

# Antioxidant Plastics based upon Conducting Polymers

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## Introduction: Active Packaging

The packaging industry increasingly is turning to polymer chemists and engineers to develop novel plastic materials with added active functions. In addition to containing a food product or pharmaceutical, the packaging then assists in prolonging the product's shelf-life or improving convenience, *e.g.* through moisture or oxygen control. Further active agents can include ethylene scavengers and antimicrobial compounds such as ascorbic acid. One of the most widespread types of active packaging involves the addition of oxygen scavengers. In the food industry, these scavengers are designed to lessen oxidative damage, such as rancidity in oils and fats, discolouration of meats, and loss of nutritive elements. To be effective, the scavengers need to be able to absorb large quantities of oxygen, be economically priced and preferably recyclable, and, importantly, contain no toxic products that will come in contact with the consumer.

One of the most effective means of removing oxygen from within a package is the inclusion of small sachets containing powdered iron. In other cases an active oxygen scavenger is embedded in the packaging itself. The active material then lowers the internal oxygen concentration by removing oxygen that would otherwise migrate through the plastic. Examples include nylon MXD6 as a high gas barrier resin that is easy to recycle, and which can be prepared as a single layer blend with a beverage plastic such as PET (polyethylene terephthalate) or as a multilayer construction where the scavenger is included within an inner layer. In some cases a cobalt catalyst is added to improve the scavenging properties of the nylon. Another alternative is to incorporate small molecule antioxidants, such as ascorbic acid or sulfites, or to employ an unsaturated organic polymer that can be oxidised and thereby remove oxygen coming through the packaging. In trials on red wines stored in PET bottles with the inclusion of a polyester copolymer oxygen scavenger, the oxygen permeability was found to be decreased by more than 10-fold.<sup>1</sup> Tests over 170 days showed that SO<sub>2</sub>, anthocyanin and flavanol retention was greatest in the PET containers with the oxygen scavenger included. The containers performed even better than storage in glass and this is ascribed to the ability of the scavenger within the PET to remove oxygen already dissolved in the wine.

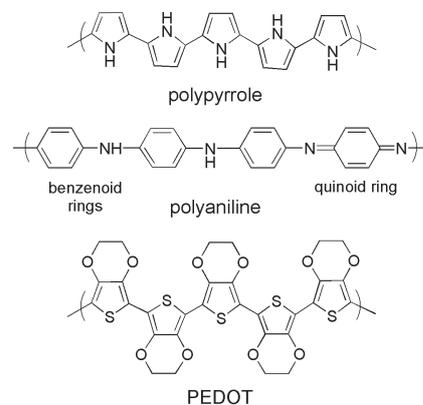
A further related concept in active packaging is the inclusion of antioxidants with radical scavenging properties. These range from the classic antioxidant vitamins, such as  $\alpha$ -tocopherol and  $\beta$ -carotene, through to the more stable synthetic antioxidants, such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT). These antioxidants scavenge free radicals to lessen rancidification in oils and fats, and so they can be included in the plastic packaging, both to retard the oxidation and the degrada-

tion of the plastic itself, and to prolong the shelf-life of products coming in contact with the packaging. At the same time the small molecule antioxidants might leach out of the packaging material, which is not always desirable.

## Conducting Polymers

*Plastics that conduct electricity* is a concept that has become very familiar to NZ chemists, particularly following the 2000 Nobel Prize awarded to Alan MacDiarmid, Hideki Shirakawa (Japan) and Alan Heeger (USA) for work on conducting polymers. Polymers with good environmental stability that are easy to prepare, *e.g.* polypyrrole (PPy), polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT) (Chart 1), have attracted considerable research attention and are being considered in a diverse range of applications such as plastic solar cells, actuators and in biosensing.<sup>2</sup> In some cases, the high conductivity of the polymers in the doped state is important, while in others it is the ability of the polymers to be reversibly oxidised and reduced, *viz.* to be redox-active, that is the important consideration. Oxidised PPy has been found to be a suitable material for *in vitro* nerve cell culture and for the controlled release of drugs.<sup>3,4</sup> An important consideration for *in vivo* applications is the toxicity for PPy, which to date has been found to be low, pointing to good biocompatibility.<sup>5</sup> In further studies, PPy particles did not induce a cytotoxic effect in experiments on mouse cells<sup>6</sup> and showed no evidence of systemic toxicity around the rat sciatic nerve.<sup>7</sup> Biocompatibility studies have been extended more recently to consider cell proliferation on PPy substrates.<sup>8</sup>

