is able to be used in applications where dynamic stresses and strains are encountered. With these advantages in mind, the aim of this study was to design, fabricate and evaluate humidity sensors using processable polyaniline blends as the sensing medium. In particular, the sensors have been assessed for linearity, sensitivity, bulk resistance, response time, temperature response and stability within a curing epoxy environment.

2. METHODOLOGY

2.1 Sensor substrate construction

Sensor electrodes were made from 125 μ m platinum wire that was insulated with a 14 μ m polyester coating, as supplied from Goodfellow (UK). A 5cm section of wire was cut, then folded in half and its ends were twitched together to create two parallel wires electrodes connected at one end by a loop of bare platinum. The insulation coating from both ends was removed by scorching with a hot Bunsen burner flame. The parallel wire sections were glued together in a flat orientation with cross-linked poly vinyl alcohol (PVA) and left to dry before the platinum wire loop was cut. The final substrate was checked to ensure that its thickness was no more than 150 μ m and the spacing between electrode ends was less than 1mm. A typical finished sensor substrate can be seen in Figure 1.

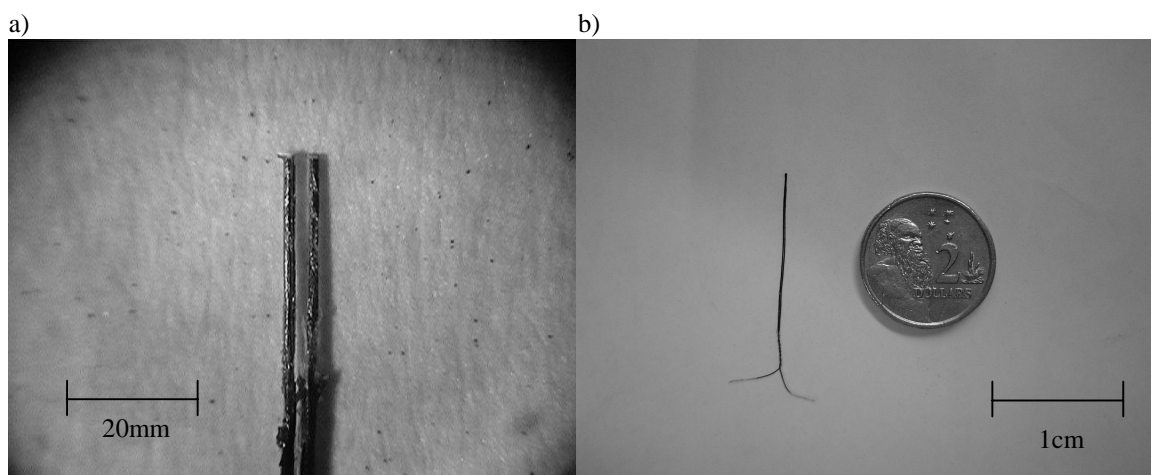
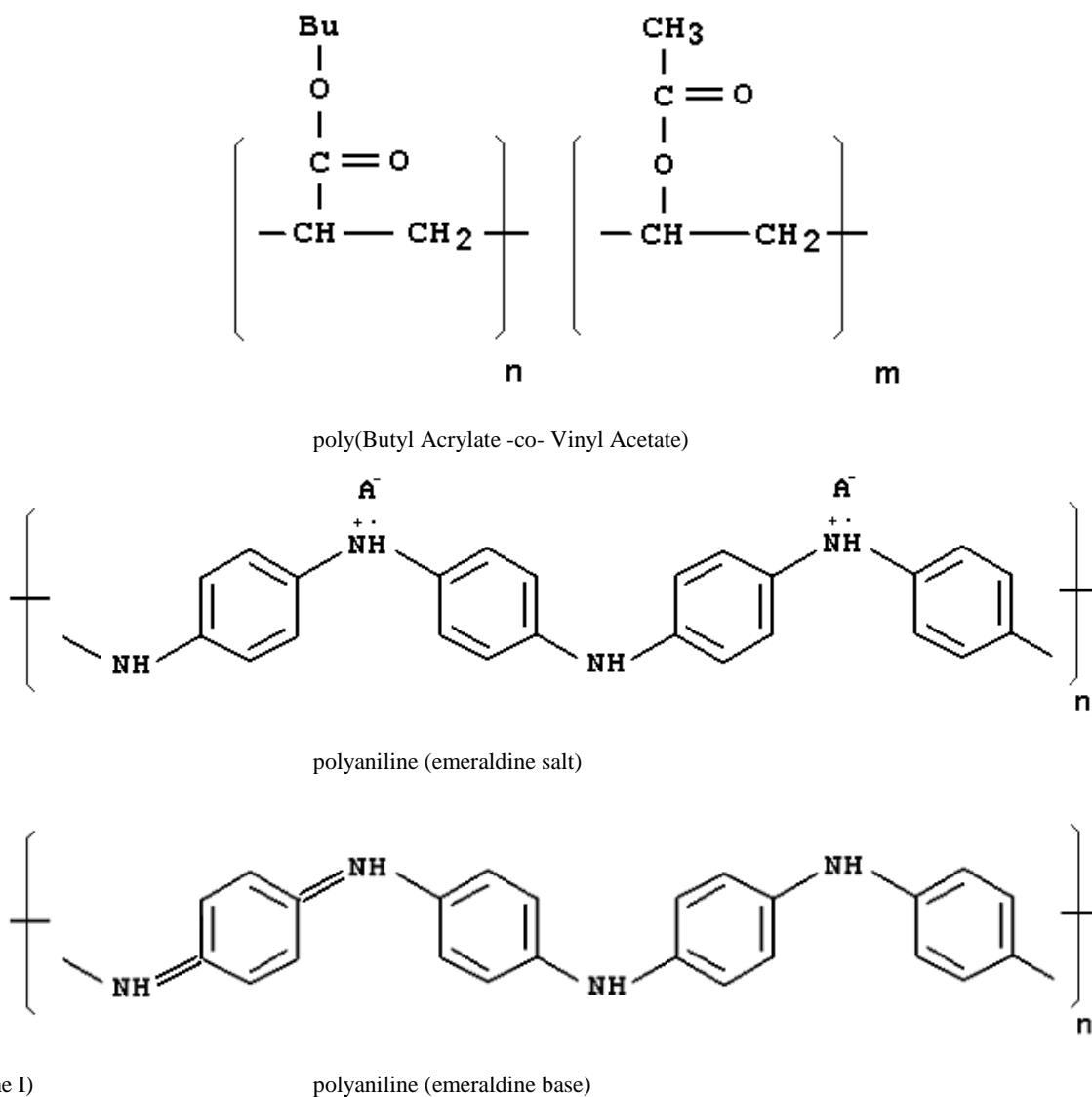


