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Preparation of Polypropylene/Silver Nano-Zeolite Plastics and Evaluation of Antibacterial and Mechanical Properties

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Abstract Polypropylene (PP)/silver nanoparticles (AgNPs)-zeolite plastics were prepared by melt blending PP with AgNPs-zeolite at various AgNPs content of 0, 40, 80 and 160 ppm in a twin-rotating-screw extruder for inducing antimicrobial activity. Mechanical properties and antibacterial efficacy of the prepared PP/AgNPs-zeolite plastics were investigated. Results indicated that yield strength and tensile strength of PP/AgNPs-zeolite plastics were almost unchanged in comparison with that of the control PP while elongation at break was reduced from 562% (0 ppm) to 443% (160 ppm). The highly antibacterial efficiency (η~100%) was observed for the PP/AgNPs-zeolite plastics samples containing from 80 to 160 ppm of AgNPs. Thus, the prepared PP/AgNPs-zeolite masterbatch can be suitably used to fabricate a number of products like food containers, chairs, vials, etc. with highly antimicrobial activity.

Keywords Polypropylene, Silver, Nanoparticles, Zeolite, Antibacterial

1. Introduction

Silver nanoparticles (AgNPs) with broad-spectrum antimicrobial activity have been most commonly used in consumer and medical products including clothing, respirators, household water filter, contraceptives, antibacterial spays, cosmetics, detergents, dietary supplements, cutting boards, sox, shoes, cell phones, laptop keyboards, food packaging, wound dressing, children's toys, ect [1-6]. In addition, Mannewattanapinyo et al. reported that AgNPs could be relatively safe when administrated to oral (LD_{50} > 5,000 mg/kg body weight), eye and skin of the animal models [7]. Polypropylene (PP) and polyethylene (PE) are among the most commercially important thermoplastic polymers with wide applications in the automotive, food and packaging industry, household appliances, and construction [8]. Several studies on the mechanical properties and antibacterial properties of polymers/silver composites have been carried out [8-11]. Typically, results of Aalaie et al. study indicated that PE/nanosilver film exhibited highly antibacterial efficiency (η>99.9%) for *E. coli* and *S. aureus* bacteria [8]. In addition, tensile strength and elongation at break of the PE/nano silver films with nanosilver filler from 0.5 to 1.5% were almost unchanged in comparison with that of the control PE film.

In this study, PP was first mixed with AgNPs deposited in zeolite framework (AgNPs-zeolite) by extrusion compounding process to prepare PP/AgNPs-zeolite masterbatch. Then, PP/AgNPs-zeolite plastics with various AgNPs contents were prepared by mixing PP/AgNPs-zeolite masterbatch with PP resin. The mechanical properties and antibacterial efficacy of as-prepared PP/AgNPs-zeolite plastics were investigated. The development of these composite materials is with the purpose of fabricating them into a number of applications like food containers, chairs, vials, etc. with antimicrobial activity.

2. Experimental

2.1. Preparation of AgNPs-zeolite and PP/AgNPs-zeolite Plastics

PP pellets (QR6701K), MFI = 10g/10 min and d = 905kg/m^3, were a product of Sabic, Saudi Arabia. AgNPs-zeolite with the AgNPs size of about 30 nm and silver content of 1.2% (w/w) was a product synthesized by our research group as described in a previous paper [6]. In brief, 1.05 kg of zeolite 4A was suspended into a glass beaker containing 1.3 L water. Then, 1.05 L of HNO_3 2N in water was added into zeolite suspension mixture for neutralization to pH ~6 and for final volume of about 4.2 L. 17.5 g of $AgNO_3$ was dissolved in 300 ml water and then poured slowly into neutralized zeolite suspension mixture.

