Preparation and Characterization of Antibacterial Zeolite–Polyurethane Composites

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ABSTRACT: In this study, antibacterial properties were induced in polyurethane (PU) films by the incorporation of Ag^+-loaded zeolites as fillers. The mechanical and thermal properties of the prepared composites were also investigated. For this purpose, two different types of zeolite microparticles, high-silica zeolite beta crystals and low-silica zeolite A crystals, were synthesized. Ag^+ was added by ion exchange, and these particles were incorporated into the PU prepolymer, which was prepared from its main components of toluene diisocyanate and polypropylene ethylene glycol (medical purity). Microbiological tests revealed that both types of composites, prepared by the addition of Ag^+-containing zeolite beta or zeolite A to the PU matrix, had antibacterial properties. It was demonstrated for the first time that a high-silica zeolite (zeolite beta) and its composite film could be effectively employed as antibacterial materials. Furthermore, mechanical and thermal characterization of the composites showed that the zeolites enhanced the mechanical properties of the polymer and did not cause any deterioration in its thermal properties. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2854–2861, 2008

Key words: composites; polyurethanes; zeolites

INTRODUCTION

Polyurethanes (PUs) are among the best choices for biomedical applications because of their desirable mechanical properties and biocompatibility. The hardness, strength, elasticity, and other mechanical characteristics of PUs can be varied greatly according to the chemical composition and microstructure of the polymers.[1,2] The mechanical characteristics of PUs (hardness, strength, and elasticity) as well as their physical form (elastomer, foam, adhesive, fiber, etc.) can be varied greatly in the desired direction.[3,4]

Enhanced mechanical performances of PUs can be achieved through the incorporation of inorganic materials into the polymer matrix, and zeolites have been shown to be alternative inorganic fillers for this purpose.[5,6] Unlike traditional fillers (e.g., clays, glass, and silica particles[7,8]), the conditions of zeolite synthesis can be greatly altered, and this provides a broad range of potential properties and the ability to tailor the functions of composite materials. As inorganic fillers, zeolites have been shown to increase the mechanical strength of polymers in several studies.[5,6] In previous studies, it was observed that composite films prepared with the incorporation of zeolite beta into PU had improved mechanical properties with respect to the original PU, and the effect was more pronounced with calcined zeolite beta crystals.[6]

Zeolites can be used as effective antibacterial agents because the native cations in the zeolite structure can be exchanged with heavy-metal ions that have antibacterial activity.[10,11] Among them, silver ions are the most attractive because of their strong activity, wide spectrum, and low human toxicity.[12] Therefore, zeolites have attracted interest for biomedical applications, including antidiarrheal agents, hemorrhage control, detoxicants, and antibacterial agents.[10] In different applications, antibacterial PU is obtained by either the coating of PU with silver[13,14] or by silver particle impregnation.[15–18] Using silver-ion-loaded zeolites as antibacterial agents offers an advantage over the other methods because silver ions are more effective than metallic silver atoms.

In this study, two types of zeolites, zeolite A and zeolite beta, were synthesized and modified to have antibacterial properties. Inorganic–organic composites were prepared by the incorporation of these zeolites into a PU matrix, which was synthesized from its main components of toluene diisocyanate (TDI) and polypropylene ethylene glycol without the addition of any catalyst, any solvent, or any other ingredient. The mechanical and thermal properties of the prepared composites were determined, and their antibacterial properties were tested on *Escherichia coli*. In this way, the antibacterial activity of the Ag^+-loaded high-silica zeolite beta was tested against low-silica zeolite A, whose Ag^+-exchanged form is a well-known antibacterial agent. To the best of our knowledge, this is the first report on the preparation of antibacterial zeolite beta incorporated PU composites, which are believed to be alternative candidates for use in daily life and for biomedical applications with their improved mechanical and antibacterial properties.

