

Preparation and Characterization of Zeolite Beta–Polyurethane Composite Membranes

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ABSTRACT: Incorporation of zeolite into polyurethane (PU) membranes was investigated by using as-synthesized and calcined zeolite beta particles at two different loading contents (0.1 and 1 wt %). The chemical interaction between the zeolite beta crystals and PU was observed by ATR-FTIR spectroscopy. The SEM results suggested that the calcined zeolite beta crystals were more homogeneously dispersed in the composite membranes than the as-synthesized zeolite beta crystals. DMA results demonstrated that all composite membranes had higher storage modulus in the rubbery state and higher stability towards thermal and mechanical degradation with respect to the

control groups. Tensile testing results also showed increased tensile strength and elongation at break for all composite membranes. This study suggests that incorporating zeolite beta in its as-synthesized or calcined forms and at different amounts can be applied as an alternative method for tailoring the mechanical properties of PU membranes without changing its structural characteristics. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3378–3387, 2007

Key words: zeolite beta; polyurethanes; composites; mechanical properties

INTRODUCTION

Polymer based organic/inorganic composites are becoming increasingly important due to the fact that the resultant material shows superior performance in terms of mechanical toughness, permeability, selectivity, and photoconductivity for various applications.^{1–8} There are different types of inorganic materials used as fillers, such as clays,¹ SiC particulates,³ ceramic microspheres,⁵ and particularly silica particles.^{7,8} Pure silica does not contain framework charge since silicon is tetravalent. On the other hand, aluminosilicates have negatively charged oxide frameworks that require balancing of the extra framework positive ions. Thus, using zeolites as fillers could be challenging, since zeolites offer different parameters (i.e., Si/Al ratio, ion-exchange properties) that can be used as tools for tailoring the properties of the composite membranes for the desired purpose.

Zeolites are microporous crystalline aluminosilicates and are being used as fillers in organic/inorganic composites mostly to improve the gas separa-

tion performances because of their uniform molecular-sized pores.^{9–11} They are also being used in many further applications due to their high thermal and mechanical stabilities.^{12,13} Generally preparation of a stable zeolite involves the calcination of the as-synthesized materials.^{14–17} Calcination is usually done by heat treating the zeolite sample at 500°C or at higher temperatures. Zeolites offered various challenges in different areas with their unique properties; however, the powder forms of these materials limit their use in several applications especially in the manufacturing field. Their incorporation into polymers creates a very promising field of investigation in the field of nanotechnology.

Polyurethanes (PUs) are one of the most commonly used polymers in technological and medical applications due to their extensive structure/property diversity. They can be synthesized from diisocyanates and polyols in many different forms including foams, adhesives, coatings, fibers, resins, and elastomers.^{18,19} Physical properties, mechanical strength, and surface structure as well as the chemistry of the membranes can be very important depending on the usage area. These properties can be altered and tailored by varying the preparation composition, molecular weight of polyol component, type and the structure of diisocyanates, and with addition of inorganic fillers such as zeolites.

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To assess the proper use of zeolite-PU composite membranes in certain applications, knowledge of their mechanical/thermal properties and their morphology is essential. In the current study, zeolite beta, which is a large-pore and high silica zeolite, possessing a three-dimensional 12-membered ring channel system^{20,21} was chosen as the inorganic filler. Unlike other types of zeolites that are currently under investigation in the field of composite membranes,⁹ zeolite beta can be synthesized with a wide range of Si/Al ratios from ~ 10 to more than 100 and is known to be thermally stable showing high resistance to high calcination temperatures without loss of crystallinity.^{12,22} In this study, the effect of adding zeolite beta particles into PU membranes in as-synthesized or calcined forms at two different loading contents were studied by Fourier-transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), and characterized by their mechanical properties. To the best of our knowledge, this is the first report on the preparation and characterization of zeolite beta-PU composite membranes.

EXPERIMENTAL

Material synthesis

Zeolite synthesis

The zeolite beta formulation used ($2.2\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:60\text{SiO}_2:4.6(\text{TEA})_2\text{O}:445\text{H}_2\text{O}$, where TEA \equiv tetraethylammonium) was prepared from two precursor solutions. For this purpose, sodium aluminate precursor solution was prepared firstly by dissolving sodium aluminate (52.9 wt % Al_2O_3 , 45.3 wt % Na_2O , Riedel de Haën) in tetraethylammonium hydroxide (35 wt % TEAOH in water, Aldrich) solution. To this solution, colloidal silica (40 wt % suspension in water, Sigma Aldrich, SiO_2) was added and the resulting solution was put into the teflon-lined autoclaves. The autoclaves were kept at 150°C under static conditions for 10 days. After cooling, the formed zeolite crystals were filtered, washed, and dried.