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Stirring was carried out for 2 h at RT for completed Ag^+ exchange. A freshly prepared 50 ml hydrazine 25% (w/v) solution was added dropwise to the above Ag^+/zeolite under stirring for 4 h at RT. Reduction reaction was stopped and let standing overnight for AgNPs/zeolite settling down at ambient temperature. Finally, AgNPs/zeolite product was filtered off using cotton fabric and dried at 110°C till to constant weight. PP resin in ground powder form (9 kg) and AgNPs-zeolite powder (1 kg) were premixed and melt blended in a twin-rotating-screw extruder (Brabender, Germany) for preparation of PP/AgNPs-zeolite masterbatch in form of pellets. Then, three PP/AgNPs-zeolite plastic samples with estimated AgNPs content at 40, 80 and 160 mg/kg were prepared by mixing a required amount of masterbatch with PP pellets in the extruder as mentioned above.

2.2. Characteristics of AgNPs-zeolite and PP/AgNPs-zeolite Plastics

The as-prepared AgNPs-zeolite in powder form was characterized by transmission electron microscopy image (TEM, on a JEM 1010, JEO, Japan); by absorption UV-Vis spectrum (UV, on an UV-2401PC, Shimadzu, Japan); and by X-ray diffraction pattern (XRD, on a X Per' Pro, PA Nalytical, Netherlands) for observation of formation and size determination of AgNPs on zeolite [6].

The plastic samples in sheet form were prepared by heating pressure. The plastic sheets with thickness of about 2 mm were prepared for mechanical properties measurement on a Tensile tester Zwick/Roell Z 005, Germany according to ASTM D 638. The silver content in PP/AgNPs-zeolite plastic samples was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Perkin-Elmer, Optima 5300 DV. AgNPs-zeolite aggregated on the surface of PP/AgNPs-zeolite plastic typically for sample with silver content of 160 mg/kg was visualized using scanning electron microscope (FE-SEM, Hitach S-4800, Japan).

2.3. Antibacterial activity of PP/AgNPs-zeolite Plastics

The antibacterial activity of PP/AgNPs-zeolite plastic samples against *E. coli* was evaluated following the method of Ahmadi et al. [12] with some modifications. Scheme of the antibacterial test was shown in Figure 1.

Firstly, the PP/AgNPs-zeolite plastic samples of 2 mm thickness, 15 mm diameter, and Ag content of 40, 80 and 160 ppm were sterilized at 121°C for 20 min in autoclave and then artificially contaminated with *E. coli* by soaking in 10^7 CFU/ml *E. coli* bacteria suspension for 30 sec. The neat PP sample was also treated with the same process and used for the control. Consequently, the contaminated plastic samples were dried inside sterilized petri dishes at ambient temperature for 10 min and then shaken in 10 ml sterilized water at 150 rpm for 15 min (Figure 1). After that, the washing water was collected for determination of the bacterial contamination with spread plate method [13]. The antibacterial efficiency of PP and PP/AgNPs-zeolite plastic samples was calculated according to Eq. (1).

$$\eta(\%) = (N_o - N) \times 100/N_o \quad (1)$$

Where N_o and N are survival number of bacteria in washing water of the control and studied samples, respectively [12, 13].

3. Results and Discussion

In the UV-Vis spectrum of AgNPs-zeolite solution, a maximum absorption peak was appeared at λ_{max} 429 nm which was confirmed to be a characteristic plasmon resonant peak of AgNPs [14], while the such a peak was destitute in Ag^+-zeolite before reduction (Figure 2). Moreover, the XRD patterns shown in Figure 3 indicated that the AgNPs-zeolite has four typical diffraction peaks corresponding to 111, 200, 220, 311 crystal planes of silver with face centered cubic (fcc) structure [6, 18], whereas these peaks were not appeared in zeolite 4A. The UV-Vis spectra (Figure 2) and XRD patterns (Figure 3) authenticated the presence of AgNPs in zeolite framework.