EXPERIMENTAL

Materials

In zeolite synthesis, sodium aluminate (50.8 wt % Al_2O_3, 43.4 wt % Na_2O; Riedel de Haën, Seelze, Germany) as an aluminate source, a Ludox HS-40 colloidal silica solution (40 wt % SiO_2 suspension in water; Sigma–Aldrich) or sodium metasilicate pentahydrate ($Na_2O \cdot SiO_2 \cdot 5H_2O$, 29 wt % Na_2O, 28 wt % SiO_2, 43 wt % H_2O; Fluka AG) as a silica source, and NaOH powder (>97 wt %; J. T. Baker) as a soda source were used. For zeolite beta synthesis only, tetraethyl ammonium hydroxide (TEAOH; a 35 wt % TEAOH aqueous solution; Aldrich) was used as the organic structure directing agent. Ag^+-exchange stock solution was prepared with solid $AgNO_3$ (J. T. Baker). In all synthesis and ion-exchange procedures, deionized water (resistivity > 18 MΩ cm) was used. PU samples were prepared from TDI (a mixture of 2,4-TDI and 2,6-TDI in a ratio of 80 to 20; Dow Chemical Co.) and polypropylene ethylene glycol (polyol, molecular weight ∼ 3500; Dow Chemical).

Preparation of the zeolites

Synthesis

Zeolite beta (Na Beta) and zeolite A (Na A) were hydrothermally synthesized from gel solutions with molar compositions given in Table I. A sodium aluminate precursor solution for zeolite beta was prepared by the dissolution of NaOH and sodium aluminate in deionized water. Then, a TEAOH solution was added, and the precursor solution was stirred thoroughly. A colloidal silica solution was added to the aluminate precursor solution and mixed

TABLE I
Sample Codes and Descriptions

Code	Description
NaBeta	Molar composition of the synthesis gels: 2.2 Na_2O/Al_2O_3/20 SiO_2/4.6 (TEA)$_2$O/444 H_2O
	Experimental conditions: 150°C and 8 days[6]
NaA	Molar composition of the synthesis gels: 3.39 Na_2O/Al_2O_3/1.77 SiO_2/116.9 H_2O
	Experimental conditions: 100°C and 4 h[20]
cAgBeta	Silver-ion-exchanged and calcined NaBeta
AgA	Silver-ion-exchanged NaA
PU	PU film
PU–cAgBeta	PU composite film prepared by the addition of cAgBeta to PU
PU–AgA	PU composite film prepared by the addition of AgA to PU

thoroughly before being placed into Teflon-lined stainless steel autoclaves. The autoclaves were kept statically at 150°C in a conventional oven for 8 days. The resulting solid crystals were vacuum-filtered, washed with deionized water, and dried at 80°C.

Zeolite A was synthesized according to the published procedures[19] with sodium metasilicate pentahydrate and sodium aluminate as silicate and aluminate sources, respectively. These solutions were put into polypropylene bottles and kept statically at the designated temperatures (Table I). Crystals were obtained after vacuum-filtration, washing, and drying steps as in the synthesis of zeolite beta.

Ion exchange and calcination

For the cation-exchange process, 1 g of a zeolite sample was put into a solution of $AgNO_3$ (0.05M, 25 mL), and the resulting suspension was stirred in the dark for 24 h at room temperature. Zeolites were removed by centrifugation at 3700 rpm and then washed with repeated centrifugation and redispersion in deionized water to remove excess $AgNO_3$. Ag^+-loaded zeolites, that is, AgBeta and AgA, were obtained after drying at 80°C. AgBeta was calcined at 550°C for 6 h before the composite was made to remove the organic structure directing agent, and it was named cAgBeta.

PU synthesis

PU films were prepared from TDI and polyol without the addition of any other ingredients such as a solvent, catalyst, or activator in a closed vacuum system, as described previously.[6] In this process, the polyol (20 mL) was put into the reactor chamber, which was attached to a vacuum and was kept at 90°C for at least 1 h for the removal of water. Afterwards, TDI (5 mL) was added dropwise, and the total solution was stirred for 6 h at 90°C *in vacuo*.

For the PU film preparation, the formed viscous prepolymer solution was poured into glass Petri dishes, and they were placed in a vacuum oven, in which they were kept at 80°C for 3–4 days. The films were easily removed from the Petri dishes after solidification.