The calcined zeolite beta samples were prepared from the parent zeolite beta by heat treating the as-synthesized material at 500°C for 10 h in a conventional oven. Two different types of zeolites, the as-synthesized and the calcined forms, were used for the preparation of the zeolite beta-PU composite membranes. For each type of zeolite beta sample, two different percent loadings (0.1 or 1 wt %) were studied.

PU synthesis

PU membranes were prepared from toluene diisocyanate (TDI; Dow Chemical Company, USA) as a

mixture of 2,4 and 2,6 toluene diisocyanate in the ratio of 80 : 20) and polypropylene ethylene glycol (polyol; Dow Chemical Company; $M_w \sim 3500$) without adding any other ingredients (solvent, catalyst, or activator) in a closed vacuum system as briefly described previously.²³⁻²⁵ In this process, 20 mL of polyol was put into the reactor chamber, heated at about 90°C , and evacuated for at least 2 h to avoid volatile chemicals especially water. Afterwards, 5 mL of TDI was added drop wise and the total solution was stirred for 6 h at 90°C under vacuum. The formed viscous solution was poured into glass petri dishes, closed, and placed into vacuum oven where they are kept for ~ 10 days at 90°C for complete curing.

Preparation of zeolite beta-PU composite membranes

The PU membranes were prepared as described earlier, except zeolite particles were added after the viscous polymer solution was poured into glass petri dishes in the form of thin films. Before incorporating into the PU, zeolite beta particles were kept in the oven at 110°C for an hour to remove the adsorbed humidity. Desired amounts were screened (0.1 or 1 wt %) using a sieve of 120-mesh to avoid larger crystals to be included into the polymer matrix and then loaded into the PU solutions. Afterwards, the mixtures were kept in the ultrasonic bath for 15 min to obtain a good dispersion. Then they were placed into vacuum oven and kept at 90°C for curing until they form solid films (~ 10 days). The preparation scheme of the zeolite beta-PU composite membranes is shown in Figure 1, and the summary of the sample codes with their compositions is given in Table I. The procedures were repeated twice for each experiment to assure the results were reproducible.

Characterization

Attenuated total reflectance-FTIR (ATR-FTIR) spectra were obtained on a Bruker IFS 66/S spectrometer equipped with a ZnSe crystal at 45° . The samples were analyzed over $500\text{--}4000\text{ cm}^{-1}$ range with the resolution of 4 cm^{-1} . All spectra were averaged over 32 scans.

SEM was used to study the morphology of the zeolite beta-PU composite membranes. Electron micrographs were obtained using a JSM-6400 Electron Microscope (JEOL). Prior to the measurement, the specimens were coated with gold. Energy dispersive X-ray spectroscopy (EDX) analysis was carried out utilizing a Phoenix EDAX X-ray analyzer equipped with sapphire super ultrathin window detector attached to the JSM-6400 SEM.

DMA measurements were carried out using a Perkin-Elmer Pyris Diamond DMA. The samples were

measured over a temperature range from -100 to 120°C at a heating rate of $5^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. An oscillation frequency of 1 Hz was applied. The storage modulus (E'), loss modulus (E''), and $\tan \delta$ values were recorded versus temperature. The T_g values of the composite membranes were obtained from the peaks of $\tan \delta$ curves.

Mechanical properties of zeolite beta-PU composite membranes were studied by Lloyd LRX 5K Mechanical Tester, controlled by a computer running program (WindapR). Zeolite beta-PU composite membranes (thickness $1.20 \pm 0.05\text{ mm}$, width: $10.0 \pm 0.05\text{ mm}$, length $40.0 \pm 0.05\text{ mm}$) were attached to the holders (gauge length: 10 mm) of the instrument. A constant extension rate of $10\text{ mm}/\text{min}$ was applied. The load deformation curve was printed for each specimen. The tensile strength was obtained from equation $\rho = F/A$, where ρ is the tensile strength (MPa), F is the maximum load applied (N) before rupture, and A is the initial area (m^2) of the

