Original Article

Iron oxide-entrapped solid lipid nanoparticles and poly(lactide-co-glycolide) nanoparticles with surfactant stabilization for antistatic application

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ABSTRACT

Polymers with very low surface conductivity can easily accumulate an electric charge through surface friction. If the charged entities are grounded with conductive materials, they may discharge electricity associated with sparks that will interrupt the production process, and more seriously, cause industrial disasters. In order to avoid damage from electrical sparks, an antistatic agent (ASA) is employed with the polymer during production. In this study, conductive iron oxide (Fe₃O₄) nanoparticles (NPs) with hydrophobic modification by oleic acid (OA) were prepared using a co-precipitation method. Fourier transformed infrared spectra and thermogravimetric analysis confirmed that OA-Fe₃O₄ was formed through chemisorption interactions between OA and Fe₃O₄. Fe₃O₄ NPs were entrapped in solid lipid NPs (SLNs) and poly(lactide-co-glycolide) NPs through hydrophobic interactions to obtain new composite antistatic NPs (CANs). Surfactants and their concentration played a decisive role in the zeta potential and particles size of CANs. Sodium dodecyl sulfate (SDS) created some regular-shaped CANs, and didodecyldimethylammonium bromide (DMAB) and glycerol monostearate (GMS) created irregular-shaped CANs. 10% methanol and 1% Tween 80 yielded an appropriate contact angle with polymer films. The surface electrical resistance value of CANs was found to be in the order of SDS > DMAB > GMS. GMS-based CANs reached a lower electrical resistance value of around 10⁸ Ω/sq, and can be used as an ASA in engineering practice.

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1. Introduction

Polymers in several applications are becoming important materials in the day-to-day life of people due to their electrical insulator activity with surface resistivity from $10^{15}$ to $10^{21} \, \Omega \cdot \text{cm}^2$. This inherent property of the polymers is the major reason for the development of static charges over them. Developed static charges create serious problems, including their attraction of dust, intertwisting, electric shocks, damage to the packed electronic devices, and the initiation of explosions when powder or liquid are packed in polymer packaging materials [1-4]. The reduction of surface electrical resistance to less than $10^{11} \, \Omega$ in the plastics can bring down the electric charge [5]. This can be achieved by incorporating antistatic agents (ASAs) in the polymers, which reduce surface resistivity and eliminate static charges [6]. Soap-like molecules (including both hydrophilic and hydrophobic functional groups) are generally used as ASAs. The hydrophilic groups of an ASA absorb water vapor from the air and create a continuous water layer to promote a conductive channel for the plastics. However, soap-like molecules have the following drawbacks: they have no volume conduction beneath the surface, they are easily removed and washed out, and they have reduced activity over time [2,7]. Conductive-type ASAs, the direct addition of electrical conductors including carbon black, graphite, carbon nanotubes [2,8], conductive polymers [9], ions-ionic polymers [10] and metals (gold or silver) to the polymers, can achieve the best antistatic effects [11]. But, carbon black lacks transparency, and ionically acting ASAs are not permanent and are applicable only in a higher degree of atmospheric humidity [12].

ASAs can be divided into internal antistatic agents (IASAs) and external antistatic agents (EASAs), based on the method used. An IASA is directly mixed with polymers during the molding process, and then it migrates slowly to the surface. In addition, an IASA has the advantages of easy processing and long-term effects, and the disadvantages of being influenced by atmospheric moisture, and having an alteration in polymer property and a low dispersion of an IASA in the polymer matrix. Moreover, an EASA is used by directly spray-coating the plastics surface; it has the advantages of an invariant plastics property and is highly available for electron dissipation using a low dosage. However, an EASA has the disadvantages of easy elimination by attrition, and non-uniform coating of an EASA on the surface of products that yields various exterior shapes. Therefore, different types of ASAs, using both methods, are utilized by different industries based on their needs.