Composite preparation

Zeolites were dried at 80°C overnight, sieved (sieve no. 100, 160-μm openings) to break up zeolite lumps, and added to the freshly prepared viscous PU prepolymer. Desired amounts (10 wt %) of the sieved zeolites were added to the prepolymer with a spatula and mixed thoroughly to obtain a well-dispersed mixture. The samples were immediately placed in a vacuum oven for curing. The composites were easily removed from the glass dishes after solidification.

Material characterization

Phase identification of the synthesized zeolites was achieved with powder X-ray diffraction (XRD) analysis using Ni-filtered Cu Kα radiation (PW 1729, Philips, Eindhoven, The Netherlands). The morphological properties of the Ag^+-loaded zeolites as well as the zeolite–PU composites were examined by field emission scanning electron microscopy (Quanta 400, FEI). Energy-dispersive X-ray spectroscopy analysis was performed with an EDAX X-ray detector attached to a Quanta 400 field emission scanning electron microscope. The Ag^+ content of the ion-exchange zeolites was determined by inductively coupled plasma optical emission spectrometry (Optima 4300DV, PerkinElmer) with the atomic percentage values.

Thermal characterization of the prepared composites was carried out by thermogravimetric analysis (Pyris 1 thermogravimetric analyzer, PerkinElmer) under an N_2 atmosphere between 25 and 600°C and at a heating rate of 10°C/min. The mechanical properties were analyzed with a mechanical tester (LRX 5K, Lloyd) controlled by a computer running WindapR software. Samples were attached to the holders of the instrument (gauge length = 20 mm), and load–deformation curves were obtained. At least five samples from the same composite sample were tested, and the average values of the ultimate tensile strength (UTS), elongation at break (EAB; %), and Young's modulus were calculated.

Antibacterial testing

The antibacterial effects of the prepared samples were tested on *E. coli*. All the equipment either was available in sterile packages or was flame-sterilized before use, and transfers were done inside an aspirated cabin to satisfy aseptic conditions.

Antibacterial effects of Ag^+-ion-exchanged zeolite powders were determined with liquid medium tests. Bacterial colonies were grown on eosin methylene blue (EMB) agar plates at 37°C 1 day before microbiological tests. Grown colonies were taken with an inoculating loop under aseptic conditions and dissolved in 50 mL of deionized water. After the bacterial culture was thoroughly dispersed in the deionized water, zeolite powders (500 ppm) were added, and the solutions were gently mixed. For control purposes, a blank solution was prepared without zeolite addition. After 1 day of incubation (at 37°C) under static conditions, samples from the liquid media were taken with an inoculating loop and spread onto EMB agar by a sterile cotton swab. The agar plates were again incubated for 1 day at 37°C, and the growth of *E. coli* was examined.

Antibacterial effects of the zeolite–polymer composites were determined by the disc diffusion method. Bacterial colonies were grown on EMB agar plates at 37°C as in the case of the liquid medium tests. With the aid of a sterile cotton swab, the inoculum was taken from EMB agar plates and spread onto Muller–Hinton agar plates. Composite samples of 5-mm discs were placed on the inoculated Muller–Hinton agar both vertically and horizontally. After 1 day of incubation at 37°C, the bacterial growth inhibition zones that formed around the composite samples were recorded with photographs.

RESULTS AND DISCUSSION

Zeolite characterization

The powder XRD patterns of the synthesized zeolites matched the XRD patterns in the literature,[19] confirming that the desired crystalline phases were pure materials. The powder XRD patterns of the two types of synthesized zeolites are given in Figure 1. The broad peak between 6.5 and 8.5° and the intense peak at 22.5° are the characteristic peaks of zeolite beta. The characteristic peaks for zeolite A were also observed at 2θ values of 21.7, 24, 27.2, and 30°.[20,21] The particle sizes were approximately in the range of 1.3–1.6 μm for AgA and 0.7–1.2 μm for cAgBeta as shown in the scanning electron micrographs presented in Figure 2. The characteristic cubic shape of zeolite A particles was observed in the micrographs with slightly truncated edges. Zeolite beta crystals did not show a definite crystal shape, but they were observed as round particles with coarse surfaces.