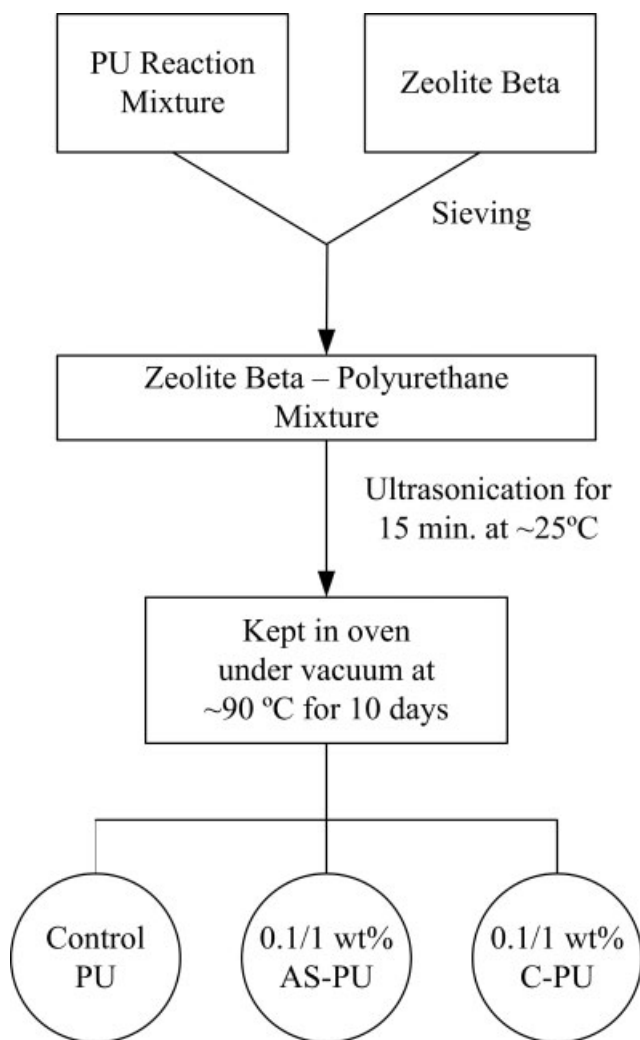


Figure 1 Preparation flowchart of the zeolite beta-polyurethane (PU) composite membranes.

TABLE I
Sample Codes and Zeolite Beta-PU Compositions

Sample code	Type and amount (wt %) of zeolite loading
Control PU	Pure PU
0.1C-PU	0.1 wt % calcined zeolite beta loaded PU composite membrane
1C-PU	1 wt % calcined zeolite beta loaded PU composite membrane
0.1AS-PU	0.1 wt % as-synthesized zeolite beta loaded PU composite membrane
1AS-PU	1 wt % as-synthesized zeolite beta loaded PU composite membrane

specimen. The load deformation curve was converted to stress-strain curve, where stress is the load applied per unit area (F/A) and strain is the deformation per unit length. Slope of straight line (elastic region of the stress-strain curve) is accepted as the Young's modulus of the specimen. For each type of sample, at least five experiments were achieved and the average values of Young's modulus, tensile strength, and percent elongation at break values were calculated.

RESULTS AND DISCUSSION

ATR-FTIR analysis

ATR-FTIR spectra of the control PU and zeolite beta-PU composite membranes are shown in Figure 2. There are two regions of interest, which are the $-\text{NH}$ absorption and $-\text{C}=\text{O}$ stretching regions as shown in Figure 2(a,b). The bands at 3300 and 1726 cm^{-1} are the two typical stretching vibrations observed for PUs.⁴ It was found that each membrane exhibited the peaks for characteristic functional groups for PU. This suggests that the incorporation of zeolite beta did not alter the chemical structure of the PU membranes.