Figure 1) (a) Finished sensor substrate ready for coating, and (b) as seen at higher magnification showing bared insulation and gap of approx. 250 μ m.

2.2 Polymer Blends

A processable polymer was made by the chemical polymerisation of aniline monomer to emeraldine salt (ES) with ammonium persulphate, in an emulsion of poly (butyl acrylate-co-vinyl acetate) P(BuA-VAc) copolymer (40 w/w%)^[26]. The P(BuA-VAc) copolymer (Scheme I) was synthesised according to previously reported methods^[27, 28] and the final polymerisation took place with camphor sulphonic acid (HCSA) being used in excess as the dopant. The end product was purified with a de-ionised water wash prior to centrifuging and the resulting solid was dried to a powder. The PAn percentage was determined from elemental analysis to be 15 w/w% in the developed PAn/ P(BuA-VAc) blend.

Some of the resulting powder was washed in ammonia solution to de-dope the PAn to emeraldine base (EB) (Scheme 1). This residue was then washed with distilled water until a neutral pH was realised with the waste water, and this was then also dried to a powder. The two polymers (ES and EB) were separately redissolved in CH_2Cl_2 solvent at 1-2% by weight to create dark green and dark blue liquids respectively which could be readily stored in an easily processable form.



Scheme 1)

2.3 Development of the sensors

The sensor substrate was dip-coated with the PAn ES blend that was to be used as the sensing material and allowed to dry completely in a desiccator. After drying, on several other sensors a second protective layer of the PAn EB was applied to the surface by dip coating. This layer was applied to stabilise the ES sensing material and protect it from the possibility of any further de-doping, which would lead to a loss in conductivity and a change in the humidity response.