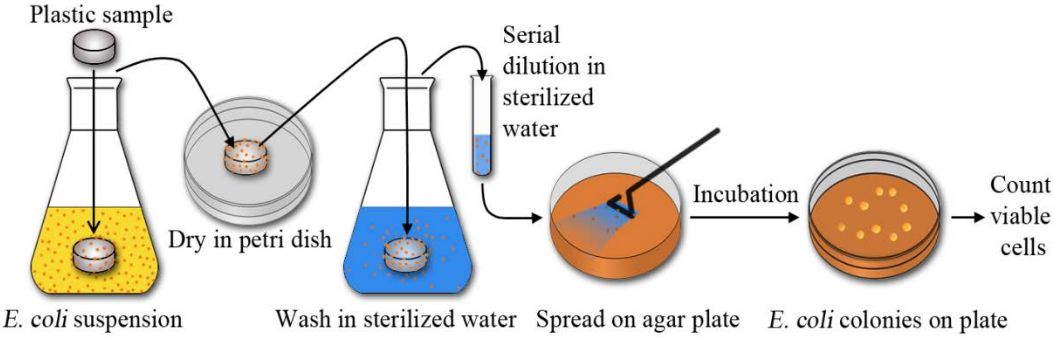

Figure 1. Scheme of the antibacterial efficiency test for plastic samples

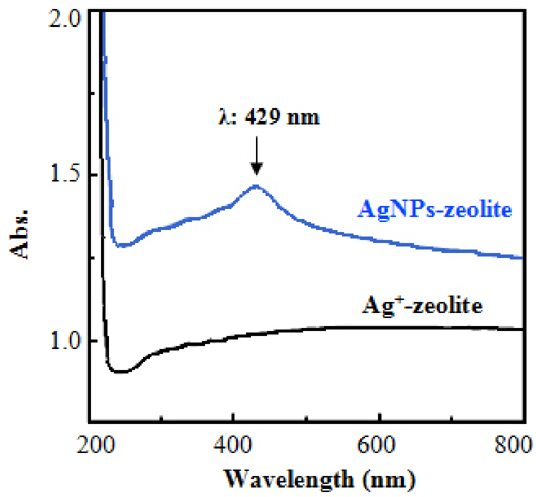

Figure 2. UV-Vis spectra of Ag^{+}-zeolite and AgNPs-zeolite

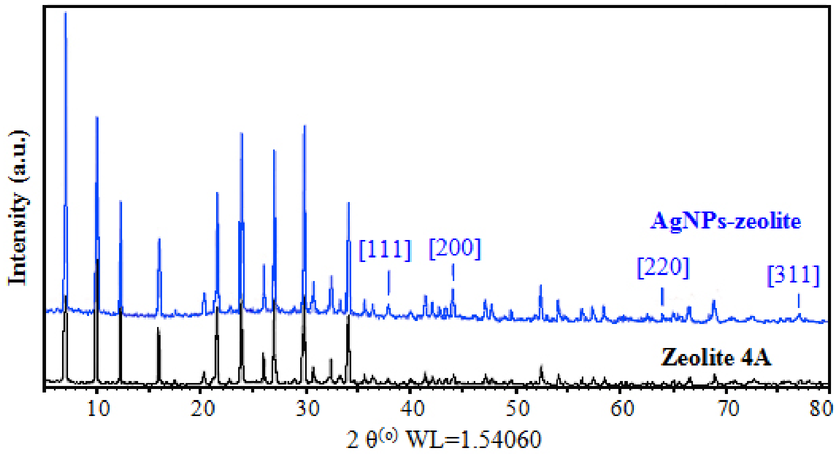

Figure 3. XRD patterns of zeolite and AgNPs-zeolite

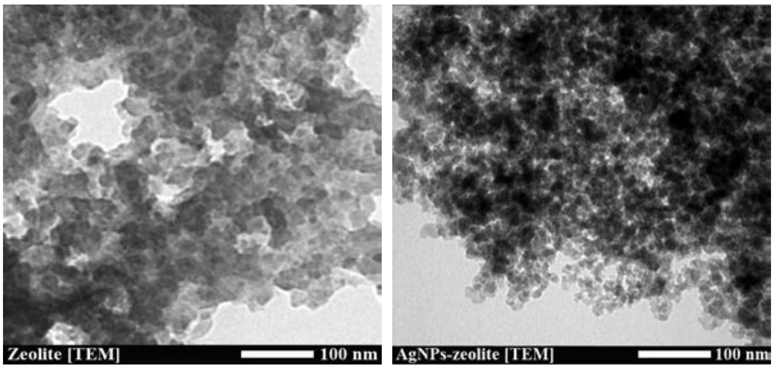

Figure 4. TEM images of zeolite (left) and AgNPs-zeolite (right)