Chart 1. Structures of three common conducting polymers



## Antioxidants and Radical Scavenging Test Procedures

Dietary antioxidants such as vitamin C, vitamin E and polyphenols appear to offer protection against cardiovascular diseases and cancers.<sup>9</sup> They can also act as preservatives in foods, and in the case of lipid-soluble antioxidants can help limit the onset of rancidity, especially for foods

rich in polyunsaturated fats. An excessive production of free radicals is thought to be responsible for high levels of oxidative damage, whereby species that contain unpaired electrons react with biomolecules to cause cellular injury and death.<sup>10</sup> The mechanism of action of antioxidants can include chelation of pro-oxidative metals, oxygen scavenging and free radical termination.<sup>11</sup> Antioxidants can then be defined as compounds present in foods or in the body in small amounts that prevent or inhibit reactions promoted by oxygen and radicals such as peroxides.

As the ultimate effects of a good dietary supply of antioxidants in the body or the inclusion of preservative antioxidants, such as SO<sub>2</sub> or ascorbic acid, in beverages is only realized over a time-frame of years, more rapid antioxidant capacity tests have been developed for food and biomedical studies. These rapid bench-top assays, many of which provide a measure of the free radical scavenging of the antioxidant compounds present, have inevitable limitations but can be used to provide an indication of the potential, or capacity, for antioxidant activity, *e.g.* of a glass of red wine. The main antioxidant capacity test procedures have been classified as either single electron transfer (ET) assays or hydrogen atom transfer (HAT) assays.<sup>12</sup> An example of an ET-based method, in which antioxidants reduce a supplied oxidant radical, is the 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) assay, based upon their reaction with the ferrylmyoglobin radical, formed through activation of metmyoglobin by hydrogen peroxide, or alternatively by the reaction of ABTS with potassium persulfate, to produce the coloured radical cation ABTS<sup>•+</sup>.<sup>13</sup> Antioxidants can quench the ABTS<sup>•+</sup> radical and thereby decolourise the reaction mixture, which is monitored by a spectrophotometer at 753 nm. The ABTS assay is applicable to both lipophilic and hydrophilic phases.<sup>13</sup> A further ET method is the  $\alpha,\alpha$ -diphenyl- $\beta$ -picrylhydrazyl (DPPH) assay, in which a more effective radical scavenger removes the purple coloured DPPH radical more rapidly and/or more completely.<sup>14,15</sup> Both of these assays have been widely applied to measure the total antioxidant capacity of foods and beverages.<sup>16</sup> An example of an HAT-based assay is the oxygen radical absorbance capacity (ORAC), in which the antioxidants and a substrate compete for peroxy radicals generated by the decomposition of azo compounds. A further approach to testing the effectiveness of antioxidants is to set up accelerated aging trials in which a beverage or food oil is heated for several weeks, and the browning of the beverage, or degradation of the oil with build-up of peroxides, is monitored.

### Conducting Polymers as Free Radical Scavengers

The role of polyanilines, alongside aromatic amines, in stabilising rubber mixes has been demonstrated, whereby polyaniline or poly(methoxyaniline) slowed down the rate of oxidation of the rubber itself.<sup>17</sup> Our interest in conducting polymers as antioxidants was stimulated by a recognition of the similar oxidation potentials of several polyphenol antioxidants, such as catechin and many of the common conducting polymers, indicating a similar strength as reducing agents.<sup>18</sup> This led us to test a number

of commercially available *soluble* conducting polymers in the DPPH assay over a 30 minute test period, and the conducting polymers were found to be very effective free radical scavengers.<sup>18,19</sup> By using electrochemical tests to evaluate the potential at which the DPPH radical is reduced in a methanolic test solution, itself a weak oxidising agent, the high effectiveness of the conducting polymers relative to the original aniline and pyrrole monomers could be understood. Likewise, the high scavenging activity in the DPPH assay of certain groups of polyphenols, namely those with more readily oxidizable catechol and galloyl groups, was also explained relative to the low response observed for polyphenols with more isolated phenol groups that are more difficult to oxidise. This observation is important in understanding differences obtained with the DPPH assay for food and beverage extracts compared to measures of polyphenol content such as the Folin-Ciocalteu assay.<sup>20</sup>

In further investigations various spectroscopic measurements were applied to solid conducting polymer samples, mainly polyaniline, before and after exposure to a DPPH test solution, including EPR, XPS, and solid state NMR, using both <sup>13</sup>C and <sup>15</sup>N NMR studies. For this work and in subsequent studies, the conducting polymer powders were prepared using ammonium persulfate as the oxidising agent to effect the required chemical polymerisations. The various spectroscopic studies confirmed that polyaniline was oxidised in the course of the DPPH test and that, indeed, it had acted as a reducing agent, while no evidence was seen for additional chemical binding or trapping of the DPPH radicals within the polyaniline structure.<sup>21,22</sup>

