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Study on the synthesis of antibacterial plastic by using silver nanoparticles doped in zeolite framework

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Abstract: Silver nanoparticles (AgNPs) doped in the zeolite framework (AgNPs/Z) were successfully synthesized by γ-irradiation in ethanol solution of silver ion-zeolite (Ag^+/Z) prepared by ion exchange reaction between silver nitrate ($AgNO_3$) and zeolite 4A. The effects of the Ag^+ concentration and irradiation dose on the formation of AgNPs/Z were also investigated. AgNPs/Z with the silver content of about 10,000 ppm and the average particle size of AgNPs of about 27 nm was characterized by ultraviolet-visible spectroscopy, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM). Firstly, AgNPs/Z was added into PP resins for creation of PP-AgNPs/Z masterbatch (Ag content of ~10.000 ppm) and then PP-AgNPs/Z plastics were preapared by mixing masterbatch with PP resins. The antibacterial activity of the PP-AgNPs/Z plastics was investigated against Gram-negative bacteria *Escherichia coli* (*E. coli*). The results showed that PP-AgNPs/Z plastic contained 100 ppm of Ag possessed a high antibacterial property, namely the bactericidal effect was more than 96 % on the platic surface. In conclusion, possessing many advantages such as: vigorously antibacterial effect and good dispersion in plastic matrix, AgNPs/Z is promising to be applied as bactericidal agent for plastic industry.

Keywords: *Zeolite, silver nanoparticles, ion exchange, γ-irradiation, antibacterial plastic.*

I. INTRODUCTION

Nowadays plastics become one of the most popular materials of human society. Therefore, the development of additives for plastic is inevitable. According to Allied Market Research of (USA), worldwide consumption of plastic additives is estimated of about 12.6 million tons in 2013 and it is expected to increase to 17.1 million tons by 2020 [1]. In this field, antimicrobial systems serve as indispensable contribution, namely the consumption of plastic biocides was 25 million kg corresponding to $25 million in 2001 [2]. Recently, considerable interest has arisen in the use of silver nanoparticles (AgNPs) based on high antimicrobial activity and easy-incorporation ability into other materials, such as clay, montmorillonite, silica and zeolite [1-4], for special applications. The AgNPs-clay and the AgNPs-zeolite exhibited a higher antimicrobial activity than untreated samples [3,6], while the AgNPs deposited on silica were mingled with PP resins for antibacterial plastic masterbatch [5]. Interestingly, AgNPs were synthesized effectively on montmorillonite by γ-irradiation method [4].

Zeolite A, known as Linde Type A, belongs to low silica zeolite. It has abundant extra-framework cations, ion Na^+. For that reason, zeolite A is considered as an excellent substrate for ion-exchange purpose. In this study, ion Ag^+ was firstly loaded into zeolite

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4A by ion exchange from silver nitrate and then irradiated by Co-60 gamma ray for forming AgNPs/Z. Subsequently, AgNPs/Z was mixed with PP resins and bactericidal tests of PP-AgNPs/Z plastics were carried out against Gram-negative bacteria *E. coli*.

II. EXPERIMENTAL

Materials and chemicals

Zeolite 4A was purchased from China. $AgNO_3$ and ethanol of analytical grade were from Shanghai Chemical Reagent Co. Ltd, China. Polypropylene resins were provided by HMC Polymers Co. Ltd, Thailand. The Luria-Bertani medium and agar plates used for bacteria incubation were purchased from Himedia, India. The *E. coli ATCC 6538* was provided by University of Medicine and Pharmacy, Ho Chi Minh City and cultivated and preserved at biology laboratory, VINAGAMMA, Ho Chi Minh City.

Preparation of Ag^+/Z

Ag^+/Z were prepared by ion-exchange method. Zeolite 4A was suspended in water (pH~ 6), following the suitable amount of $AgNO_3$ was supplied into the mixture for the final Ag content on zeolite of ~ 10.000 ppm and stirred at 60^0C continually for 2 h. The suspension was filtered to harvest the solid Ag^+/Z and then washed with water before drying overnight at 110^0C.

Preparation of AgNPs/Z

The Ag^+/Z prepared above were suspended in ethanol solution (10%) for the final Ag contents of 15, 20, 25 and 30 mM. The suspensions were irradiated by γ-rays to required dose (30-60 kGy) with the dose rate of 3.2 kGy/h at Dalat Nuclear Research Institute. After removing the liquid, the obtained AgNPs/Z was washed and dried overnight at 110^0.