Iron oxide (Fe$_3$O$_4$) nanoparticles (NPs) with a particle size of 10 nm to 100 nm are widely used in coating and plastics dyeing, and a size <20 nm is used in the medical field in nuclear magnetic imaging and as a drug carrier due to their super-paramagnetic behavior. Fe$_3$O$_4$ is a semiconductor material ($10^{-2}$-$10^{-5} \, \Omega \cdot \text{cm}^2$), since electrons can be transferred between Fe$^{3+}$ and Fe$^{2+}$ [13] and the electrical resistance range of ferric oxide can be defined as antistatic and static dissipation [14]. Therefore, with its good conductivity, Fe$_3$O$_4$ has the potential of being utilized as an ASA. However, Fe$_3$O$_4$ is not used as an ASA in the market due to its tinting strength and hiding power [15]. The external addition of Fe$_3$O$_4$ to plastics required the fixation of resin on the surface to form an electroconductive thin film [16]. However, the internal addition of Fe$_3$O$_4$ required a higher concentration of 3-5%, which can easily change the properties of polymers, for example, diminishing their transparency. Hence, the particle size of Fe$_3$O$_4$ should be <100 nm to be optically transparent [17]. The antimony-doped tin oxide (ATO; particle size 10 nm) coated on poly(methyl methacrylate) produced an antistatic layer with a thickness of about 10 nm to 25 nm. Further, optical transparency was maintained using a 0-0.04 volume fraction of ATO with surface electrical resistance of $10^{8}$-10$^{10} \, \Omega \cdot \text{cm}^2$ in relative humidity of 40% [18].

In this study, as a new approach, Fe$_3$O$_4$ was entrapped in solid lipid NPs (SLNs) and poly(lactide-co-glycolide) (PLGA) NPs and used as composite antistatic NPs (CANs). The SLNs and PLGA NPs with entrapment of Fe$_3$O$_4$ were easily absorbed on the surface of the polymers due to the hydrophobic interactions of the CANs. The hydrophobic interactions helped to release the Fe$_3$O$_4$ slowly onto the plastics surface and improve antistatic aging [19]. The degradation rate of PLGA NPs may also control the ability to release Fe$_3$O$_4$ [20,21].

2. Materials and methods

2.1. Preparation of Fe$_3$O$_4$ NPs

Liphophilic Fe$_3$O$_4$ NPs were prepared using a co-precipitation method. 0.25 g of FeSO$_4$·7H$_2$O (J.T. Baker, Phillipsburg, NJ) and 0.44 g of FeCl$_3$·6H$_2$O (J.T. Baker) were added to 20 mL of deionized (DI) water and stirred at 500 rpm and at room temperature. 1 N aqueous NaOH (Mallinckrodt Baker, Hazelwood, MO) was added to the Fe$^{2+}$/Fe$^{3+}$ mixture with continuous stirring until the pH reached 10. After that, 2 mL of oleic acid (OA; Sigma-Aldrich, St. Louis, MO) was added and stirred for 1 h at room temperature. The temperature of the reaction mixture was increased to 95 °C at a rate of 2 °C per min, and then immediately cooled down to room temperature followed by the addition of 0.1 N aqueous nitric acid (General Chemical, Parsippany, NJ) to decrease the pH to 5. The supernatant of the reaction mixture was removed, DI water was added and stirred at 200 rpm for 5 min, and the supernatant was removed again. This was repeated five times followed by acetone (Mallinckrodt Baker) treatment five times. Finally, the black precipitate was dissolved in 10 mL of n-hexane (Macron Fine Chemicals), filtered twice, and then the n-hexane was removed by concentration under reduced pressure to obtain hydrophobic OA-coated Fe$_3$O$_4$.

2.2. Preparation of CANs

2.2.1. Fe$_3$O$_4$-SLNs
The 15 mL of water phase included 0.5 mM, 1 mM, 1.5 mM, and 2 mM of didodecyl(dimethyl)ammonium bromide (DMAB; Sigma-Aldrich), sodium dodecyl sulfate, sodium salt (SDS; Sigma-Aldrich), or glycerol monostearate (GMS; Alfa Aesar, Ward Hill, MA) was heated to 65 °C. To this, 10 mg of lecithin (Sigma-Aldrich), 6 mg of Tween 80 (Fisher Scientific, Fair Lawn, NJ), 5.5 mg of OA-Fe$_3$O$_4$ and 1.5 mg of lipid mixture (beeswax (Sigma-Aldrich) and tricaprin (Sigma-Aldrich)) dissolved in 1 mL of tetrahydrofuran (THF; Echo Chemical, Miaoli, Taiwan)
2.4. \textit{Fe}_3\text{O}_4-\text{PLGA NPs}