The amount of Ag^+ loaded into the zeolites, as determined by inductively coupled plasma optical emission spectrometry, and the ion-exchange percentage, as determined by energy-dispersive X-ray analysis, are given in Table II. The Ag^+ loading in zeolite A was approximately twice as high as the Ag^+ loading
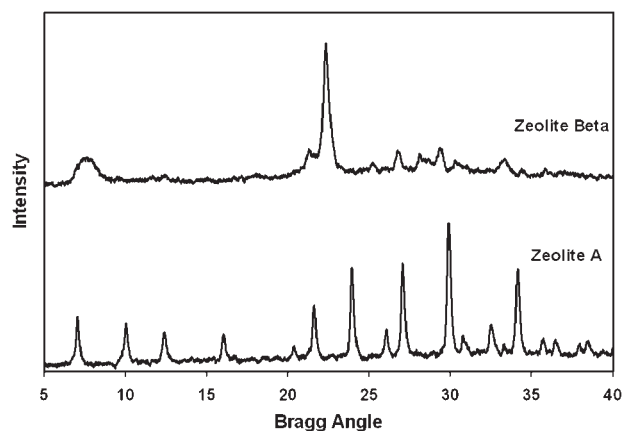
Figure 1 XRD patterns of the synthesized zeolites.

observed in zeolite beta. This was an expected result because the maximum ion-exchange capacity of zeolite beta was lower on account of the higher SiO_2/Al_2O_3 ratio of the framework structure. This was also the goal of this study because it was wondered if antibacterial activity was going to be observed even for a high-silica material such as zeolite beta and its corresponding PU composite material, which resulted in a lower Ag^+ loading with respect to zeolite A. The ion-exchange percentages for zeolite A and zeolite beta were found to be 25.5% and almost 100%, respectively, at the end of the 24-h ion-exchange process when the $AgNO_3$ concentration was low (0.05M). A higher Ag^+ loading is attainable for zeolite A if Ag^+-ion-exchange procedures are repeated or more concentrated $AgNO_3$ solutions are used. However, in this study, these procedures were avoided because of the detrimental effects of silver oxide deposited on the surface, as mentioned in the literature.[22]

Composite characterization

Morphology

Scanning electron micrographs of cross-sectional views of the composites with high magnifications are presented in Figure 3. Zeolite particles were observed to be in close contact with the polymer matrix. No voids were observed between the polymer matrix and zeolite crystals, and this held for all of the composites. Usually chemical linkers are used to increase the interactions between the inorganic fillers and polymer,[23] but in this study, a homogeneous dispersion of zeolite particles and good interaction between inorganic and organic compounds were observed without the addition of any linker. This interaction was investigated in our previous study, and it was found that the dispersion of the zeolite crystals upon calcinations was more homogeneous.[6] Furthermore, Figure 3 shows that the zeolite beta particles had better interactions with the polymer matrix with respect to the zeolite A particles. According to Figure 3(c,f), it is more likely that there were more voids created upon the incorporation of zeolite A particles in comparison with zeolite beta particles. This may be due to the fact that there was better compatibility between the high-silica zeolite beta and PU with respect to the low-silica zeolite A. A higher Si/Al ratio led to a more hydrophobic material, and this resulted in better compatibility between the zeolite and the polymer. One way of understanding whether any interaction between organic and inorganic compounds really exists is to observe an enhancement in the mechanical properties upon the incorporation of the inorganic material into the polymer matrix.
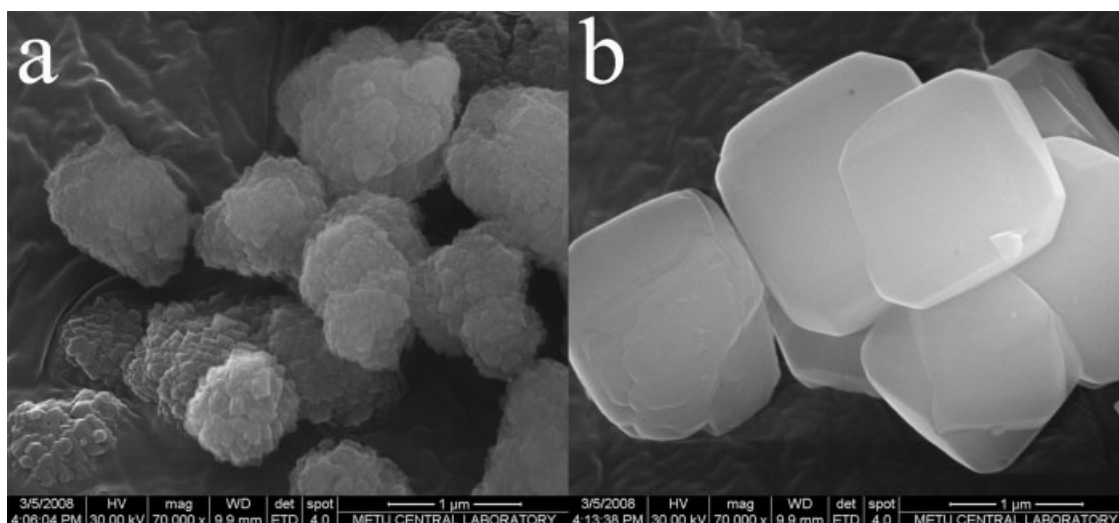