With this overall design the width of the conducting electrodes was the main limiting factor to the overall size. The width was kept to a minimum by aligning the electrodes under a microscope ensuring that no short circuits were present

using a standard multimeter. The width was thus kept to around 500 μ m or less before the process of polymer dip-coating. The polymer coating thickness was examined under a microscope and was estimated to be 25 μ m or less for each of the polymer coatings (PAn P(BuA-co-VAc) ES and PAn P(BuA-co-VAc) EB) on the produced sensors.

2.4 Testing the sensors

An Agilent 34401A Multimeter was used to measure resistances across the sensors when placed in chambers of varying humidity. The relative humidities (RH) in each chamber were created using saturated salt solutions of LiCl, MgCl₂, Ca(NO₃)₂, NaNO₃, and Distilled water which correspond to relative humidities of 11, 33, 51, 74 and 95% respectively [29]. A chamber containing silica gel was also used and was found to give a 3% RH after checking with a commercial humidity sensor. The resistance for each humidity level was measured after equilibration in each of the humidity chambers to produce an overall bulk resistance calibration curve for each sensor. The resistance reading at 95%RH for each sensor was set as a baseline and the % change in resistance was then calculated for each RH and second calibration curve produced.

3. RESULTS AND DISCUSSION

3.1 Linearity/ Sensitivity

A standard calibration curve for 15 w/w% PAn ES blend was found to show an exponential response from 3 to 95%RH and showed high sensitivity with over a 300% resistance change from 11 – 74%RH. Calibration curves for the 15 w/w% PAn ES blend with EB protective coating responses were also found to be exponential and from 11 – 74%RH showed that both the overall response and sensor sensitivities were not compromised when compared to uncoated sensors. A high sensitivity was recorded with over a 300% resistance change from 11 – 74%RH.

Each of the sensor types were especially sensitive for low RH changes. The %change in resistance calibration curves were repeated many times for each blend and the average values can be seen in Figure 2) along with the standard deviation at each RH level.

3.2 Effect of Electrode Separation

The final spacing of the conducting electrodes was found to be the main factor in determining the resulting sensor resistance. With electrodes that were less than 1mm apart, each blend gave sensors that showed bulk resistance measurements (at 3% RH) less than 10 k Ω , making it an appropriate transducer for practical applications.

3.3 Response Time

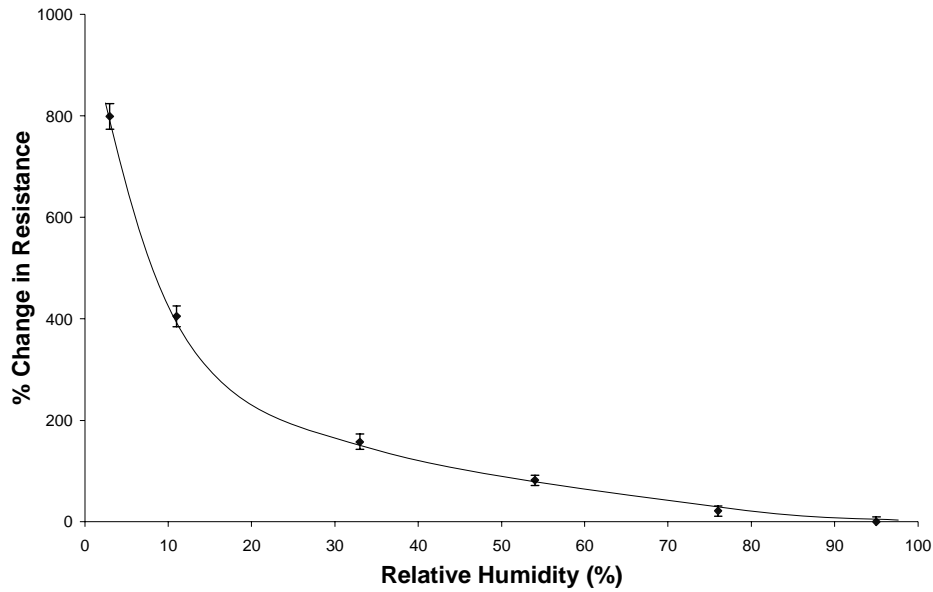
The rate of water ingress into or out of the polymer was seen to be dependant on the differential between the current concentration of water in the sensor and the concentration of water in the surrounding atmosphere. As could be expected, the larger this differential, the longer the time needed to reach equilibrium in the sensor and the times required to reach equilibrium for humidifying stages were much faster than that for desiccating stages. It was seen for the largest differential (from 3 to 95% RH) the uncoated sensors took approximately 4 to 5 hours to reach 90% of the equilibrium resistance on humidifying, whereas 24 hours was required to reach 90% of the equilibrium resistance on desiccating. As could be expected, the EB coated sensors took longer for each of these steps taking approximately 6 to 7 hours to reach 90% of the equilibrium resistance on humidifying and 30 hours was required to reach 90% of the equilibrium resistance on desiccating.

