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Role of stilbene-triazine sulfonic acid sodium salts in tuning electro-conductivity of polypyrrole-paper composites

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ABSTRACT

Electro-conductive paper-based products can suit the needs of various end-use applications, e.g., antenna and energy-storage devices. Here, the concept of using stilbene-triazine sulfonic acid sodium salts (STAS) as dopants for enhancing the conductivity of polypyrrole-paper composites and mitigating the decay of conductivity was demonstrated. Noticeably, the combined use of hexa-sulfonic STAS and 9,10-anthraquinone-2-sulfonic acid sodium salt (AQSAS) as dopants delivered significant enhancement of conductivity. Meanwhile, the decay of conductivity during storage was substantially mitigated. Moreover, the effectiveness of hexa-sulfonic STAS was much more pronounced than the other two types of STAS, i.e., di-sulfonic STAS and tetra-sulfonic STAS.

1. Introduction

The development of electro-conductive products for various end-use applications is an active research area [1–8]. Conducting polymers, including polyaniline (PANI), polypyrrole (PPy), polythiophene (PTH), and poly (*p*-phenylene vinylene) (PPV), have a number of envisaged applications. Examples of possible applications include electromagnetic shielding, electronic and optical devices, energy-storage devices, rechargeable batteries, catalysts, and light emitting diodes [9–21].

Basically, the electro-conductivity of conducting polymers or their composites can be tuned by doping with appropriate agents (either *n*-type (electron-rich) or *p*-type (electron-poor)) [22–26]. Indeed, PPy is one of the most extensively studied conducting polymers, which can be formed into various composites [27–29]. PPy can be produced on the basis of electrochemical and chemical oxidative polymerization processes [30–32]. For PPy or its composites, efforts have been made to enhance the conductivity and mitigate the decay of conductivity by using such dopants as chloride, sulfate, anthraquinone sulfonic acid, polystyrene sulfonic acid, sodium bis (2-ethylhexyl) sulfosuccinate, dodecyl benzene sulfonic acid, sodium dodecyl sulfate, 2-naphthalene-sulfonic acid, and indigo carmine [32–40].

Stilbene-triazine sulfonic acid sodium salts (STAS) are effective UV absorbents/screeners due to their unique structures, and they are widely used in the paper industry as optical brightening agents (known as OBAs) to increase pulp brightness and protect paper sheets from harmful UV-radiation [41,42]. STAS have sulfonic groups (-SO_3Na), and the number of these groups may vary, depending on the applications [43]. The presence of these groups indicates that STAS may potentially be used as dopants for conducting polymers such as PPy. However, to the best of our knowledge, the use of stilbene-triazine sulfonic acid sodium salts (STAS) as dopants has not been reported.

The effective utilization or proper disposal of renewable resources is essential for a green economy and a sustainable future [44,45]. In fact, bio-based resources can be converted into various products for diversified applications [46–51]. Cellulosic paper-based products are derived from renewable lignocellulosic feedstocks, and they are widely used in printing/writing, households, industrial processes, etc. Composites of conductive polymers and cellulosic paper are attractive products, since they are fully recyclable, lightweight, and can be manufactured at a low cost [52]. Basically, the fabrication of conductive paper can be performed via in-situ oxidative polymerization of pyrrole in the presence of pulp fibers or anchoring conducting materials onto paper surface [52–61]. Due to the oxidative PPy degradation, the conductivity of PPy-paper composites tends to decrease during storage, which may be affected by the nature of the dopants [62]. In most cases relevant to applications of PPy-paper composites, the decay of conductivity somehow needs to be substantially mitigated.

In the current study, stilbene-triazine sulfonic acid sodium salts (STAS) were investigated as dopants in the in-situ oxidative polymerization process pertaining to the formation of PPy-paper composites. It

