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Preparing poly (styrene-co-acrylic acid) - carbon black –silver nanocomposite as anti-bacterial digital printing ink

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Abstract

Silver nanoparticles and carbon black were incorporated into poly (styrene-co-acrylic acid) using eco-friendly emulsion aggregation (EA) approach, with final application as an anti-bacterial electrophotographic printing ink, called toner. This approach was based on dispersing and coagulating the nanosilver (nAg) and carbon black particles in styrene-co-acrylic latex (previously synthesized by the emulsion polymerization). XRD, and SEM-EDX revealed the silver nanoparticles to be located in the polymeric structure of toner. The antibacterial properties were determined using the agar-well diffusion method against gram-negative (Escherichia coli). The nanocomposite produced via emulsion aggregation method showed highly potent antibacterial activity toward bacteria compared with the neat black toner, which makes it useful in anti-bacterial printing application. The antibacterial property was, also, observed to increase with the concentration of the silver powder in nonlinear behavior.

Introduction

Nanotechnology is currently known as one of the most promising areas for technological improvement in the 21st century [1]. Moreover, nanocomposite materials have become a rapidly expanding area of research, which cover an unlimited variety of systems with potentially novel material properties [2]. When compared with pure polymers, polymer nanocomposites possess many attractive properties [3] increased module and strengths [4], and color properties [5], and antibacterial properties [6, 7]. The introduction of silver-based antimicrobial polymers represents a great challenge for both academic world and industry [8].

Antimicrobial action of silver (Ag) is considered to be the result of three major pathways: (a) adhesion of nanoparticles on the surface, causing deformation of the membrane which leads to an increase in the membrane permeability, (b) silver particle penetration into the bacterial cell results in DNA damages, and (c) dissolution of silver particles releases antimicrobial Ag ions. It is apparent that the combination of free silver ion withthiol (SH) groups of cellular components, such as protein, causes the inactivation of bacteria [8, 9]. Interestingly, Gram-positive bacteria are less susceptible to nanosilver than Gram-negative bacteria [10], which may be explained by the much thicker peptidoglycan cell walls of Gram-positive bacteria than those of Gram-negative bacteria [11]. Silver-based antimicrobials have captured much attention not just because of the non-toxicity of the active Ag^+ to human cells, but as well because of their novelty; they are a long lasting biocide with high temperature stability and low volatility [8]. Therefore, Silver is well known as a significant resource for antimicrobial properties in many applications such as packaging [12], coating [13], and printing ink [14, 15].

Historically, printing has been introduced and used since the eighth century in China and has delineated as a permanent, vivid, visual communication medium, including all the ideas, methods, and devices used to manipulate or reproduce graphic visual messages. The printing process is accomplished by applying an inked image carrier to the substrate as it operates through a high speed press. Letterpress, lithographic, gravure, flexographic, and screen are examples of conventional methods of printing, and electrophotographic and ink jet is some of digital printing methods [16]. Electrophotographic printing was invented in 1938 as a copying technology by C.F. Carlson, who named it xerography [17]. Electrophotographic, which is utilized in the copying machine and laser printer, has attracted interest in recent years as one of the major technologies for printing, servicing a broad reach of market applications [18]. Total cost of ownership, convenience, and quality today favor the use of this technology over its alternatives in many applications such as packaging [19]. The package printing industry, which comprises about a third of the global printing market, serves an important role in the supply chain of various industries and conventional printing methods is no longer the only option for the package printing industry. Digital printing methods are the newer and sometimes cheaper method for this industry. In particular the lack of prepress and make-ready costs for digital mean this is a more cost-effective option for short runs; here digital printing has allowed greater customization of packaging than ever before [20]. In many packaging applications such as pharmaceutical and food packaging, microbial contamination has been regarded as a serious issue. In previous studies, the anti-bacterial properties of lithographic and flexographic ink in the presence of nanosilver (nAg) and nanoZinc oxide (nZnO) were studied [14,15]. Despite the importance of digital printing, there are very limited studies on the antibacterial printing toner expect some patents [21]. However, as far as the authors are concerned, it is for the first time in this paper that the antibacterial ink was introduced for electrophotographic printing. The electrophotographic ink which is called toner is a composite of polymer, colorant, and other additives, essential for the printing process [19]. For this manner, monodisperse semi-spherical nanocomposite was prepared from poly (styrene-co-acrylic acid), carbon black, and nnaosilver (nAg) with an eco-friendly method named emulsion aggregation (EA) [22] which can be used as an electrophotographic printing ink.

