

Conductive polymer/silver-coated textile composites with antibacterial properties

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*A composite made up of a conductive polymer, poly(*o*-anisidine), and metallic silver particles imparts antibacterial activity and electrical conductivity when deposited on a nonwoven textile fabric.*

Conductive textile composites have potential for use in a range of applications, including antistatic apparel and household goods, EMI shielding, sensors, and for medical purposes.^{1–9} Such composites are generally prepared by in situ oxidative polymerization. In this method, polymerization occurs on the textile surface when it is dipped into a polymerization solution, thus enabling homogeneous polymer deposition. This technique has a number of advantages, the most significant of which is the facile one-step synthesis and homogeneous polymer deposition (e.g., onto a fabric) that it enables. This technique also requires relatively simple and economic devices compared to other methods such as electropolymerization.

Among the various oxidizing agents that are used in polymerization, silver nitrate (AgNO_3) is promising because it enables the simultaneous deposition of metallic silver particles and a conductive polymer. Thus, by using this method, composites gain versatile properties (e.g., antibacterial activity and improved conductivity).^{10–12} The oxidizing ability of AgNO_3 is relatively low, however, and additional chemicals (such as phenylenediamines and secondary oxidants) may also be used.^{13,14} Further, additional processes are required, such as the non-economical treatment of UV light for shortening the polymerization time.^{11,12}

In our study, we prepared a nonwoven composite comprising poly(*o*-anisidine), silver, and poly(ethylene terephthalate)—POA/Ag/PET—by polymerization of *o*-anisidine with AgNO_3 . POA is one of the most conductive derivatives of polyaniline and has a number of other useful properties, such as its ability to provide a homogeneous surface coating.¹⁵ We investigated the effects of polymerization conditions on both the POA/Ag content and the volume resistivity of the composite. We also evaluated the antibacterial activity of POA/Ag/PET by comparing it with a POA/PET composite.

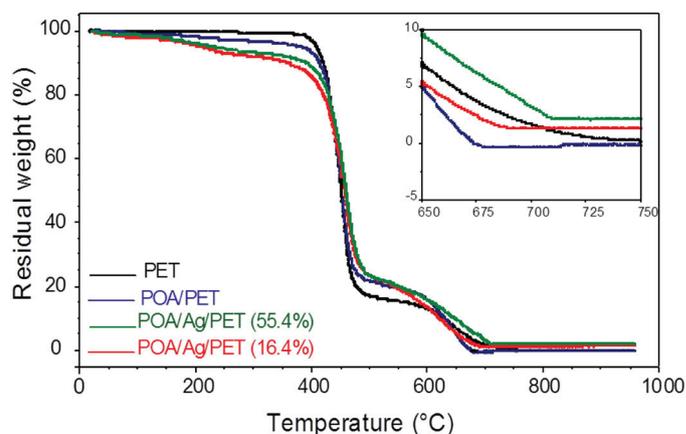


Figure 1. Thermogravimetric analysis curves of non-woven PET and non-woven PET coated with composites of POA/PET and POA/Ag/PET (with POA/Ag contents of 55.4 and 16.4%). The inset shows a close-up view of the material behavior between a temperature range of 650 and 750°C. PET: Poly(ethylene terephthalate). POA: Poly(*o*-anisidine). Ag: Silver.

To accelerate the polymerization of *o*-anisidine, we used ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, or ferric nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ —both of which prevent the formation of unwanted silver salts—as a secondary oxidant. When $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was used, the resulting composites had a relatively higher POA/Ag content and exhibited lower resistivity. In this case, the deposited silver particles were also visible to the naked eye.

To investigate the effect of acid type on POA/Ag content and the resistivity of the resulting composite, we selected nitric acid (HNO_3) and various sulfonic acids—such as *p*-toluene sulfonic acid, camphor sulfonic acid, and dodecyl benzene sulfonic acid—because their side groups do not allow the precipitation of unfavorable silver salts, and act as an anionic dopant for POA.^{16–19} We found that the POA/Ag contents of the composites obtained using sulfonic acid were higher than

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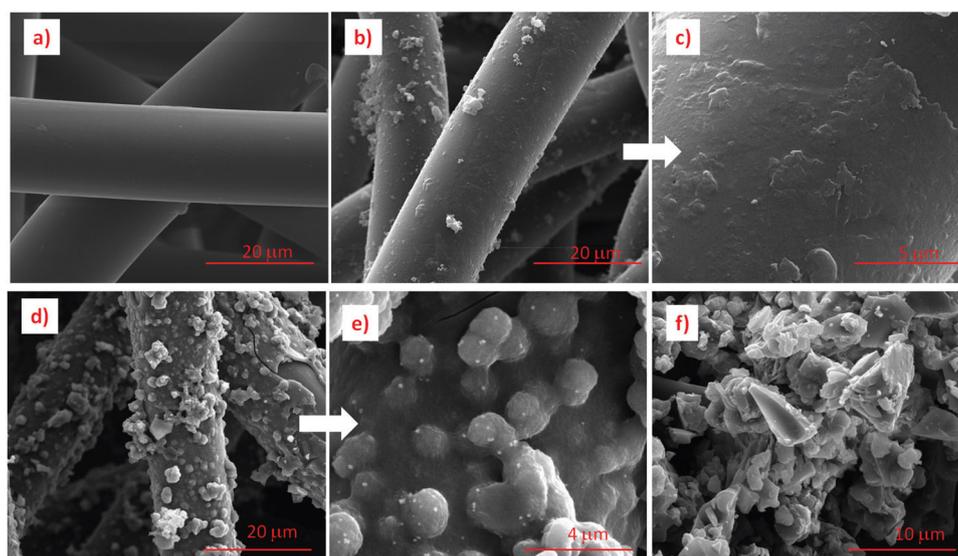