The 15 mL of water phase, including 0.5 mM, 1 mM, 1.5 mM, and 2 mM of DMAB, SDS, or GMS, was prepared. To this, 10 mg of lecithin, 8 mg of Tween 80, 5 mg of OA-Fe₃O₄ and 1.5 mg of PLGA (Sigma-Aldrich) dissolved in 1 mL of THF were added slowly and stirred at 1050 rpm for 30 min. Then, the solution was filtered through filter paper and centrifuged at 8000 x g to remove the excess surfactant. Finally, the obtained Fe₃O₄-PLGA NPs suspension was set at a concentration of 2 mg/mL.

2.3. Characterization of functional group and surface morphology

The powder X-ray diffraction (XRD) pattern of Fe₃O₄ and OA-Fe₃O₄ was obtained by direct coating of NPs over the glass slide using an X-ray powder diffractometer (XRD-6000, Shimadzu, Tokyo, Japan) equipped with Cu Kα (λ = 1.5418 Å) radiation. Fourier transform infrared (FTIR; IRprestige-21 FTIR, Shimadzu) spectra of Fe₃O₄ and OA-Fe₃O₄ were obtained by mixing KBr (FTIR grade, Sigma-Aldrich) with Fe₃O₄-PLGA NPs or Fe₃O₄-PLGA NPs at a 5:1 ratio and at a wavelength of 400-4000 cm⁻¹. The thermal stability of NPs was obtained using a thermogravimetric analyzer (TGA; TGA-50, Shimadzu) with a scan range of 50-600 °C under a nitrogen atmosphere. The morphology of Fe₃O₄-PLGA NPs was determined using a transmission electron microscope (TEM; JEM-1400, Jeol, Tokyo, Japan). The samples were dispersed using sonication for 1 min, followed by coating of 10 μL samples over a copper mesh, and drying to observe the TEM analysis.

2.4. Determination of particle size and zeta potential

A 2 mL Fe₃O₄-PLGA NPs suspension solution with a concentration of 2 mg/mL was placed in a 4-sided transmission quartz channel to determine particle size, D and zeta potential, ζ. The parameters were set in a Zetasizer 3000 (Malvern, Worcestershire, UK), then the 4-sided cells were inserted into the detection chamber and analyzed by dynamic light scattering.

2.5. Contact angle measurement

0%, 0.5%, 1%, 1.5%, and 2% Tween 80 solution was prepared in 0%, 5%, and 10% (v/v) methanol solution. Five different polymer films, including low-density polyethylene (LDPE; Chung Kai Development, Chia-Yi, Taiwan), high-density polyethylene (HDPE; Chung Kai Development), polypropylene (PP; Chung Kai Development), polyvinyl chloride (PVC; Chung Kai Development), and polyethylene terephthalate (PET; Chung Kai Development), were fixed on the slide with a double-sided adhesive, and the wetting properties of the different concentrations of solvent to the polymers were measured using a drop shape analyzer (Kruss GmbH, Hamburg, Germany).

2.6. Antistatic test of CANs on different plastics

LDPE, DPE, PP, PVC and PET were cut into 8 cm x 7 cm rectangular shapes and fixed on a double-sided adhesive hard plate. 200 μL of a 2 mg/mL concentration of Fe₃O₄-PLGA NPs or Fe₃O₄-PLGA NPs suspension was placed at the center of the plastics rectangles, evenly coated using a cotton swab, and then dried and placed in a dry box before measuring the surface resistivity of the coated films using a surface electrical resistance meter (Dr. Schneider FC, King Glory Technology, Guangdong, China) at room temperature and atmospheric humidity.