Experimental

Materials

The polymer used in this study was a styrene-acrylic resin (R579; ResinFam Co., Iran) which, according to supplier, had a medium pH value, Tg of 51°C, and mean particle size of 220 nm. A polyethylene emulsion wax (EE 95, Kala Kar Co., Iran) and a carbon black pigment (Printex U, Degussa-Evonik, Germany) were, also, employed. Polyaluminum chloride was used as coagulation agent. All the above mentioned materials were used as received. A spherical nano colloidal silver (nAg) disperse in water (3780 ppm), confirmed by Ion Coupled Plasma (ICP), with an average diameter of ~50 nm confirmed by TEM, was obtained from the Sharif Nano Pigment Co (Tehran, Iran).

Antibacterial Toner Production Procedure

Antibacterial Toner nanocomposite was produced via a stepwise procedure, in accordance with previous work [22]. First (step a), a 1-liter beaker was filled with 24.5 g styrene-acrylic latex, 2 g carbon black, 3 g wax, and 120 g deionized water; then the contents were mixed manually at room temperature for about 15 min. In step b, the resulting suspension obtained in a mixed using a Homogenizer for 5 min. Next step, that is c, was started by continuous mixing of ingredients at room temperature for about 1 h followed by the addition of a solution of 0.6 g coagulation agent in nitric acid, and were mixed again over 10 min until the pH value of the mixture reached 2. In this manner, a gel was seen to be formed, as a consequence of changing the viscoelastic nature of the suspension from a Newtonian water-like fluid to a shear thinning paste-like gel. In step d, the temperature of the mixture was raised to 50°C for about 30 min while the gel was continually mixed. The mixture was held at this temperature for another 60 min in step e, where the temperature of the mixture was increased to 96°C for 30 min. The last step, denoted as g, was started by holding the product of step f, at 96°C for a further 60 min. The ultimate mixture was neutralized with sodium hydroxide solution and cooled down to 25°C, after which the produced microparticles were isolated from the water, washed to remove divalent ions, filtered, and dried with a frizzed dryer.

Based on the above procedure, sets of experiments were undertaken with different amount of nAg to produce antibacterial toner. Various amounts of nAg, namely, 0%, 0.5%, 1%, and 5%, were applied by the weight of toner. Such an antibacterial toner was then named as AT0, AT0.5, AT1, and AT5. The resultant antibacterial toners in the powder form are used for future investigation. The variation of pH and temperature over the course of the toner synthesis process and the scheme of the preparation is shown in author previous work [23].

To confirm the printability of the produced toner, The resultant antibacterial toner nanocomposites were printed in a controlled environment [23°C, 50% relative humidity (RH)] using a monochrome laser-jet printer (HP 1100, Laser-jet printer). This printer was changed to only have a hot roll fusing system containing two metal rolls covered with silicone rubber and was heated from inside the rolls.

Characterization of Antibacterial Toner

To investigate the localization of carbon black and nanosilver into the manufactured toner and particle size of nAg, transmittive electron microscopy (TEM, Zeiss EM 900, Germany) was used. The particle size of silver was determined utilizing image-J software. Prior to TEM measurements, the resulting powder toners were centrifuged and dispersed in water, followed by sonication for about one minute to break up aggregations.

Scanning electron microscopy in combination with energy-dispersive X-ray spectrometry (SEM/EDX S360, Cambridge Instruments Ltd., UK) was, also, conducted to investigate the existence and distribution of nanoAg. The EDX measurements were conducted by using primary electron beam with an acceleration voltage of 20 kV to detect Ag.

The agar-well diffusion method was employed to determine the antimicrobial activities of powder toner in accordance with ISO 22196. Escherichia coli (E. coli); ATCC 8739 was used to conduct the antimicrobial tests.

Color measurement of the printed toner was conducted on a GretagMacbeth Color Eye 7000A spectrophotometer (USA). The spectral reflectance factor of all samples was determined and then transformed into CIELAB colorimetric coordinates (L*, a*, b*) using CIE standard illuminant D65 and a CIE 1964 standard colorimetric observer. It is well-known that an increase in the L* indicates the higher lightness of the sample. The a* axis in colorimetric coordinate is green at one extremity (-a*) and red at the other (+a*), while b* axis has blue and yellow extremes, respectively. Therefore, a positive Δa^* signifies a color shift toward red, while a negative Δa^* feature a color shift toward green. Likewise, a positive Δb^* signifies a color shift toward yellow and a negative Δb^* indicates a color shift toward blue.

Result and Discussion

TEM Analysis

Size, shape, surface charge, and aggregation status of nanomaterials significantly affects their interactions with biological systems [24]. As to nanosilver, these parameters are of great importance to its antibacterial activity [10]. Nanosilver with a smaller size possesses higher surface to volume ratio, exposing more silver atoms on its surface and further facilitating the release of silver ions [24]. In addition, small nanosilver enters into bacteria more easily and its high surface energy can promote the generation of reactive oxygen species (ROS), causing much stronger oxidative stress in bacterial cells than a large one [10, 24]. The particle size of nAg reported by the company was examined and confirmed using transmission electron microscope (TEM). The TEM images (figure 1a, b) showed that the particle size of colloidal silver nanoparticles dispersion was in the range of 50 nm utilizing image J software (also confirmed by datasheet of obtaining product). Although some aggregations of nanoparticles are also noticeable in the TEM micrograph.