Figure 2 Scanning electron micrographs of Ag^+-zeolites: (a) cAgBeta and (b) AgA.

TABLE II
Amounts of Ag⁺ Loaded into the Zeolites by the Cation-Exchange Process

Zeolite type	SiO₂/Al₂O₃ ratio of the synthesis gel	Si/Al[a]	Loaded Ag⁺ (wt %)	Ag⁺-ion exchange (%)[b]
cAgBeta	20	9.4 ± 1	5.53 ± 0.02	98.3
AgA	1.77	1.2 ± 1	10.58 ± 0.01	25.5

[a] Energy-dispersive X-ray analysis.

[b] $\text{Ag exchange } (\%) = \frac{\text{Ag (atom \%)}}{\text{Ag (atom \%)} + \text{Na (atom \%)}} \times 100$.

Mechanical properties

Characteristic mechanical parameters showing the strength, elasticity, and ductility of the prepared composites are given in Table III. An increase was observed in the UTS, modulus of elasticity, and EAB values for all of the composites in comparison with the pure PU films. The enhancement of mechanical properties upon the incorporation of inorganic species in organic polymer matrices is a well-known situation, and the results obtained in this study are in agreement with the literature.[5,6] The increase in the mechanical properties indicated that the zeolites increased the resistance of the polymer material against elastic deformation. Furthermore, the UTS and EAB values were slightly higher for PU–cAgBeta than for PU–AgA. These results suggested that cAgBeta particles had better compatibility than AgA particles with the PU matrix. These results also correlated with the SEM results, showing a more pronounced inorganic–organic interaction between the cAgBeta particles and the polymer matrix than between the AgA particles and the polymer matrix.