3. Results and discussion

3.1. Characterization of Fe₃O₄ NPs

Co-precipitation of Fe³⁺ and Fe²⁺ at a 2:1 ratio under an alkaline condition is an easy and economical way to prepare Fe₃O₄ NPs, because Fe₃O₄ is composed of ferric (Fe³⁺) and ferrous (Fe²⁺) iron at a ratio of 2:1 [22]. In this study, the experiment was designed at a 1.95:1 ratio (Fe³⁺:Fe²⁺). Fe²⁺/Fe³⁺ is present in the form of Fe(OH)₂/Fe(OH)₃ under an alkaline condition and undergoes dehydrogenation to produce Fe₃O₄ [23]. OA has a negative charge at the hydrophilic end under alkaline conditions. Fe₃O₄ has an isoelectric point of 6.5 [24] and exhibits a positive charge on the surface at pH 5, which produces a static charge on the negative charge force to form OA-coated hydrophobic Fe₃O₄ through electrostatic interactions. Even though OA is protonated under acidic conditions, there is still enough charged OA to bind to the Fe₃O₄ surface, due to the pKa (9.85) of OA [25], and further analysis supports OA attachment to the Fe₃O₄.

Fig. 1(A) shows the XRD pattern of Fe₃O₄ and OA-Fe₃O₄. The XRD pattern of Fe₃O₄ (Fig. 1(A)) showed sharp main characteristic peaks at 30.1° (220), 35.5° (311), 43.1° (400), 53.4° (422), 57° (511), and 62.2° (440), as reported in the literature, and matched well with file number 82-1533 in Joint Committee on Powder Diffraction Standards database, which confirmed the formation of the crystalline Fe₃O₄ phase. In the case of OA-Fe₃O₄, noisy peaks were observed due to the presence of amorphous OA, which decreased the crystallinity of Fe₃O₄ and confirmed the presence of OA over Fe₃O₄ [26,27]. Further, the characteristic peaks of (311), (511) and (440) were still observed, which proved that the OA did not affect the internal structure of the iron.

Fig. 2(B) shows the FTIR spectra of OA and OA-Fe₃O₄. FTIR helps to understand the mechanism coupling OA onto the surface of Fe₃O₄. OA-Fe₃O₄ showed characteristic CH₃ stretching peaks at 2930 cm⁻¹ and 2858 cm⁻¹, which confirmed the presence of OA. Further, the characteristic intense C=O peak of OA at 1710 cm⁻¹ shifted to 1642 cm⁻¹ in OA-Fe₃O₄. This was attributed to the interactions of C=O with the Fe atom of Fe₃O₄, and the peak at 1642 cm⁻¹ was characteristic of COO⁻ stretching. This study suggested that OA is chemisorbed onto Fe₃O₄ through carboxylate [28,29].
TGA analysis of Fe₃O₄ and OA-Fe₃O₄ (Fig. 2(C)) further supported the chemisorptions of OA onto the Fe₃O₄ surface. Weight loss was observed in a temperature range below 100 °C due to the evaporation of physically absorbed water of both Fe₃O₄ and OA-Fe₃O₄. After that, no significant weight loss was observed in the case of Fe₃O₄. However, weight loss was observed below 260 °C in OA-Fe₃O₄ due to the physically adsorbed OA, and weight loss was observed between 260 °C to 400 °C due to the chemisorbed OA [26].

3.2. Particle size and zeta potential analysis of CANs

Fig. 2(a) and (b) shows the effect of different types and various concentrations of surfactants on the particle size of SLNs and PLGA NPs. The particle size of SLNs was decreased with increased concentrations of SDS. The increased concentrations of SDS reduced the surface tension between the oil and water phase and decreased the particle size. However, no significant particle size reduction was observed in the case of PLGA NPs. It is possible that the surface of PLGA was saturated with the surfactant. Thus, PLGA NPs maintained the same size. Compared with DMAB, SDS showed a smaller particle size of SLNs and PLGA NPs. SDS has a larger hydrophilic-lipophilic balance (HBS) value than DMAB, which resulted in decreased surface tension and a reduction in particle size [28]. The HBS value of GMS is lower than that of SDS and DMAB, and the particle size of SLNs increased with increases in GMS concentration.

Fig. 2(c) and (d) shows the effect of different types and various concentrations of surfactants on the zeta potential of SLNs and PLGA NPs. SDS and DMAB are anionic and cationic surfactants, respectively. Hence, the surface of the synthesized NPs was negatively and positively charged. The increased concentration of SDS increased the surface charge density, which increased the more negatively charged zeta potential of SLNs and PLGA NPs. In the case of nonionic GMS surfactant, SLNs and PLGA NPs showed decreased zeta potential, because the surface of the partially negatively charged OA carboxylate group was covered by nonionic GMS.