Solid conducting polymer samples created some difficulties with standard DPPH test protocols, where 1.5 mL of a 72  $\mu$ M solution of coloured DPPH radicals (with an initial absorbance maximum at 516 nm of around 0.65 units) was typically employed. The first issue centered around a nearly complete removal of DPPH radicals within a couple of minutes when just 1 mg of conducting polymer was employed. This means that conducting polymer samples could not be differentiated using the existing methodology. The final form of the DPPH assay now involves 20 mL of a 255  $\mu$ M solution of DPPH radicals and 1.0 mg conducting polymer samples with controlled shaking during the reaction period.<sup>23</sup> Even though the initial absorbance reading is around 2.6 units, final readings in the 0.5 to 1.0 range are typically obtained, allowing comparisons between conducting polymer samples to be made. Under these conditions, the scavenging of DPPH radicals continues well beyond the 30 minute test period typically employed for small molecule antioxidants in solution. Differences between soluble antioxidants and the solid conducting polymers contribute to this effect, along with the wide range of oxidation potentials of the conducting polymer structural units (seen also in the broad oxidation curves typical of cyclic voltammograms). The test procedure has thus been extended to 24 hours of reaction time before the final readings are taken.

Owing to variations in the performance of the antioxidant capacity assays, there is a current trend to apply a range of test procedures to confirm experimental findings. The

ABTS assay has thus been adapted for use with conducting polymer powders in a 3 hour test procedure.<sup>24</sup> Likewise, the ORAC assay has been adapted for use with conducting polymer-containing films.<sup>25</sup> With these test procedures in place, it has been possible to assess the radical scavenging efficiency of different conducting polymers. In their as-prepared, partially oxidised forms, polypyrrole and polyaniline showed more effective radical scavenging than PEDOT, both on a mass basis, and in the number of monomer units required to scavenge each free radical (Table 1). Similar results were obtained using both DPPH and ABTS assays, although the polymers were able to scavenge more DPPH than ABTS radicals. This trend was observed despite that fact that the ABTS radical is a stronger oxidizing agent than the DPPH radical, suggesting that further properties are at work in determining the extent of radical scavenging than oxidation strength alone.<sup>24</sup>

**Table 1.** Comparison of DPPH<sup>•</sup> and ABTS<sup>•+</sup> scavenging activity of the as-prepared conducting polymers, expressed as the ratio of the number of monomer units required per free radical scavenged.<sup>a</sup>

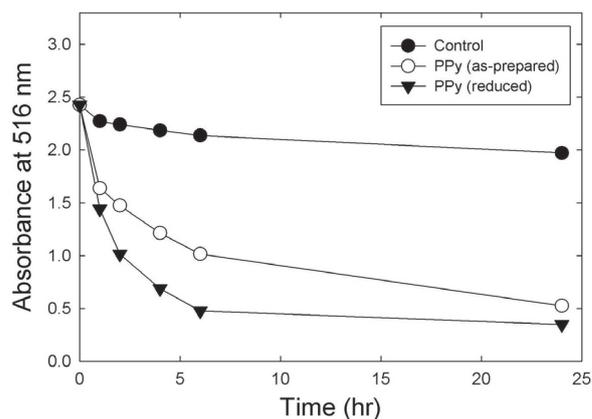
	<i>PPy</i>	<i>PANI</i>	<i>PEDOT</i>
ABTS <sup>•+</sup>	6:1	4:1	7:1
DPPH <sup>•</sup>	3:1	2:1	8:1