The stretching band at 3300 cm^{-1} observed for the control PU and the composite membranes are known to be the hydrogen bonded $\text{N}-\text{H}$ stretching vibrations. The small shoulder observed at $\sim 3480\text{ cm}^{-1}$ band is due to free stretching $-\text{NH}$ groups. As shown in Figure 2(a), the intensity of the free $-\text{NH}$ groups decreased for samples 1C-PU and 0.1C-PU and disappeared for samples 1AS-PU and 0.1AS-PU upon the incorporation of zeolite beta into PU. These results suggest that $\text{N}-\text{H}$ groups in all membranes were partly and sometimes completely hydrogen bonded.¹ The band appearing at 1733 cm^{-1} is due to free urethane $\text{C}=\text{O}$ while the peak at 1726 cm^{-1} is assigned to hydrogen bonded $\text{C}=\text{O}$. The 1726 cm^{-1} band can be explained by formation of hydrogen bondings between the hydroxyl (OH) groups of zeolites with oxygen containing carbonyl ($\text{C}=\text{O}$) or

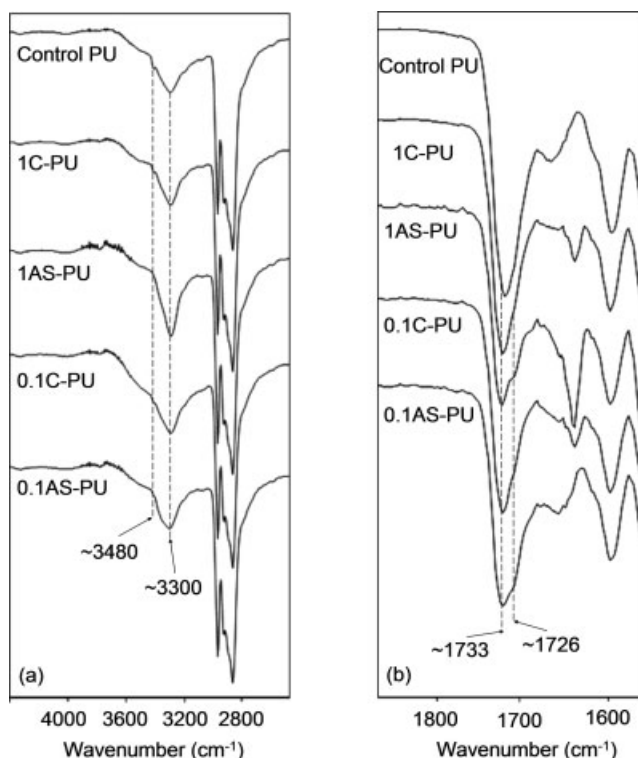


Figure 2 ATR-FTIR spectra of control PU and zeolite beta-PU composite membranes of -NH absorption (a) and -C=O stretching (b) regions.

ether (C-O-C) groups of urethanes.¹ The interaction between the zeolite and the PU can also be observed from the slight shift ($\sim 8 \text{ cm}^{-1}$) observed in the peak position of the carbonyl band of the control PU and the composite membranes represented by the 1733 cm^{-1} band [Fig. 2(b)]. However, a direct correlation cannot be made in the intensity differences among samples as a function of the loading content (0.1 wt % versus 1 wt %). The FTIR results suggest that there is a chemical interaction between zeolite beta particles and PU upon the incorporation of zeolite beta while the chemical structure of PU was maintained.

Morphology

The SEM analysis (Fig. 3) indicated that the as-synthesized zeolite beta particles were predominantly in the $1\text{--}1.5 \mu\text{m}$ size range. Calcination of the parent zeolite beta did not change the particle size and the morphology of the particles as expected. The EDX analysis showed identical Si/Al ratio ($\text{Si/Al} = 30 \pm 1$) for the as-synthesized and calcined zeolite beta samples.

The surface morphologies of composite membranes, upon 1 wt % loading of as-synthesized (AS-PU) or calcined (C-PU) zeolite beta, are presented in Figures 4 and 5, respectively. All membranes

exhibited smooth surfaces from top and bottom portions. Figure 4 shows the morphologies of the 1AS-PU composite membranes from top [Fig. 4(a)], bottom [Fig. 4(b)], and cross-sectional [Fig. 4(c)] views. These results show that the as-synthesized zeolite beta crystals were dispersed in a nonhomogeneous way in 1AS-PU membranes. This is more clearly observed from the cross-sectional view in Figure 4(c), which showed that some of the as-synthesized zeolite beta crystals precipitate and accumulate towards the bottom portion of the composite membranes. The reason for the different views between top and bottom faces is the precipitation, agglomeration of some of the as-synthesized zeolite crystals, and the fact that they were more submerged into the bottom face of the membranes creating a more spheroidal view. This was not observed for the 1C-PU composite membranes.