3.3. Shapes and surface morphology of CANs

Fig. 3(a)–(g) shows the TEM images of SLN-based CANs. In the case of SDS and DMAB, most of the Fe₃O₄ NPs were uniformly dispersed in the SLNs. However, GBM as a surfactant was less consistent in the distribution of Fe₃O₄ in the SLNs. The shapes of the SLNs appeared in elliptical, irregular and broken patterns. The difference in diffusion rates between the sizes of the Fe₃O₄ and the sizes of the lipid in the process of forming the particles resulted in a non-circular or even irregular SLN.
shape [26]. The HLB of the surfactants affected the wetting of the surface of the Fe$_3$O$_4$ NPs and led to an uneven distribution of Fe$_3$O$_4$ in the SLNs [28]. Fig. 3(h)–(l) shows the TEM images of PLGA NP-based CANs. The results were similar to those with SLNs. When using SDS as a surfactant, Fe$_3$O$_4$ NPs were distributed evenly, similar to those with SLNs. When using DMAB and GMS as surfactants, the Fe$_3$O$_4$ was coated on the PLGA NPs rather than being evenly dispersed in the particles. This was because PLGA long chains are free to unfold and Fe$_3$O$_4$ was deposited in the core of the particles during their formation. In addition, apart from cubic crystals of Fe$_3$O$_4$, few needle-like crystals were observed due to the by-products of FeOOH during co-precipitation.

3.4. Contact angle analysis of polymers film

Table 1 shows the effect of surfactant and solvent concentration on contact angle with different polymer films. Methanol was used as a solvent, because the production of thin film with an ASA using a spray-drying process requires rapid evaporation, and methanol increases the evaporation rate. The methanol concentration should not exceed 20% (v/v) to avoid damaging the SLNs. Among the five polymer films tested in this experiment, PET and PVC were amorphous, and HDPE, LDPE, and PP were semi-crystalline. The surface of amorphous plastics and that of semi-crystalline plastics contain different tiny holes that result in a slight difference in contact angle, and amorphous plastics possess a slightly lower contact angle than semi-crystalline plastics [30]. Increasing the concentration of methanol alone can reduce the contact angle, but this can be limited when using an ASA, and requires a surfactant. An increased concentration of methanol and Tween 80 decreased the contact angle. The concentration of methanol at 10% and Tween 80 at 2% yielded a lower contact angle. However, in terms of economy, a concentration of methanol at 10% and Tween 80 at 1% has been recommended.

3.5. Surface resistivity of CAN-coated polymer films

Fig. 4 shows the surface resistivity of CAN-coated plastic films. The surface resistivity of untreated polymer films was found to be above $10^{12}$ $\Omega$Sq. By comparison, OA-Fe$_3$O$_4$-containing SLNs and PLGA NPs-coated polymers showed a lower surface electrical resistance value. However, the electrical resistance value did not decrease effectively due to the lower conductivity of the OA. Fe$_3$O$_4$ is usually added as an IASA at more than 5% to reduce the surface electrical resistance to $10^6$ $\Omega$Sq [17]. Hence, an increased concentration of OA-Fe$_3$O$_4$ might decrease the electrical resistance value. Further, the surface electrical resistance value of Fe$_3$O$_4$-SLNs and Fe$_3$O$_4$-PLA NPs was higher than that of bare OA-Fe$_3$O$_4$. This might be attributed to the higher deposition of Fe$_3$O$_4$-SLNs and
Fig. 3 – TEM images of SLNs and PLGA NPs with entrapment of Fe₃O₄. (a–f) SLNs; (g–l) PLGA NPs. (a and g) C_{SDS} = 0.5 mM; (b and h) C_{SDS} = 2 mM; (c and i) C_{DMAB} = 0.5 mM; (d and j) C_{DMAB} = 2 mM; (e and k) C_{GMS} = 0.5 mM; (f and l) C_{GMS} = 2 mM. (a–f) (*–1) scale bar = 200 nm; (*–2) scale bar = 50 nm, (g–l) (*–1) scale bar = 200 nm; (*–2) scale bar = 100 nm.
Table 1 – Effect of surfactant and solvent concentration on contact angle with different plastic films.