In general, the sensors required several hours to equilibrate after a step change in RH. It is expected that producing thinner coatings over a substrate with a smaller gap between platinum wire electrodes could further reduce the sensor response time.

3.4 Temperature Response

The sensors have been found to be slightly responsive to temperature as shown by the calibration curve from temperature changes of 5 to 60 $^{\circ}$ C in constant 3% RH, seen in Figure 3). Similar resistance decreases have been reported with increases in temperature [30-32] and likewise have been attributed to an increased mobility and movement of either conducting electrons or un-doped dopants.

a)



b)

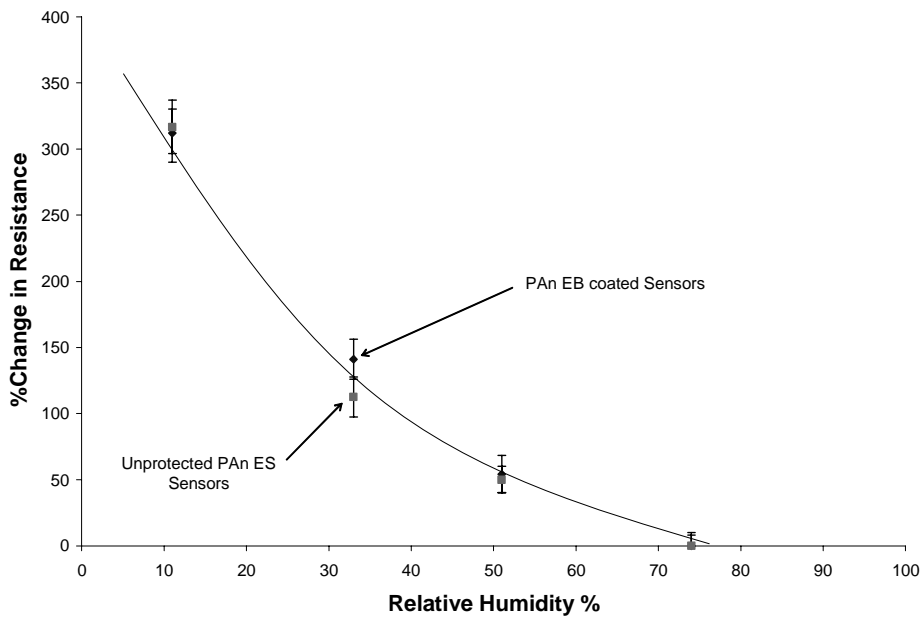


Figure 2) %Change in resistance calibration curve for a) PAn P(BuA-co-VAc) ES sensors and b) PAn P(BuA-co-VAc) ES sensors with and without EB protective coating over varying relative humidity

3.5 Sensor response inside epoxies

Sensors were embedded inside the epoxy polymer Araldite 2015 (Huntsman) to ascertain the stability of the performance for possible use in measuring water content in epoxy composites. Initially it was discovered that a sudden, unrecoverable increase in resistance was recorded with the embedding of PAn ES sensors (uncoated) that pushed the resistance out of range of the multimeter and creating a virtual open circuit. This phenomenon was attributed to a de-