Thermal properties

Thermogravimetric analysis (TGA) results for a pure PU sample and composites are shown in Figure 4. The TGA graphs had similar characteristics, showing thermal degradation of the samples starting at about 250°C and completing at 425°C. Zeolite addition to the PU matrix did not cause any negative effect on the resistance of the polymer against thermal degradation. Actually, slight shifts to higher values were observed in the degradation temperatures for all the composites compared to the pure PU samples. In a study by Chou et al.,[16] it was shown that upon the incorporation of a very small amount of silver nanoparticles (ca. 10^{-3} wt %) into a PU matrix, the
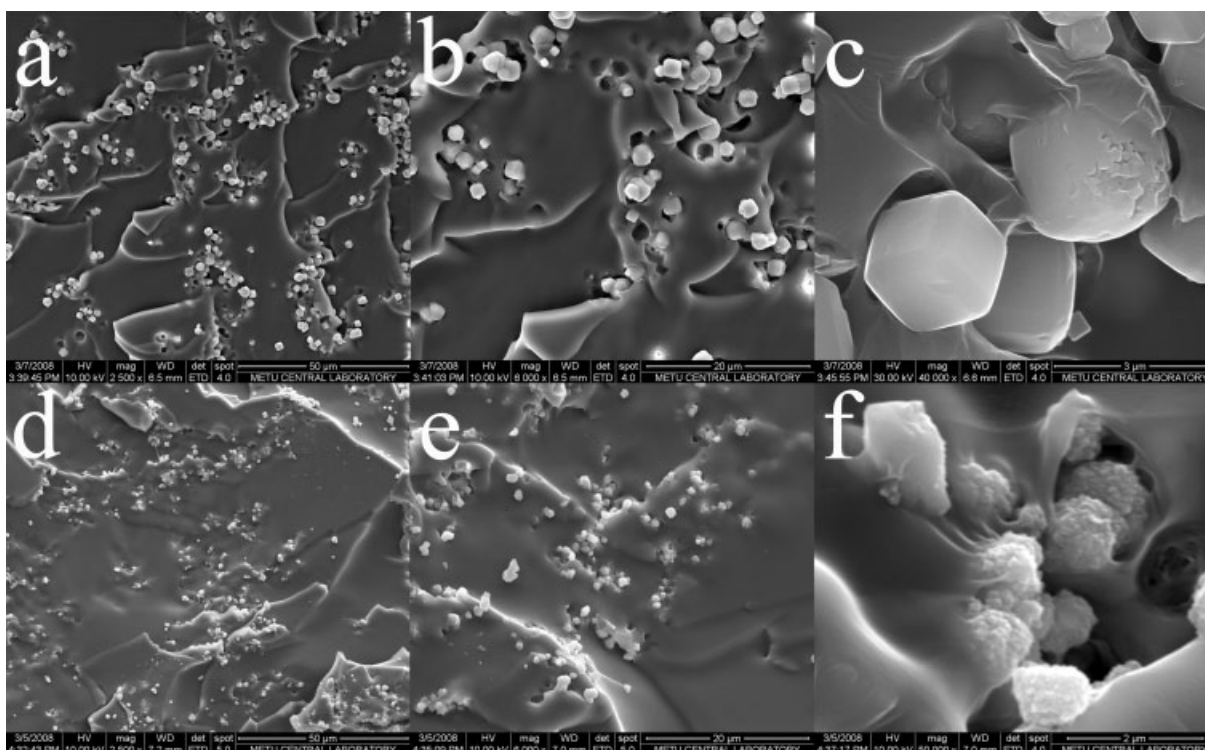

Figure 3 Cross-sectional SEM images of (a–c) PU–AgA and (d–f) PU–cAgBeta at magnifications of (a,d) 2500×, (b,e) 6000×, and (c,f) 40,000×.

Name	UTS (MPa)	Modulus of elasticity (MPa)	EAB (%)
PU	0.70 ± 0.15	3.72 ± 0.21	17.90 ± 3.87
PU–cAgBeta	1.19 ± 0.11	5.78 ± 0.37	22.64 ± 1.83
PU–AgA	1.17 ± 0.10	6.99 ± 0.94	18.70 ± 2.28

degradation temperature of the composites increased from 370 to 438°C. This much of an increase was explained by the fact that the silver nanoparticles served as nucleation sites for the enhanced crystallization of the PU matrix. In this study, the effect was not significant.