Figure 4 showed the TEM images of zeolite and AgNPs-zeolite. It can be seen from TEM image of AgNPs-zeolite that the AgNPs diameter synthesized in the cavities of the zeolite was fairly uniform that was in agreement with the results reported by Shameli et al [14]. However, the sizes of AgNPs in the zeolite framework obtained by Shameli et al. were smaller (2 – 4 nm) compared to that of ours (~30 nm). This reason may be due to the dilution ratio of zeolite and water during reducing process. Another reason may be due to $NaBH_4$, a stronger reducing agent that was used by Shameli et al. [14] to reduce Ag^{+} instead of hydrazine hydrate. Further study should be carried out to clarify this phenomenon. Furthermore, in comparison with the AgNPs size of ~30 nm calculated from XRD pattern (Figure 3) based on Debye-Scherrer's formula [6], the sizes of AgNPs from TEM image in Figure 4 were in the range of 10 – 30 nm, smaller than 30 nm. The color of AgNPs-zeolite is grey (Figure 5).

Figure 5. Photographs of zeolite and AgNPs-zeolite

Reaction of Ag^+ reduction by hydrazine hydrate ($N_2H_4.H_2O$) is shown in reaction below [15].

$$4Ag^+ + N_2H_4 + 4OH^- \rightarrow 4Ag^o + N_2 + 4H_2O$$

This reducing reaction lowers the pH of the solution and it remains in weak base due to reducing agent ($N_2H_4.H_2O$) is added in more three time excess, according to stoicheiometry of the above reducing reaction. Dimitrijevic et al. also reported that hydrazine hydrate has been considered as preferred reducing agent and used for industrial scale production of silver powder for decades [15]. Therefore, this synthesis process of AgNPs-zeolite can be potentially to carry out on large scale. The schematic illustration of the synthesis of AgNPs into the zeolite framework from Ag^+-zeolite by chemical reduction was also described by Shameli et al [14].

Table 1. The actual content of silver in PP/AgNPs-zeolite plastic samples

Estimated Ag content, mg/kg	Actual Ag content, mg/kg
40	38.2 ± 2.7
80	76.4 ± 4.5
160	153.7 ± 6.4

The actual content of silver in PP/AgNPs-zeolite plastic samples was shown in Table 1. The obtained results of silver content in all three PP/AgNPs-zeolite plastic samples were slightly smaller in comparison with estimated values. Mechanical properties of PP/AgNPs-zeolite plastics were presented in Table 2.

Table 2. Mechanical properties of PP/AgNPs-zeolite plastics

AgNPs contents (ppm)	Tensile strength (MPa)	Elongation (%)	Yield strength (MPa)
0 (PP)	25.7	562	31.5
40	25.2	487	31.4
80	25.5	464	30.6
160	25.4	443	29.8

It was obvious from the results in Table 2 that the yield strength and tensile strength of PP/AgNPs-zeolite plastics with AgNPs content in the range of 0 – 160 ppm were almost unchanged. Conversely, the elongation at break was reduced from 562% (0 ppm) to 443% (160 ppm).

The obtained results were consistent with the results of Aalaie et al. for PE/nanosilver composite film prepared by extrusion compounding process by means of masterbatch [8]. However, it was different from the results reported by Jang et al. [9] that they prepared PP/silver nanocomposites by simultaneous *in situ* synthesis of AgNPs during extrusion compounding process. Accordingly, yield strength, tensile strength and elongation at break were all increased with the silver content from 100 to 1000 ppm. It can be observed in SEM photos (Figure 6) that the AgNPs-zeolite was clearly aggregated on the PP/AgNPs-zeolite plastic surface compared to neat smoothly PP surface.