<table>
<thead>
<tr>
<th>Plastics</th>
<th>$C_{\text{Twee}n}$ (%)</th>
<th>$C_{\text{MeOH}}$ (%)</th>
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<tbody>
<tr>
<td></td>
<td>0</td>
<td>5</td>
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<tr>
<td>LDPE</td>
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<td>47.1 ± 2.0</td>
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<td>43.8 ± 1.5</td>
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<td>41.0 ± 1.0</td>
<td>42.4 ± 1.1</td>
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<td></td>
<td>35.4 ± 2.4</td>
<td>41.1 ± 0.7</td>
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<tr>
<td></td>
<td>82.1 ± 1.8</td>
<td>71.9 ± 1.8</td>
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<td>43.0 ± 0.9</td>
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<td>44.0 ± 1.5</td>
<td>42.4 ± 0.9</td>
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<td></td>
<td>39.8 ± 1.6</td>
<td>40.7 ± 0.6</td>
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<td>42.5 ± 1.0</td>
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<td></td>
<td>44.4 ± 0.6</td>
<td>39.3 ± 1.1</td>
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<td>41.1 ± 1.6</td>
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<td>PET</td>
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Fe$_2$O$_4$-PLGA NPs than that of bare OA-Fe$_2$O$_4$, due to the strong hydrophobic interactions. GMS had a lower electrical resistance value of around $10^8$ Ω·sq, and SDS and DMAB had electrical resistance values in the range of $10^9$–$10^{11}$ Ω·sq. These values meet the required surface resistance of standard antistatic materials: $10^8$–$10^{14}$ Ω·sq from military handbook DOD-HDBK-263, and $10^3$–$10^{12}$ Ω·sq and $10^4$–$10^{11}$ Ω·sq from industry standards ANSI/EIA-541-1988 (USA) and ANSI/ESD S541-200 (USA), respectively [31]. In addition, the surface resistance value of CANs obtained was comparable to the previously reported antistatic agents; including, $1.74 \times 10^7$ Ω·sq for 15 wt% graphene nanoplatelet-incorporated polyaniline nanocomposites on HDPE [31], $3.63 \times 10^2$ Ω·sq for 12 wt% ZnO whisker on PET [32], $10^9$–$10^{10}$ Ω·sq for sulphonated polyaniline on PET [33], $3.0 \times 10^8$ Ω·sq for quaternary ammonium salt/poly(ethylene oxide) on PVC [34], and $10^{11}$ Ω·sq for organo-montmorillonite on PP [35]. The electrical resistance value of materials in the range of $10^8$–$10^{12}$ Ω·sq can reach a static dissipation level, and electrical resistance values of $10^5$–$10^8$ Ω·sq can reach an antistatic level. Hence, CANs using GMS as a surfactant can be a good ASA, and SDS and DMAB as surfactants can reach a static dissipation level.

Fig. 4 – Surface resistivity of polymer film after treatment with CANs. NP concentration was 2 mg/ml; surfactant concentration was 2 mM; $n = 3$.

SLNs and PLGA NPs containing OA-Fe$_2$O$_4$ (as CANs) were successfully developed using a micro-emulsion and solvent diffusion method and utilized as an ASA for the first time. The particle size of SLNs and PLGA NPs was found to be in the range of 200–340 nm, and the size was controlled by concentrations of various types of surfactants. Fe$_2$O$_4$ was uniformly distributed in SLNs and non-uniformly distributed in PLGA NPs. The solvent and surfactant ratios for coating synthesized CANs on different plastics were optimized as the concentration of methanol ($C_{\text{MeOH}}$) was 10% and the concentration of Tween 80 ($C_{\text{Twee}n}$) was 1%. The surface electrical resistance

4. Conclusions
of CAN-coated polymers was in the range of $10^8$–$10^{11} \, \Omega/cm^2$. Of the three surfactants, only GMS-based CANs showed a surface electrical resistance value of around $10^8 \, \Omega/cm^2$, which can be employed as an ASA. In addition to their antistatic performance, Fe$_3$O$_4$-SLNs and Fe$_3$O$_4$-PLGA NPs can be used in the biomedical field, since SLNs and PLGA NPs have the advantage of being drug carriers. Moreover, the super-paramagnetic properties of Fe$_3$O$_4$ render it useful in nuclear magnetic resonance imaging.

**Conflicts of interest**

The authors declare no conflicts of interest.

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