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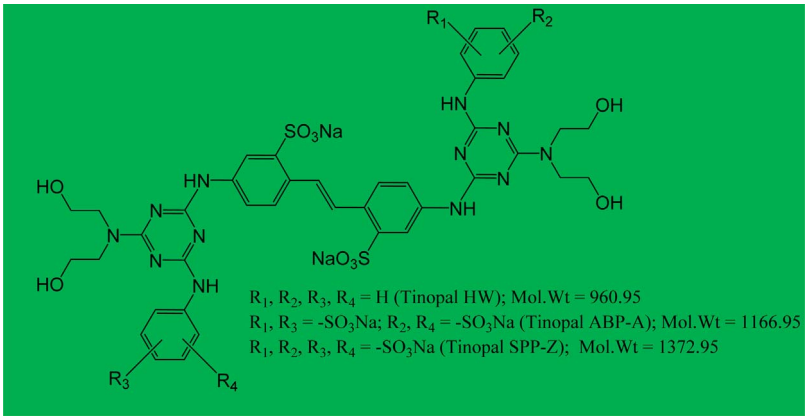

Fig. 1. Chemical structure of stilbene-triazine sulfonic acid sodium salts (STAS).

Table 1
Definitions of sample IDs of PPy-paper composites.

PPy-paper composites
PPC: PPy-AQSAS-paper composites (without STAS)
PPC2A: PPy-20% STAS-2-paper composites – (without AQSAS)
PPC2B: PPy-40% STAS-2-paper composites – (without AQSAS)
PPC2C: PPy-AQSAS-20% STAS-2 paper composites
PPC4: PPy-AQSAS-20% STAS-4 paper composites
PPC6: PPy-AQSAS-20% STAS-6 paper composites

Note: "20%" or "40%" indicates the dosage of STAS relevant to the amount of pyrrole.

was hypothesized that the presence of sulfonic groups would enable the use of STAS as effective dopants, and their role in inhibiting UV-induced PPy degradation would help to mitigate the decay of conductivity upon storage. Encouragingly, the conductivity of the composites was significantly improved, while its decay during storage was inhibited, when hexa-sulfonic STAS was used in combination with 9,10-anthraquinone-2-sulfonic acid sodium salt (AQSAS) as dopants.

2. Experimental

2.1. Materials

Hardwood-derived bleached kraft pulp (a typical paper-grade pulp) was obtained from a pulp and paper mill in Eastern Canada. Pyrrole (98%, Aldrich) was freshly distilled under reduced pressure and stored at 4 °C prior to use. All other chemicals including 9,10-anthraquinone-2-sulfonic acid sodium salt (AQSAS) (Aldrich), $FeCl_3$ (Aldrich), STAS samples (20–25% of aqueous solution, Ciba, Switzerland) were used as received. The STAS samples used in the formation of PPY-paper composites are: (1) Tinopal HW (STAS-2), (2) Tinopal ABP-A (STAS-4), and (3) Tinopal SPP-Z (STAS-6). It is noted that the numbers 2, 4, and 6 were used here to indicate three types of STAS having -di, -tetra and -hexa sulfonate groups (Fig. 1).

2.2. Formation of PPy-paper composites

Ten grams of pulp fibers (oven-dry basis) were dispersed in deionized water, which were added into a plastic bag. AQSAS was then added, and the mixture was hand kneaded for 5 min. Subsequently, STAS, $FeCl_3$, and pyrrole were sequentially added. The addition of each of these three components was followed by hand kneading for 5 min. It should be noted that the total amount of water in the reaction medium was 90 ml, and the final consistency of the aqueous slurry was 10%. It is also noted that the amount of pyrrole was 6%, relative to the dry weight of pulp fibers; the $FeCl_3$/pyrrole molar ratio and the AQSA/pyrrole molar ratio were 2/1 and 13/50, respectively. Upon the completion of the in-situ polymerization reaction, the resultant PPy-engineered pulp fibers were washed with deionized water.

The aforementioned PPy-engineered pulp fibers were formed into paper-sheets (target basis weight: 100 g/m^2) (Table 1) with a laboratory sheet former. The wet paper-sheets were pressed at 50 psi for 7 min, and then dried at room temperature for 24 h. For comparison purposes, unmodified pulp fibers were also made into paper-sheets under otherwise identical conditions.

2.3. SEM/FT-IR/TGA analyses

For FT-IR analyses, samples were made into pellets using KBr as supporting materials. Fourier-transform infrared (FT-IR) spectra in the

Fig. 2. Schematic of converting cellulosic fibers into polypyrrole-engineered fiber product (i.e., paper-based product) involving the use of stilbene-triazine sulfonic acid sodium salts.