Characterization of AgNPs/Z

AgNPs/Z dispersed in 2% polyvinyl alcohol (PVA) solution was used to demonstrate the formation of AgNPs on zeolite by UV-Vis absorption spectrum measurement on the Jasco-V630 spectrophotometer, Japan. The mean size of AgNPs was determined by X-ray diffraction (XRD) on D8 Advance Brucker, Germany. The microstructure of the AgNPs/Z was studied by using scanning electron microscopy (Hitachi S-4800, Japan) and transmission electron microscopy (JEOL JEM-1010, Japan). The Ag content in AgNPs/Z was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on an Optima 5300 DV Perkin- Elmer, USA. The presence of silver in AgNPs/Z was also assessed by energy dispersive X-ray spectroscopy (EDX) on JEOL 6610 LA, Japan.

Preparation antimicrobial plastic

AgNPs/Z prepared by 50 kGy-irradiation of Ag^+/Z 25 mM with the Ag content of 10.000 ppm was chosen for mixing with PP resins. Firstly, the mixture of AgNPs/Z- PP with 10% AgNPs/Z was loaded by extruder Brabender DSE 20, Germany for creating masterbatch P-AgNPs/Z with the Ag content of ~ 1.000 ppm. Subsequently, the masterbatch was mixed with PP resin at suitable ratios for preparation of PP-AgNPs/Z products containing suitable silver contents.

Bactericidal activity evaluation

The bactericidal activity of PP-AgNPs/Z plastic was carried out against *E. coli* ATCC 6538, as an indicator of fecal contamination of water [7, 8] by two tests. The first test studied on the influence of Ag content on antibacterial activity of PP-AgNPs/Z: The PP-AgNPs/Z samples with different Ag contents (35, 70 and 100 ppm) were contaminated artificially with *E. coli* before washed by sterilized water. Survial cells of contaminated sample surfaces were detemined inderectly by the bacterial contamination of washing waters throught spread plate technique. The PP sample was used as a control sample. The second test, the samples of PP-AgNPs/Z (~ 100 ppm Ag) with surface areas about 10, 20 and 30 cm^2 were exposed to *E. coli* suspension overnight. The *E. coli* contamination in each suspension was evaluated by spread plate technique. The bactericidal effect was calculated using the equation: $\eta(\%) = (N_0 - N)\times 100/N_0$, where N_0 and N are survival number of bacteria in the control and studied samples, respectively [9, 10].

III. RESULTS AND DISCUSSION

The influence of irradiation dose and Ag^+ concentration on AgNPs formation into zeolite framework

The Fig. 1 showed that when irradiated Ag^+/Z suspension (Ag^+ concentration ~ 25 mM) in the dose range of 20-60 kGy, UV - Vis spectra of AgNPs/Z dispersed in 2% PVA solution had the maximum absorption wavelength (λ_{max}) in the range 455-429 nm respectively, whereas in control sample (zeolite), maximum absorption peak did not appear in this wave range. According to Ramnani et al., silver clusters show characteristics absorption band in the visible region (λ_{max} ~ 390–450) [11]. Therefore, the UV-Vis spectra demonstrated that the formation of AgNPs in irradiated samples. Moreover, the nearly resembled maximum absorptions of 50- and 60-kGy-irradiated samples prove that 50 kGy is the saturation dose for 25 mM Ag^+/Z suspension. Thus, the complete conversion dose of 1 mM Ag^+ to AgNPs is 2 kGy, higher than the dose 1.8 kGy in report of Ramnani et al. [11].