<sup>a</sup>Data taken from ref. 24

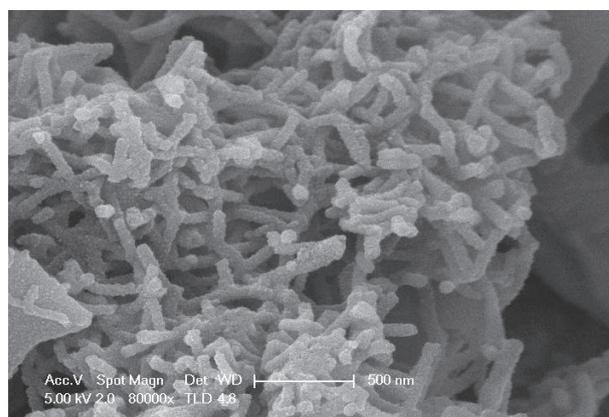
It was further established that pre-reduced forms of the conducting polymer powders, obtained by reduction with hydrazine, were even more effective free-radical scavengers than the as-prepared partially oxidised forms (Fig. 1), consistent with the expected redox interaction involved.<sup>24,26</sup> The available surface area is also expected to be important in determining the extent of radical scavenging: PANI nanofibres of decreasing average diameter have been shown to exhibit a greater radical scavenging ability in the DPPH assay.<sup>27</sup> The enhanced antioxidant activity was attributed to the increased surface area of the PANI nanofibres, a result obtained in a further study on PANI nanofibres.<sup>28</sup> We have also found that PANI prepared conventionally in the presence of a strong acid such as sulfuric acid, consisting of granular PANI particles, was less effective than PANI prepared without added acid, in which high surface area nanotubes are formed (Fig. 2). This was seen in the DPPH assay (Fig. 3), and in the ABTS assay.<sup>24</sup> That said, the higher scavenging of DPPH radicals of the nanotube form may be related as much to the initial oxidation state of the PANI products, as to the surface area of the different polymer forms.

### Conducting Polymer Blends

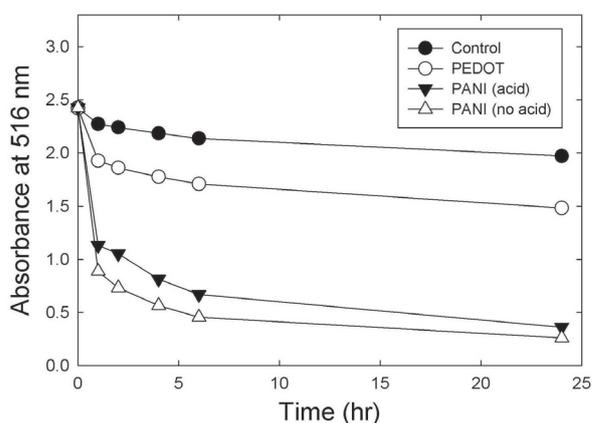
Conducting polymers on their own are not immediately suitable as a plastic packaging materials, as they lack the necessary mechanical properties. Forming blends between conducting polymers and food-grade plastics is the next step to consider, with the aim of retaining the mechanical properties of the packaging material and the radical scavenging activity of the conducting polymer. Blends between conducting polymers and both ethyl cellulose and polyethylene have been developed at the University of Auckland and form the basis of a provisional patent.<sup>25,29</sup>



**Fig. 1.** Decline in the 516 nm absorbance of a 225  $\mu$ M methanolic solution of DPPH radicals with 1.0 mg of PPy powders added.



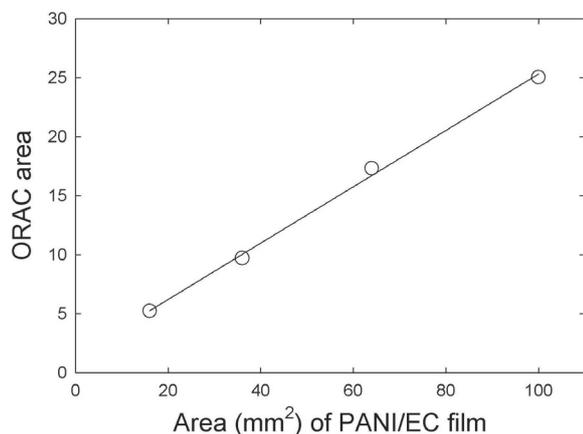
**Fig. 2.** SEM image of polyaniline nanotubes from oxidation of aniline by ammonium persulfate in the absence of strong acids (500 nm scale bar).



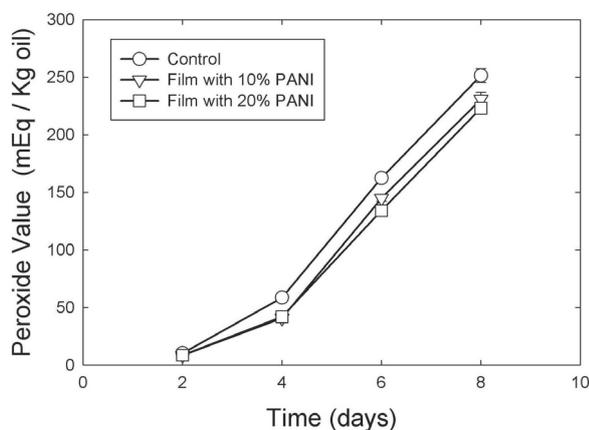
**Fig. 3.** Decline in the 516 nm absorbance of a 225  $\mu$ M methanolic solution of DPPH radicals with 1.0 mg of PANI and PEDOT powders added.