Figure 2. Scanning electron micrographs of (a) uncoated nonwoven PET, and nonwoven PET coated with: (b) and (c) a POA/Ag/PET composite containing 13.5% POA/Ag; (d) and (e) a POA/Ag/PET composite containing 55.4% POA/Ag; and (f) POA/Ag powder obtained from solution polymerization in nitric acid.

those obtained using HNO_3 . We believe that this result may arise due to the incorporation of bulky dopant anions.^{17,20} Although we could not correlate the resistivity with the type of acid used, we obtained the lowest resistivity by using HNO_3 . We found a solution of 1.0M HNO_3 to provide the most suitable medium in terms of achieving the lowest resistivity in the resultant composite.

We used thermogravimetric analysis to determine the silver weight fractions in the nanocomposites' POA/Ag content: see Figure 1. Silver weight fractions were calculated from residual weight values of the composites at 800°C. We found that although the POA/Ag contents of the composites increased, the content of silver particles decreased, thus showing that the contribution of POA to the POA/Ag content was rather higher than that of the silver particles.

We used scanning electron microscopy to evaluate the surface morphology of non-woven PET, and non-woven PET coated with POA/Ag/PET composites containing low (13.5%) and high (55.4%) amounts of POA/Ag, and POA/Ag powder (see Figure 2). The micrographs of the composites show the smooth non-woven PET fabric surface—see Figure 2(a)—covered with homogeneous film-like POA layers and silver particles: see Figure 2(b) and (d). The thickness of the POA coating increased with the POA/Ag content. This increase was evident from the cracks that formed on the nonwoven surface, reflecting our previous findings.¹⁵ Interestingly, the deposited silver particles were interspersed as shiny areas on the granular POA aggregates: see Figure 2(e). We estimated the diameter of these silver particles to be around 75nm. In contrast to the POA/Ag coatings on the composites,

Table 1. Antibacterial activity of POA/Ag/PET and POA/PET composites, given by the composites' zone of inhibition diameter.

Composite	Organism	Zone of inhibition diameter (mm)
POA/Ag/PET	<i>E. coli</i>	10
	<i>S. aureus</i>	10
POA/PET	<i>E. coli</i>	0
	<i>S. aureus</i>	0

the POA/Ag powder showed a different bulk structure and the silver particles could not be easily distinguished: see Figure 2(f).

We investigated the antibacterial activity of the POA/Ag/PET composite against *E. coli* and *S. aureus* by comparing its zone of inhibition with that of a POA/PET composite. The results are compiled in Table 1, and optical images of the composites are shown in Figure 3. We observed a high amount of bacterial growth on the POA/PET composite, suggesting that there was no antibacterial activity against the organisms. In contrast, as a result of the presence of silver particles, the POA/Ag/PET composite showed an efficient level of antibacterial activity (with a zone of inhibition of 10mm diameter). This indicates that the POA/Ag/PET composite could be of use in applications that require both antibacterial activity and electrical conductivity.

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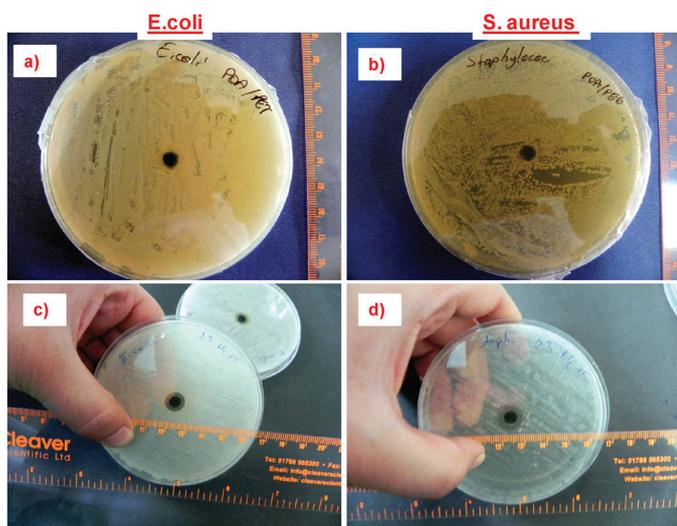


Figure 3. Optical images showing the antibacterial activity results of the POA/PET composite against (a) *E. coli* and (b) *S. aureus*, and the POA/Ag/PET composite against (c) *E. coli* and (d) *S. aureus*.

We used a facile polymerization method to create a composite comprising POA (one of the most conductive polyaniline derivatives) and metallic silver particles, and demonstrated its use as a surface coating on non-woven PET fabric. The volume resistivity was significantly affected by the type of acid used as polymerization medium. We found that using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as a secondary oxidant led to a high POA/Ag content and low volume resistivity. We were also able to detect the presence of deposited silver particles on the surface of the fabric by naked eye. Finally, the antibacterial activity of the POA/Ag/PET composite suggests that it could be useful in antibacterial applications that also make use of its electrical properties. By changing the type of conductive polymer and deposited metallic nanoparticles used, various textile composites with altered or improved properties could be prepared for a variety of applications, such as biomedical treatments and diagnostics, and antistatic applications.^{12, 21} We continue to undertake further investigations and experiments into the preparation of different conductive textile composites to improve their electrical properties and introduce versatile properties.

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