TEM images of antibacterial toner (AT5) are presented in Figure 1c, d. From the image, the core–shell structure of nanocomposites could be seen. The migration of some components from the inner part of the particle to the surface of it, can be attributed to the different surface tensions of the toner ingredients and Brownian motion, which provides sufficient driving force for pushing the particles from the inner side towards the interface [25] (Figure 1c).

The results also show that the particle size of toner measurements is in an appropriate range for printing (To achieve the perfect reproduction of an image at 600 and 1200 dpi resolutions, the average particle sizes of about 5 and 3 microns are essentially needed respectively [26]). As can be seen, the composite particles of toner are closely spherical, which is necessary for applications with high quality [19, 26].

SEM-EDX

For better understanding of the presence of nAg in polymer matrix of antibacterial toner, SEM – EDX was used. To support the existence of nAg in the toner composite, the EDX spectrum and the EDX mapping were conducted and shown in Figure 2. EDX mapping is a valuable tool to indicate the quality of the nAg dispersion. The EDX spectrum of the toner showed that the element of silver was detected on the toner which confirmed that nAg was added into the toner. The Ag values determined by EDX showed an increase with increasing the amount of silver in the toner. The dispersion of the nAg can, also, be characterized by the EDX mapping technique. The EDX mapping of the element of silver proved the uniform dispersion of these silver-loaded particles.

Antibacterial Properties

The typical procedures to evaluate the antibacterial activity of toner were as below [30]. The bacterial cultures were grown overnight in a nutrient agar medium. The grown cultures were then transferred to a flask containing a nutrient broth in which they were allowed to grow at 35 °C for 16 to 20 h. At the beginning of the logarithmic phase, they were centrifuged and washed twice with a saline solution to yield a final bacterial concentration of approximately 5×106 CFU (colony-forming unit) ml-1. The samples were placed into a vial containing saline solution, and the bacteria cells were then pipette into the vial. The samples were then allowed to grow at the 35 °C for 24 h, after which they were counted to determine the number of viable bacteria. At the end of the incubation period, the samples were gently rinsed three times in a sterile solution of NaCl (0.9 %) to eliminate the non-adherent bacteria.

Three samples were prepared for each antibacterial test. Each test was performed at least two times to ensure reproducibility for all experiments. The number of viable bacteria was monitored with a colony counter by counting the number of colony-forming units (CFUs) from the appropriate dilution on nutrient agar plates. In order to determine the relative number of removed bacteria, the term “log Reduction” was calculated according to Equation (1):

$$R = \text{log reduction} = \log A - \log B \quad (1)$$

Where, A and B are the average number of bacterial colonies on the untreated and treated samples, respectively. The bacteria’s reduction percentage was, also, calculated using equation (2):

$$R\,\% = \text{reduction percentage} = [(A - B) / A] \times 100 \quad (2)$$

The antimicrobial efficacy of the toner composites against Escherichia coli (gram negative) was tested based on the test method according to ASTM E 2149-01. As shown in table 1 adding 0.5 and 1 percent of nanosilver into the toner resulted in a bacteria reduction percentage of 99.96 % (log number of bacterial=3.1, log Reduction = 3.5) and 99.99% (log number of bacterial=2.1, log Reduction = 4.4), respectively. The outcomes indicated that the antibacterial toner with 0.5 percent nanosilver had excellent efficacy against microbes. It was, also, found that increasing the amount of nanosilver did not significantly change the antibacterial behavior, especially after adding 1 percent of nanosilver.

Colorimetric Properties of Toner Composite

Emulsion aggregation can produce toner particles with uniformly dispersed pigment particles. The uniform distribution of the pigment particles within the toner polymeric matrix results in high-quality homogeneous printed color images [31]. The spectrophotometric characteristics for antibacterial toners and images of them are presented in Figures 3. Despite the change in lightness values, All toners have a* and b* near zero, which represented the appropriate blackness of samples.

Conclusion

Monodisperse poly (styrene-co-acrylic acid) (PSA) / carbon black/ silver (0, 0.5, 1 and 5%) nanocomposite, serving as laser printing ink called toner, was synthesized via eco-friendly emulsion aggregation method. TEM demonstrated the formation of toner nanocomposite. Adding nanosilver increased residual weight of toner from 14 to 22 %. SEM-EDX analysis clearly revealed the presence of Ag nanoparticles in toner. Moreover, the antibacterial activity of the toner nanocomposites was studied against gram-negative E. coli. Bacteria. Due to their excellent antibacterial activity (bacteria reduction percentage = 99.96 % and log Reduction = 4.4 with 1% nanosilver), these nanocomposites are desirable products to own potential application in developing antibacterial ink. All nanocomposite show appropriate thermal characteristics and particle size and particle size distribution caused toners fusing in a uniform appearance.