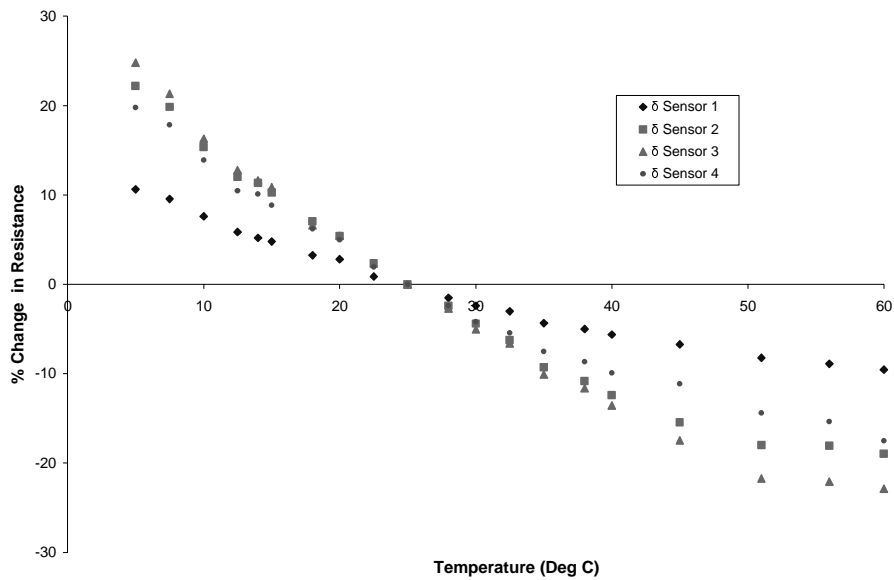


Figure 3) Typical temperature calibration curves for four different 15 w/w% PAN P(BuA-co-VAc) ES sensors in a constant 3% RH doping of the conducting polymer PAN emeraldine salt (ES), to the non conducting emeraldine base (EB) form in the presence of the alkaline, amine rich hardener component of the epoxy blend.

To verify this de-doping process, further sensors were constructed and embedded inside Araldite 2015 and the surface was ground down after curing and dry polished to view a clear cross-section of the sensor substrate. A typical image of this cross-section may be seen in Figure 4).

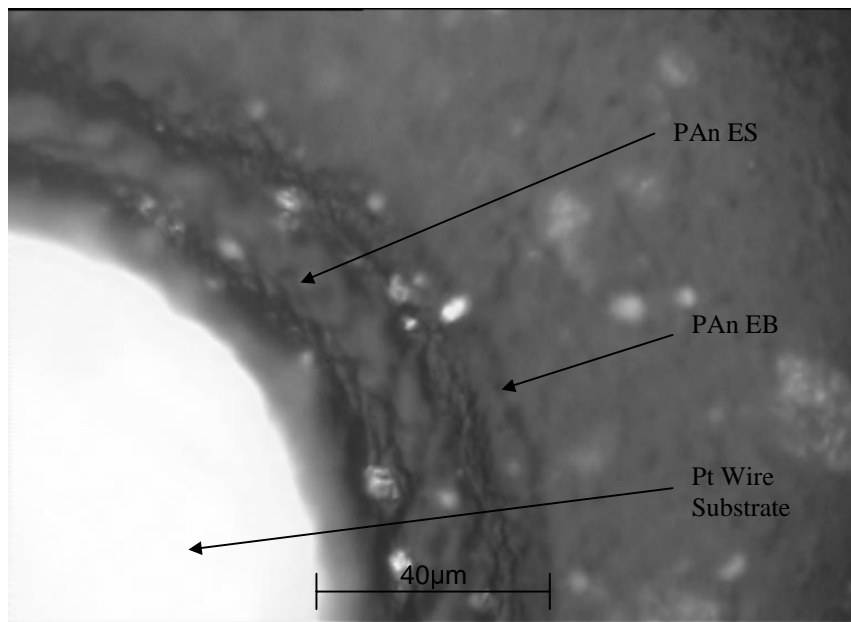


Figure 4) Typical image of a PAN P(BuA-co-VAc) ES sensor cross section after embedding in Araldite 2015

From these images it was found that the outside surface in direct contact with the Araldite 2015 showed a clear colour change and had indeed been converted to the EB form of PAn up to a depth of approximately 10-20 μm , which was further verified by examination and comparison of a map of Raman spectra across the surface.