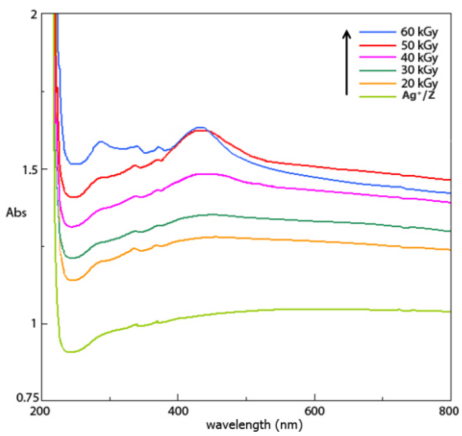

Fig. 1. UV-Vis spectra of AgNPs synthesis by different irradiation doses

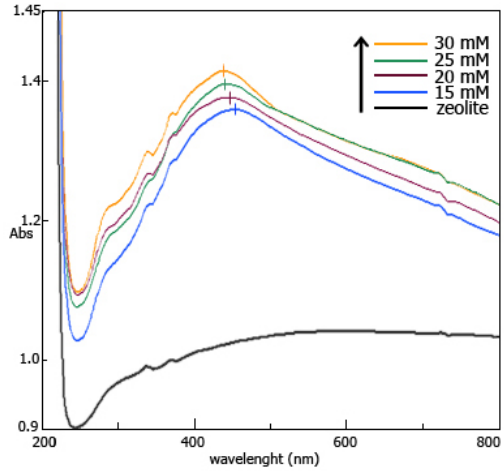

Fig. 2. UV-Vis spectra of AgNPs prepared from different Ag^+/Z suspensions

The UV-Vis spectra of AgNPs synthesized by irradiating 15, 20, 25 and 30 mM Ag^+ suspension at saturation doses of 30, 40, 50 and 60 respectively were presented in Fig. 2. The result showed that the λ_{max} of AgNPs/Z prepared from the higher Ag^+ concentration shifts to the lower wavelength, which means the formation of smaller AgNPs. This result is in agreement with report of Jiraroj et al. [12]. Moreover, the size of these AgNPs/Z were able to be estimated from XRD pattern in Fig. 3 by the Debye–Scherrer's formula: $t = 0.9\lambda/\beta\cos\theta$ as described by Jiang et al. [13]. As the result of calculation, the AgNPs sizes were about 34.6, 30.9, 27.4 and 23.6 nm for 15, 20, 25 and 30 mM Ag^+ concentration of suspension systems, respectively. The size of AgNPs decreased along with the decrease of Ag^+ concentration, so this result is suitable with above UV-Vis result.

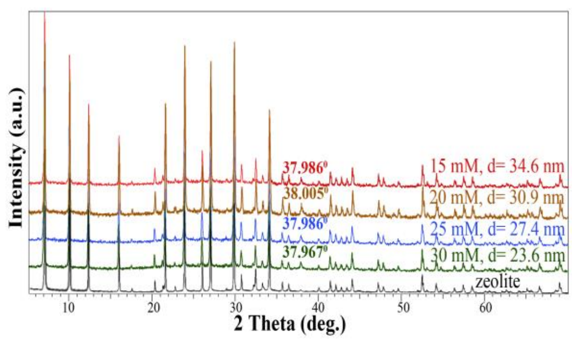

Fig. 3. XRD patterns of AgNPs/Z prepared from different Ag^+/Z suspension

Based on these results, the Ag^{+} concentration of 25 mM and irradiation dose of 50 kGy were selected for preparing the AgNPs/Z.

Characteristics of AgNPs/Z prepared by 50 kGy irradiation of Ag^{+}/Z 25 mM

The Ag content of AgNPs/Z was determine by ICP-AES (data not shown), which attained up to ~10.000 ppm. Results of energy dispersive X-ray (EDX) spectra in Fig. 4 showed that three main components of zeolite 4A were silicon, aluminum, oxygen and a small amount of sodium and potassium, but without any trace of silver, whereas the peak at 3 keV appeared in EDX spectrum confirming the appearance of silver in the composition of AgNPs/Z. In the study of Klemenčič et al. [14] and Gusseme et al. [15], the EDX spectrum was also used to confirm the presence of AgNPs in cellulose and polyvinylidene fluoride samples.

The SEM and TEM pictures of the AgNPs/Z were presented in Fig. 5 and 6, respectively. Fig. 5 showed that incorporation of AgNPs into zeolite by irradiation causes the break inside zeolite structure, whereas in the study of Jiraroj et al. [12], the formation of AgNPs on zeolite structure by chemical reduction method did not make any change in the size and shape of zeolite. In Fig. 6, the dark contrast spots just appeared on the surface of AgNPs/Z structure, this result confirmed the formation of AgNPs into zeolite framework.