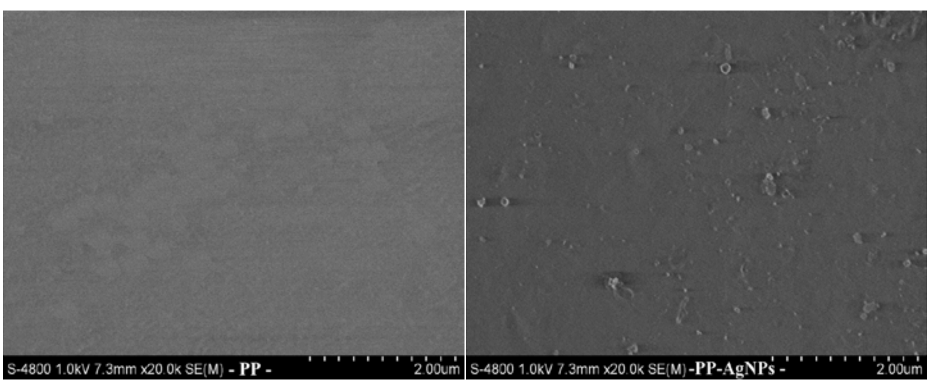

Figure 6. SEM micrographs of the neat PP (left) and PP/AgNPs-zeolite plastic (right)

Data in Figure 7 and Table 3 displayed the highly antibacterial efficiency of PP/AgNPs-zeolite plastics against *E. coli* (η ~100%), except for sample with 40 ppm AgNPs probably due to the low AgNPs content.

Table 3. Antibacterial efficiency of PP/AgNPs-zeolite plastics against *E. coli*

AgNPs contents (ppm)	CFU/ml	η (%)
0 (PP)	140,000	-
40	6,300	95.5
80	ND	100
160	ND	100

ND: not detected (non-colonies on agar plate for statistical count)

Dastjerdi et al. [16] also reported the same antimicrobial efficacy of PP/AgNPs-TiO_2 nanocomposite with the maximum antibacterial activity for sample with 75 ppm of AgNPs. Furthermore, effectively bactericidal activity of PP/AgNPs-TiO_2 was also reported by Ahmadi et al [12]. However, they used rather high AgNPs content (~500 ppm) for preparation of PP/AgNPs-TiO_2 nanocomposite. According to Fernandez et al. [17] the content of silver in the range of 20 – 100 ppm are required for realistic food packaging applications. Thus, the as-prepared PP/AgNPs-zeolite masterbatch contained 1.000 ppm of AgNPs can be conveniently used to fabricate a number of products like food containers, chairs, vials, etc.

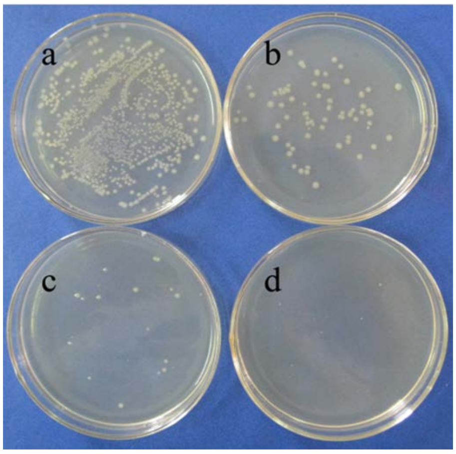

Figure 7. *E. coli* colonies from the washing water of PP/AgNPs-zeolite plastics growth on agar plates: a) control (0 ppm), b) 40 ppm, c) 80 ppm and d) 160 ppm AgNPs

4. Conclusions

The AgNPs-zeolite powder with AgNPs size of about 10 – 30 nm was successfully synthesized by hydrazine reduction method. PP/AgNPs-zeolite plastics were prepared through masterbatch by melt blending method. PP/AgNPs-zeolite plastics with AgNPs content in the range from 80 to 160 ppm exhibited highly antibacterial efficiency (η ~100%). Furthermore, the tensile strength of PP/AgNPs-zeolite plastics was almost unchanged in comparison with neat PP. Thus, the as-prepared PP/AgNPs-zeolite masterbatch can be conveniently used to fabricate various products of antimicrobial plastics such as food containers, chairs, vials, etc.

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