With larger initial coating thicknesses (greater than 30 μm), the polymer thickness directly between the conducting electrodes was found to be 60 μm or greater. Once embedded in Araldite 2015, it was seen that again the outside layer was deprotonated to a depth of 10 – 20 μm , which still left a 20 - 40 μm pathway of conducting PAn ES. In essence, these sensors should still be conductive and show a clear response. The two sensor types PAn ES (unprotected) and PAn EB coated were placed in a desiccating chamber, allowed to stabilise, and then coated with Araldite 2015. The sensor response was monitored over time and compared.

When embedded at constant RH, each of the sensors showed an initial drop in resistance (from the uncured epoxy) and started to reach stability after complete curing of the epoxy (24 hrs). This response may be seen in Figure 5). With the increased coating thickness of the unprotected sensors, it was seen that the de-doping of the polymer surface was not to the extent to irreversibly increase the overall resistance of the sensor out of range, and a clear response was recorded. It was seen though, that sensors of the same type (PAn P(BuA-co-VAc) ES – unprotected) showed quite different sensing material responses. With this in mind, concerns must be had to the stability and predictability of the unprotected sensor's performance once embedded in epoxy.

The EB coated sensors on the other hand, show responses that almost overlapped albeit with a slightly slower response. From these initial results it can be concluded that the EB coating is acting as a successful barrier to the de-protonating nature of the Araldite 2015 epoxy, and ensuring a more consistent response within the sensor.

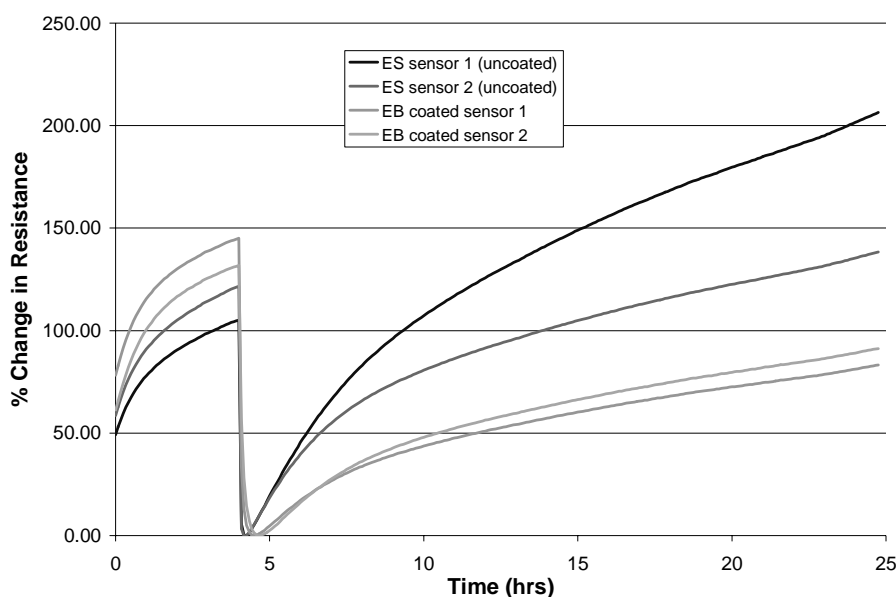


Figure 5) Sensor response of EB coated and uncoated sensors once embedded in Araldite 2015 at constant 3% RH

4. CONCLUSIONS

Micro humidity sensors were constructed from a polyester insulated platinum wire substrate to have a thickness of no more than 150 μm . Two processable polyaniline blends for substrate dip-coating were developed both with a butyl acrylate / vinyl acetate copolymer (P(BuA/VAc)), each with 15 w/w% PAn in the final sensing material. One of the blends consisted of PAn in the conducting emeraldine salt ES form and the other with PAn in the non-conducting

emeraldine base form. Two sensor types were produced that consisted of the PAn ES as the sensing material, with one type utilising a further PAn EB coating as a protective barrier layer against ES deprotonation. The sensors were investigated for their ability to sense atmospheric humidity and water content.

Both sensor types showed consistent and measurable responses. Each sensor type showed exponential responses with high sensitivity representing over a 300% resistance change from 11 – 74%RH. Calibration curves for the EB coated sensors were found to show the same shape and sensitivity was not compromised from the EB coating. Similarly, a high sensitivity was recorded with over a 300% resistance change from 11 – 74% RH.