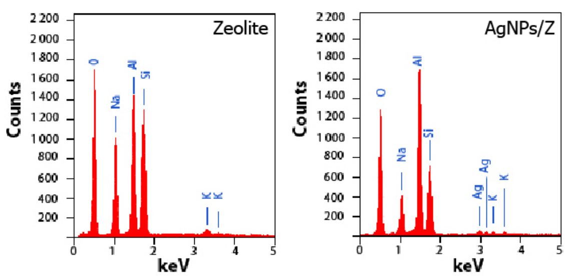

Fig. 4. EDX spectra of zeolite and AgNPs/Z

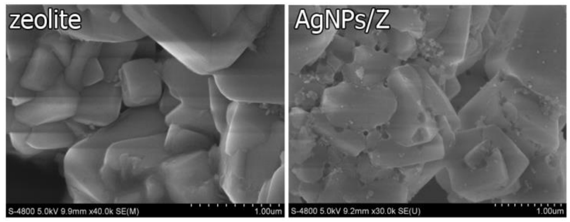

Fig. 5. SEM pictures of zeolite and AgNPs/Z

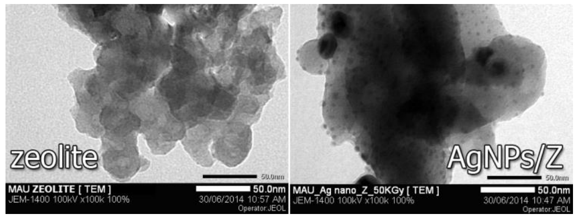

Fig. 6. TEM pictures of zeolite and AgNPs/Z

Bactericidal activity of PP-AgNPs/Z plastic

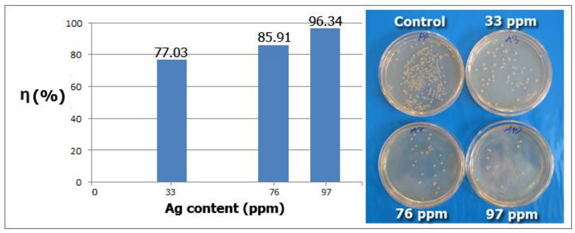

Fig. 7. The antibacterial effect of PP-AgNPs/Z platics with different Ag contents

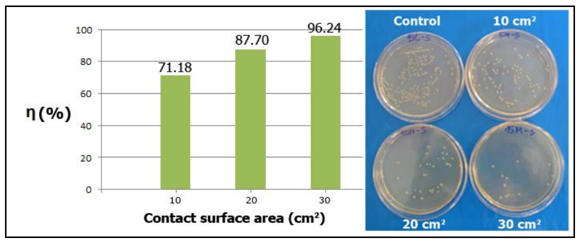

Fig. 8. The antibacterial effect of PP-AgNPs/Z platics with different contact surface areas

Results of the bactericidal activity of PP-AgNPs/Z against *E. coli* are showed in Fig. 7 and 8. In the test for estimating the influence of Ag content on anticbacterial activity of PP-AgNPs/Z, the result indicated that η% increased along with the Ag^{+} concentration and up to 96% at 97 ppm. The η value did not achieve the level 100% because the amount of *E. coli* cells contaminated on plastic surfaces was too high, about 1.000 CFU/cm^{2}. In the study of Suyen, the antibacterial effect of PP plastic added

Ag^+/zeolite 100 ppm was aslo 91% of the initial contamination of ~ 1000 CFU/ml [16].

In Fig. 8, the η% increased from ~71% to >96% when the contact surface area of PP-AgNPs/Z increased from 10 cm^2 to 30 cm^2. Due to the highly initial contamination of *E. coli* of ~ 10^7 CFU/ml, the η value of 96% inidicated the highly antibacterial effect of PP-AgNPs/Z plastic.

IV. CONCLUSIONS

The AgNPs/Z was prepared effectively by two-step process, namely the ion Ag^+ was exchanged into zeolite 4A framework and then irradiated in ethanol solution for reducing Ag^+/Z to AgNPs/Z. The functioned PP resins with AgNPs/Z of about 100 ppm AgNPs presented highly bactericidal effect against *E. coli* contaminated both on plastic surface and in cultural medium. Based on the strong antibacterial activity and easy-mixing into PP resins, the AgNPs/Z is promising to be applied as bactericidal agent for plastics.

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