Microbiological tests

Liquid medium tests for zeolites

Antibacterial effects of Ag$^+$-zeolites on *E. coli* were assessed by comparison with the effects of the Na$^+$ form of the same zeolites. A blank solution containing only *E. coli* in deionized water was also used as a blank to observe the normal growth of the bacteria on agar plates. Photographs of the agar plates were taken after 24 h of incubation and are presented in Figure 5. As shown in Figure 5(d,e), both AgBeta and AgA were effective against *E. coli* in comparison with the blank solution [Fig. 5(a)] because no bacterial colonies were observed in the agar plates. This is more clearly shown in the 100× insets of the photographs. However, as shown in Figure 5(b,c), the Na$^+$ form of the same zeolites had no significant effect on the growth. Bacterial colonies were clearly visible in the Na$^+$-zeolite-containing solutions. No signs of living cells were observed even in magnified images of the agar plates on which samples from Ag$^+$-zeolite-containing solutions were spread. These tests clearly proved the antibacterial activity of Ag$^+$-zeolites against *E. coli* even at low concentrations. These results are in correlation with the results in the literature, in which the antibacterial effect of silver ions has been clearly shown in traditional low-silica zeolites such as zeolite A.[10,22] In this study, the antibacterial effect of zeolite beta, which is among the high-silica zeolite types, has been shown for the first time.

Disc diffusion tests for composites

The efficacy of PU–Ag$^+$-zeolite composites for the inhibition of bacterial growth was tested with the disc diffusion method.[14,18,24] Figure 6 shows images of the agar plates inoculated by bacteria and incubated in the presence of composite samples. According to this figure, there were ~ 1–2-mm bacterial growth inhibition zones around the composite samples, whereas no clearance was observed around the pure PU sample. Because of the slow diffusion rate of Ag$^+$ ion in the solid-like agar medium, the observed clearance areas around the composites were evidence of antibacterial activity in the vicinity of the surface. In fact, this antibacterial effect, confined to a very limited environment, is thought to be the desired case for PU–Ag$^+$-zeolite composites because high concentrations of Ag$^+$ are toxic for animal cells and bacteria.[12]
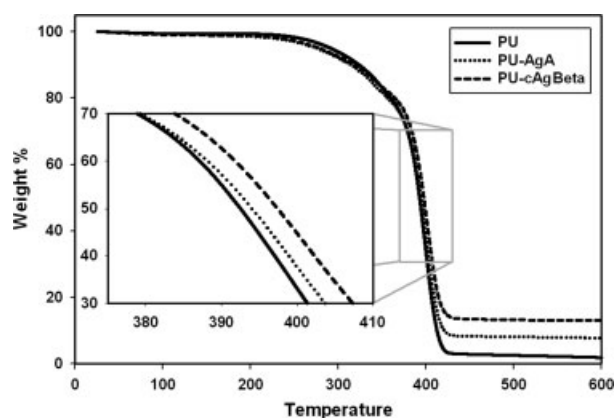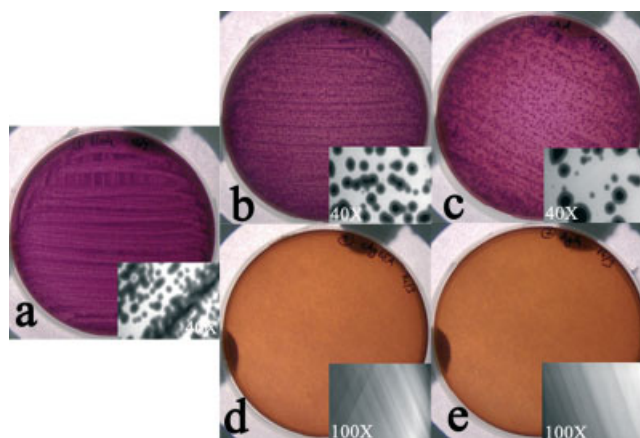

Figure 4 Comparison of the TGA results of PU and PU–Ag$^+$-zeolite composites. The inset shows the magnification of the region in which the weight-loss rate was the highest.