The EB coating on the sensors was shown not to harm the overall performance of the standard uncoated sensors and to act as a protective layer ensuring a more stable and predictable response when placed inside a curing epoxy environment. Further comparisons of resistance vs relative humidity are currently being undertaken for sensors before and after embedding in epoxy.

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REFERENCES

- [1] R. A. H. Pethrick, D.; Li, Z.-C.; Banks, W.M.; Dumolin, F.; Halliday, S.T., Dielectric and mechanical assessment of water ingress into carbon fibre composite materials., (1999) 55-74
- [2] S. R. Taylor, A non-destructive electrochemical method to detect and quantify graphite fibre/polymer matrix disbondment in aqueous and cathodically polarized conditions, *Composite Interfaces*, 2, (1995) pp. 403-417
- [3] P. B. Chiou, W.L., The effect of seawater on the fatigue edge delamination growth of a carbon/epoxy composite, 5, (1993) 516-523
- [4] K. M. Komai, Kohji; Tanaka, Kozuto, Influence of water absorption on delamination induced by low-velocity impact and CAI strength of FRPS, 2, (1997) 503-512
- [5] B. V. Kishore; Khan, B., On the utility of an instrumented impact set-up to characterize the response of discontinuous buffer strips in carbon-epoxy systems in dry and wet conditions., *Polymer Testing*, 20, (2001) pp. 453-457
- [6] M. Sato and T. Yamamoto, Sensitivity of phase velocity of a composite ZnO plate to humidity, *Sensors and Actuators B: Chemical*, 13, (1993) pp. 96-99
- [7] N. Ichinose, Humidity sensitive characteristics of the MO---WO₃ (M = Mg, Zn, Ni, Mn) system, *Sensors and Actuators B: Chemical*, 13, (1993) pp. 100-103
- [8] E. Traversa, A. Bearzotti, M. Miyayama and H. Yanagida, Study of the conduction mechanism of La₂CuO₄--ZnO heterocontacts at different relative humidities, *Sensors and Actuators B: Chemical*, 25, (1995) pp. 714-718
- [9] Y. Sakai, Y. Sadaoka and M. Matsuguchi, Humidity sensors based on polymer thin films, *Sensors and Actuators B: Chemical*, 35, (1996) pp. 85-90
- [10] Y. Sakai, Humidity sensors using chemically modified polymeric materials, *Sensors and Actuators B: Chemical*, 13, (1993) pp. 82-85
- [11] P. R. Story, D. W. Galipeau and R. D. Mileham, A study of low-cost sensors for measuring low relative humidity, *Sensors and Actuators B: Chemical*, 25, (1995) pp. 681-685
- [12] C.-D. Feng, H. Wang, S.-L. Sun, C. U. Segre and J. R. Stetter, Comparison of conductometric humidity-sensing polymers, *Sensors and Actuators B: Chemical*, 40, (1997) pp. 211-216
- [13] T. Kuroiwa, T. Hayashi, A. Ito, M. Matsuguchi, Y. Sadaoka and Y. Sakai, A thin film polyimide based capacitive type relative humidity sensor, *Sensors and Actuators B: Chemical*, 13, (1993) pp. 89-91
- [14] C. Roman, O. Bodea, N. Prodan, A. Levi, E. Cordos and I. Manovicu, A capacitive-type humidity sensor using crosslinked poly(methyl methacrylate-co-(2 hydroxypropyl)-methacrylate), *Sensors and Actuators B: Chemical*, 25, (1995) pp. 710-713
- [15] G. Vaivars, J. Pitkevics and A. Lasis, Sol-gel produced humidity sensor, *Sensors and Actuators B: Chemical*, 13, (1993) pp. 111-113