Table 1: The number of viable bacteria, in cells.cm-2, recovered from antibacterial toner nanocomposites with various amounts of nanosilver after 24 h incubation.

nAg (%)	Number of bacteria	log (number of bacteria)	log Reduction	Reductio n percenta ge (%)
0	4200000	6.623	0	-
0.5	1300	3.113	3.509	0.99969
1	150	2.176	4.447	0.999964
5	120	2.079	4.544	0.999971

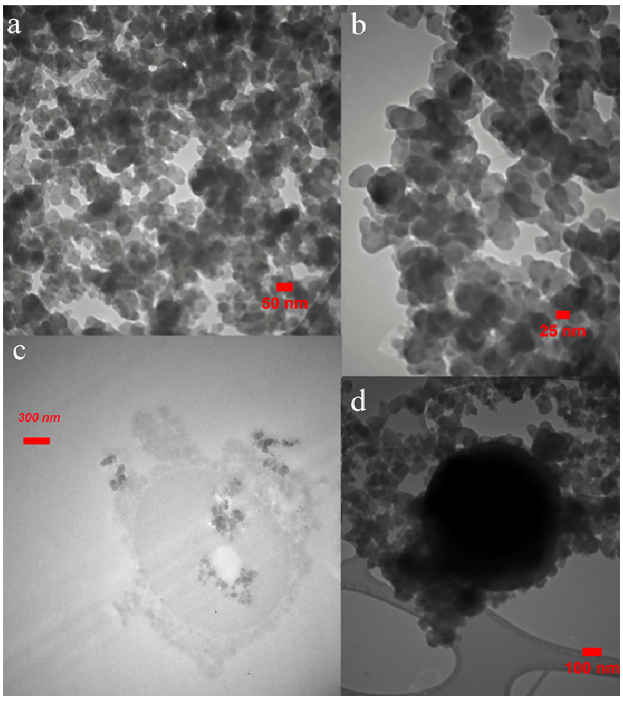

Figure 1. *The TEM micrographs of (a, b) nanosilver, (c, d) black antibacterial toner nanocomposite (AT5).*

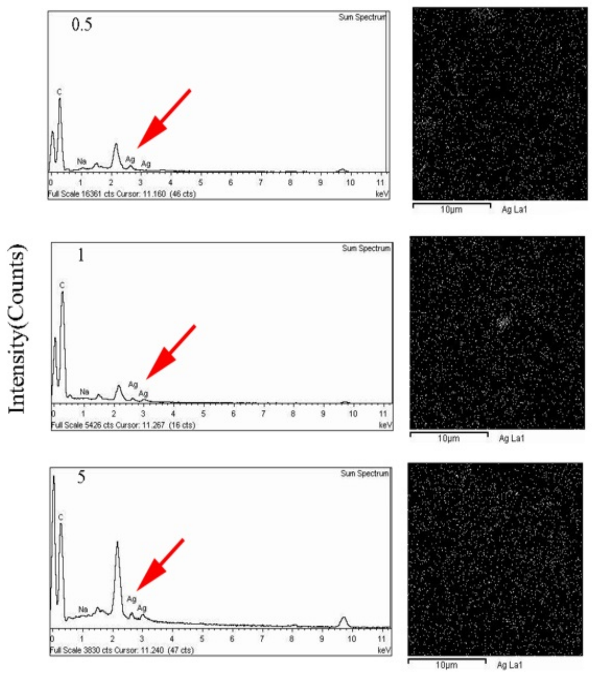

Figure 2. *EDX analysis and Map of Ag for antibacterial toner nanocomposites with various amounts of nanaosilver.*

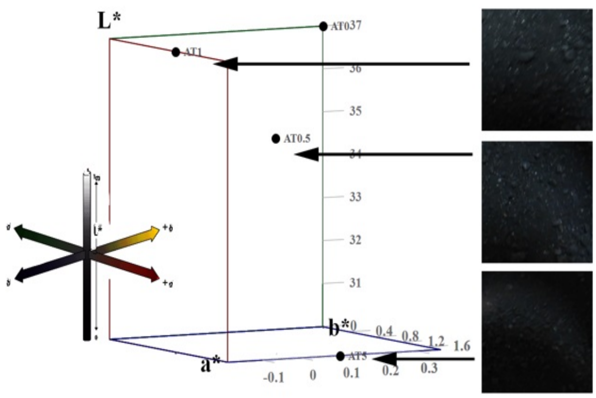

Figure 3. *Spectrophotometric parameters and images of the black printed antibacterial toners.*

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