Figure 5 Antibacterial effects of Ag$^+$-zeolite powders versus the Na$^+$ form of the same zeolites tested in liquid media. The embedded close-up figures are optical microscopy images of the agar surfaces: (a) a blank, (b) NaBeta, (c) NaA, (d) cAgBeta, and (e) AgA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
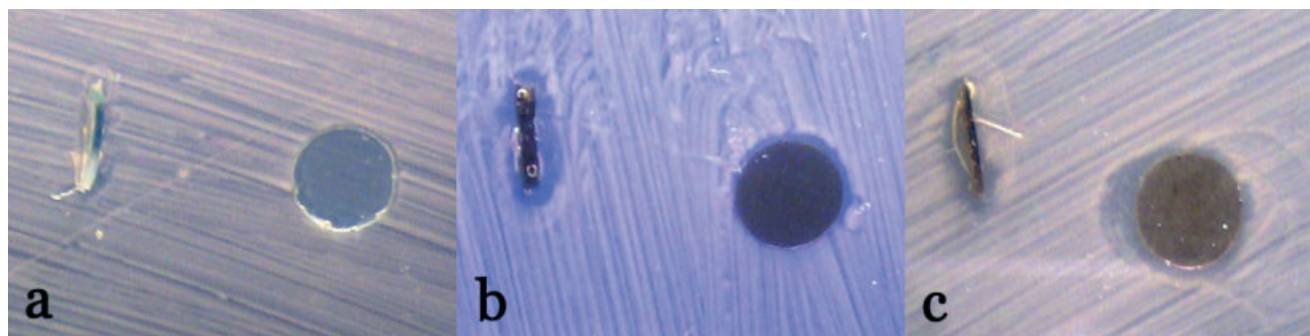
Figure 6 Pure PU and composite samples on bacteria-bearing agar plates: (a) PU, (b) PU–cAgBeta, and (c) PU–AgA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

According to the aforementioned results, although antibacterial activity was observed for all samples, no significant difference was observed among the composites prepared by the incorporation of different types and SiO_2/Al_2O_3 ratios of Ag^+-zeolites into the PU matrix. Although the purpose of this study was not to make a direct comparison of different Si/Al ratios and their effects on the antibacterial activity of a single type of zeolite, a comparison study was performed to show that a high-silica zeolite type could also be used to incorporate antibacterial effects into polymeric materials with respect to a low-silica zeolite such as zeolite A. This can be important because it is known that high-silica materials, with their more pronounced hydrophobic properties, can be better incorporated into polymeric materials in the preparation of composites.[6] Hagiwara et al.[22] performed a similar study and hypothesized that the SiO_2/Al_2O_3 ratio "in the zeolite synthesis composition" should be at most 14 and preferably 11. They proposed that although the acid resistance and alkali resistance of zeolites with a SiO_2/Al_2O_3 ratio over 14 would be better, the ions incorporated into the zeolite would not be sufficient to produce the desired antibacterial activity. In this study, the SiO_2/Al_2O_3 ratio of the zeolite beta synthesis composition was 20. In contrast to what was proposed previously, even with a low amount of silver incorporation due to the higher SiO_2/Al_2O_3 ratio, antibacterial activity was observed. This shows for the first time that even cAgBeta with its higher SiO_2/Al_2O_3 ratio and lower Ag^+ loading, in comparison with the well-known antibacterial zeolite AgA, can be effectively employed as an antibacterial filler in a PU matrix.

CONCLUSIONS

Two different zeolite types, zeolite beta and zeolite A, with Si/Al ratios of 9.4 and 1.2, respectively, were synthesized and successfully converted into antibacterial powders through the loading of Ag^+ ions. The effect of the incorporation of these zeolites into the PU matrix on the polymer's mechanical and thermal properties was studied. PU was chosen as the polymer matrix because of its desirable mechanical properties, biocompatibility, and versatile nature. The results showed that zeolite beta and zeolite A had good interactions with the polymer matrix, forming composites. Mechanical characterization of the composites in accordance with their morphology showed superior properties in comparison with the pure PU. TGA yielded very similar results, demonstrating that zeolite addition does not degrade the thermal properties of PU. Microbiological tests revealed a strong antibacterial effect of Ag^+-exchanged zeolite powders even at low concentrations in liquid media. The incorporation of Ag^+-exchanged zeolite powders into PU converted the polymer matrix into antibacterial films. In this way, a composite material of PU with not only improved mechanical properties but also antibacterial activity was obtained. Zeolite beta as a filler material was shown for the first time to possess an antibacterial effect, despite the relatively high SiO_2/Al_2O_3 ratio. We believe that these findings can be used to open up new routes for the synthesis of already existing antibacterial agents that are being consumed in all areas, such as household products and cleaning agents.

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