- [16] H.-T. Sun, Z.-T. Cheng, X. Yao and W. Wlodarski, Humidity sensor using sol--gel-derived silica coating on quartz crystal, *Sensors and Actuators B: Chemical*, 13, (1993) pp. 107-110
- [17] C.-D. Feng, S.-L. Sun, H. Wang, C. U. Segre and J. R. Stetter, Humidity sensing properties of Nafion and sol-gel derived SiO₂/Nafion composite thin films, *Sensors and Actuators B: Chemical*, 40, (1997) pp. 217-222
- [18] G. Montesperelli, A. Pumo, E. Traversa, Gusmano, A. Bearzotti, A. Montenero and G. Gnappi, Sol--gel processed TiO₂-based thin films as innovative humidity sensors, *Sensors and Actuators B: Chemical*, 25, (1995) pp. 705-709
- [19] J. Lin, M. Heurich and E. Obermeier, Manufacture and examination of various spin-on glass films with respect to their humidity-sensitive properties, *Sensors and Actuators B: Chemical*, 13, (1993) pp. 104-106
- [20] M. J. Winokur and B. R. Mattes, Structural Studies of Halogen Acid Doped Polyaniline and the Role of Water Hydration., *Macromolecules*, 31, (1998) pp. 8183 - 8191
- [21] O. N. Timofeeva, B. Z. Lubentsov, Y. Z. Sudakova, D. N. Chernyshov and M. L. Khidekel', Conducting polymer interaction with gaseous substances I. Water, *Synthetic Metals*, 40, (1991) pp. 111-116
- [22] B. Lubentsov, O. Timofeeva, S. Saratovskikh, V. Krinichnyi, A. Pelekh, V. Dmitrenko and M. Khidekel', The study of conducting polymer interaction with gaseous substances IV. The water content influence on polyaniline crystal structure and conductivity, *Synthetic Metals*, 47, (1992) pp. 187-192
- [23] S. Jain, S. Chakane, A. B. Samui, V. N. Krishnamurthy and S. V. Bhoraskar, Humidity sensing with weak acid-doped polyaniline and its composites, *Sensors and Actuators B: Chemical*, 96, (2003) pp. 124-129
- [24] K. Ogura, T. Saino, M. Nakayama and H. Shiigi, The humidity dependance of the electrical conductivity of a soluble polyaniline-poly(vinyl alcohol) composite film, *Journal of Materials Chemistry*, 7, (1997) pp. 2363 - 2366
- [25] P. S. Barker, A. P. Monkman, M. C. Petty and R. Pride, A polyaniline/silicon hybrid field effect transistor humidity sensor, *Synthetic Metals*, 85, (1997) pp. 1365-1366
- [26] A. Mirmohseni, K. Valiegbal and G. G. Wallace, Preparation and characterization of a polyaniline/poly(butyl acrylate-vinyl acetate) composite as a novel conducting polymer composite. *Journal of Applied Polymer Science* (2003), *Journal of Applied Polymer Science*, 90, (2003) pp. 2525 - 2531
- [27] D. Donescu, K. Gosa, A. Ciupitoiu and I. Languri, Semicontinuous emulsion polymerization of vinyl acetate. Part I. Homopolymerization with poly(vinyl alcohol) and nonionic coemulsifier, *Journal of Macromolecular Science, Chemistry*, A22, (1985) pp. 931 - 940
- [28] T. Makawinata, M. S. El-Nassr, J. W. Vanderhoff and C. Pitchot, Preparation, surface and colloidal properties of vinyl acetate-butyl acrylate copolymer latexes - effect of emulsion polymerization process and copolymer composition, *Acta Polymerica*, 32, (1981) pp. 583 - 592
- [29] CRC Handbook of Chemistry and Physics 76th Edition, (1995 and 1996)
- [30] S. Koul, S. K. Dhawan and S. Chandra, Conducting polymer polyaniline - effect of temperature on electrical conductivity transitions, 1, (1998) 332 - 334
- [31] S. Kim, J. M. Ko and I. J. Chung, Electrical conductivity change of polyaniline-dodecyl benzene sulfonic acid complex with temperature, *Polymers for Advanced Technologies*, 7, (1996) pp. 599 - 603
- [32] A. B. Kaiser, C.-J. Liu, P. W. Gilberd, B. Chapman, N. T. Kemp, B. Wessling, A. C. Partridge, W. T. Smith and J. S. Shapiro, Comparison of electronic transport in polyaniline blends, polyaniline and polypyrrole, *Synthetic Metals*, 84, (1997) pp. 699 - 702