Polyaniline has been blended with ethyl cellulose (EC) via dispersion in ethanol prior to casting and solvent removal to produce PANI/EC films. The ORAC assay was readily applied to the films, and it was found that the greater the size of the PANI/EC film present, the more effectively it competed with fluorescein for the peroxy radicals, leading to a longer delay in fluorescence decay and correspondingly larger *ORAC area* (Fig. 4). Once again, films containing reduced PANI were more effective

tive radical scavengers. In each case, the results indicated that active conducting polymer was available to the test solution and was not completely blocked by the presence of ethyl cellulose, even though the films themselves had very low conductivity values. To extend the test procedures to a real food sample, fish oils were subject to accelerated degradation at 60 °C in the presence of air, leading to considerable oil oxidation and the build up of peroxides. PANI/EC films were able to slow down the rate of oxidation to a measurable extent, although the benefit was only slightly better with a film containing 20% PANI compared to one prepared with 10% PANI (Fig. 5).



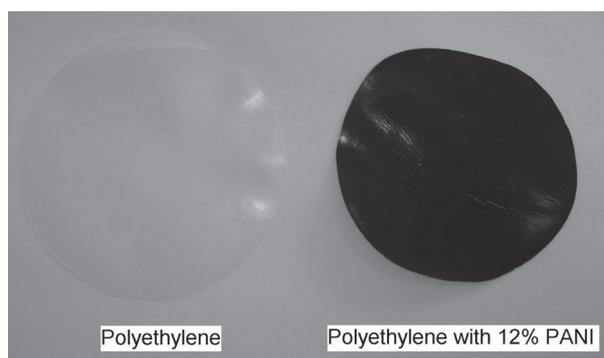
**Fig. 4.** Response of PANI/ethyl cellulose films in the ORAC antiradical assay.



**Fig. 5.** Accelerated stability test on a fish oil using PANI/ethyl cellulose films; 60 °C with exposure to the air ( $n = 3$ ).

Ethyl cellulose is an interesting cellulose derivative that can be used as a thin-film coating material, but the thermoplastic polymer polyethylene (PE) is much more widely applied, with an annual production of around 80 million tons world-wide. Blending of PANI and PE has also been achieved through compression moulding at 180 °C. With the inclusion of 12% PANI (Fig. 6), very good mechanical properties of the PE were retained and effective radical scavenging again established. Like the famous Ford Model T motor car, these films are currently available in any colour, as long as it is black! Through the inclusion of a polymeric antioxidant in the blend, rather than small molecule antioxidants, the issue of the leaching of the antioxidant out into the packaged product is minimised,

provided that high molecular weight conducting polymers are used and smaller oligomeric units are removed prior to blending.



**Fig. 6.** Photograph of two polyethylene pressed disks (11 cm diam.); that at right contains 12% PANI by weight.

## Final Remarks

Conducting polymers have been shown to be effective free radical scavengers, related to their ability to be oxidised in a similar potential range to small molecule antioxidants. Several conventional food science radical scavenging assays and accelerated storage procedures have been adapted to solid conducting polymers to evaluate the effectiveness of different samples and preparations. At the same time, the applied test assays can be considered as a useful means of assessing the available redox activity of conducting polymers when present in blends or as surface coatings. This provides important information on surface properties that can complement conductivity measurements, in particular.

The prospects for active packaging involving conducting polymers remain very promising where the effects of a solid antioxidant material can be used to extend product shelf-life. The radical scavenging property of conducting polymers also needs to be kept in mind when various biomedical applications are being developed, e.g. in nerve regeneration, wound healing and artificial muscles. This is because the scavenging of free radicals may assist in lowering levels of oxidative stress in the tissues and fluids in immediate contact with the conducting polymer.

## Acknowledgements

Research into conducting polymers as antioxidants has involved several projects over the past seven years. I am grateful to my collaborators Drs Allan Easteal and Jadranka Travas-Sejdic, and Profs. Graham Bowmaker and Ralph Cooney. The research studies of Drs. Marija Gizdavic-Nikolaidis, Chyong Fang Hsu, Zoran Zujovic, Hui Peng and Lijuan Zhang, and Corrina Thompson, Richard Delgenes, Cedric Basle and Ashveen Nand have led to the results described herein.

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