Figure 5 shows the SEM results of the 1C-PU composite membranes. Unlike the differences observed in the 1AS-PU [Fig. 4(a,b)], there were no differences

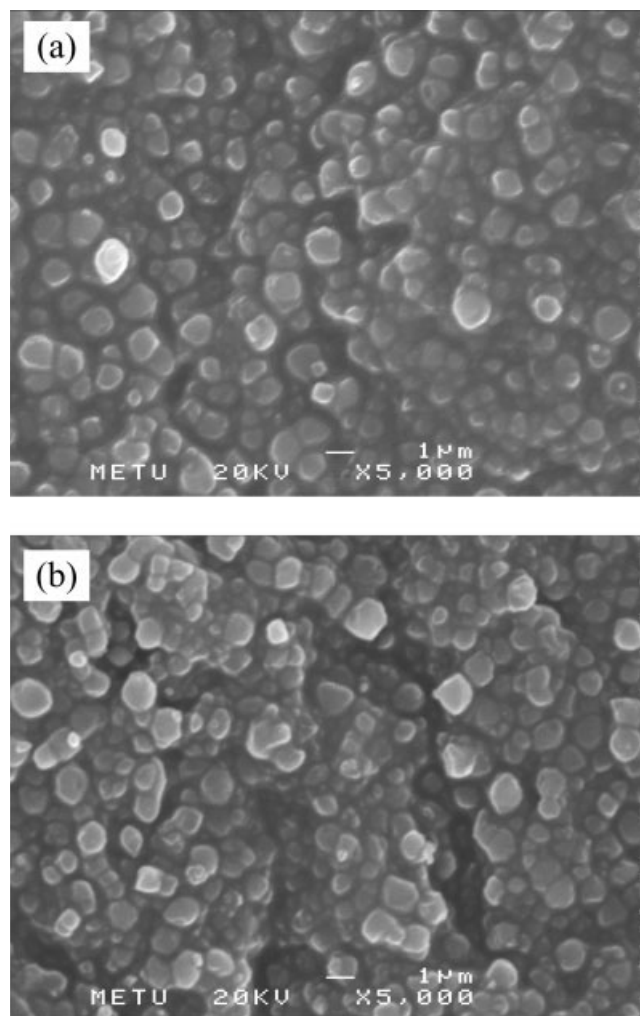


Figure 3 SEM image of as-synthesized (a) and calcined (b) zeolite beta particles.

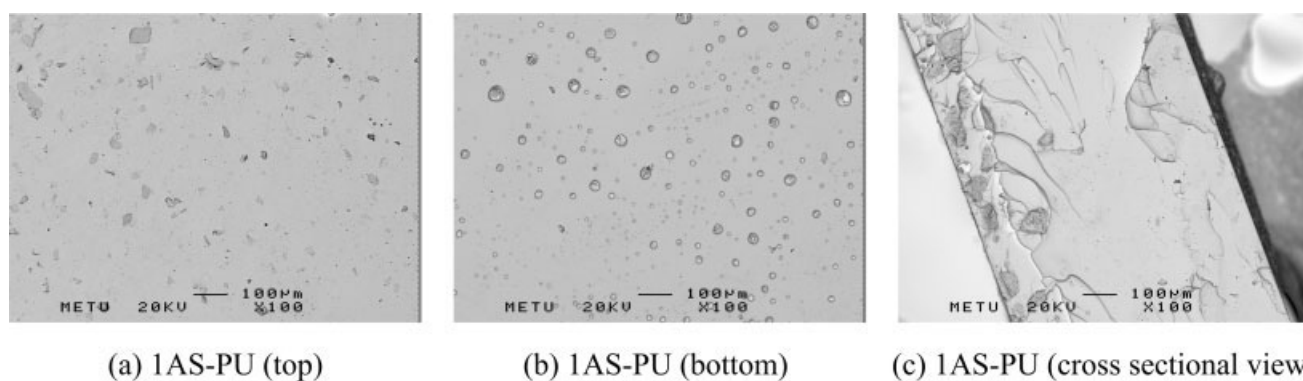


Figure 4 SEM images of 1AS-PU composite membranes.

between the top and bottom appearances of the 1C-PU composite membranes as shown in Figure 5(a,b). These results suggest that the dispersion of the zeolite crystals upon calcination was more homogene-

ous in between the top and bottom layers of the membrane with almost no accumulation and precipitation of particles. Homogeneous dispersion can also be seen from the cross-sectional views given in

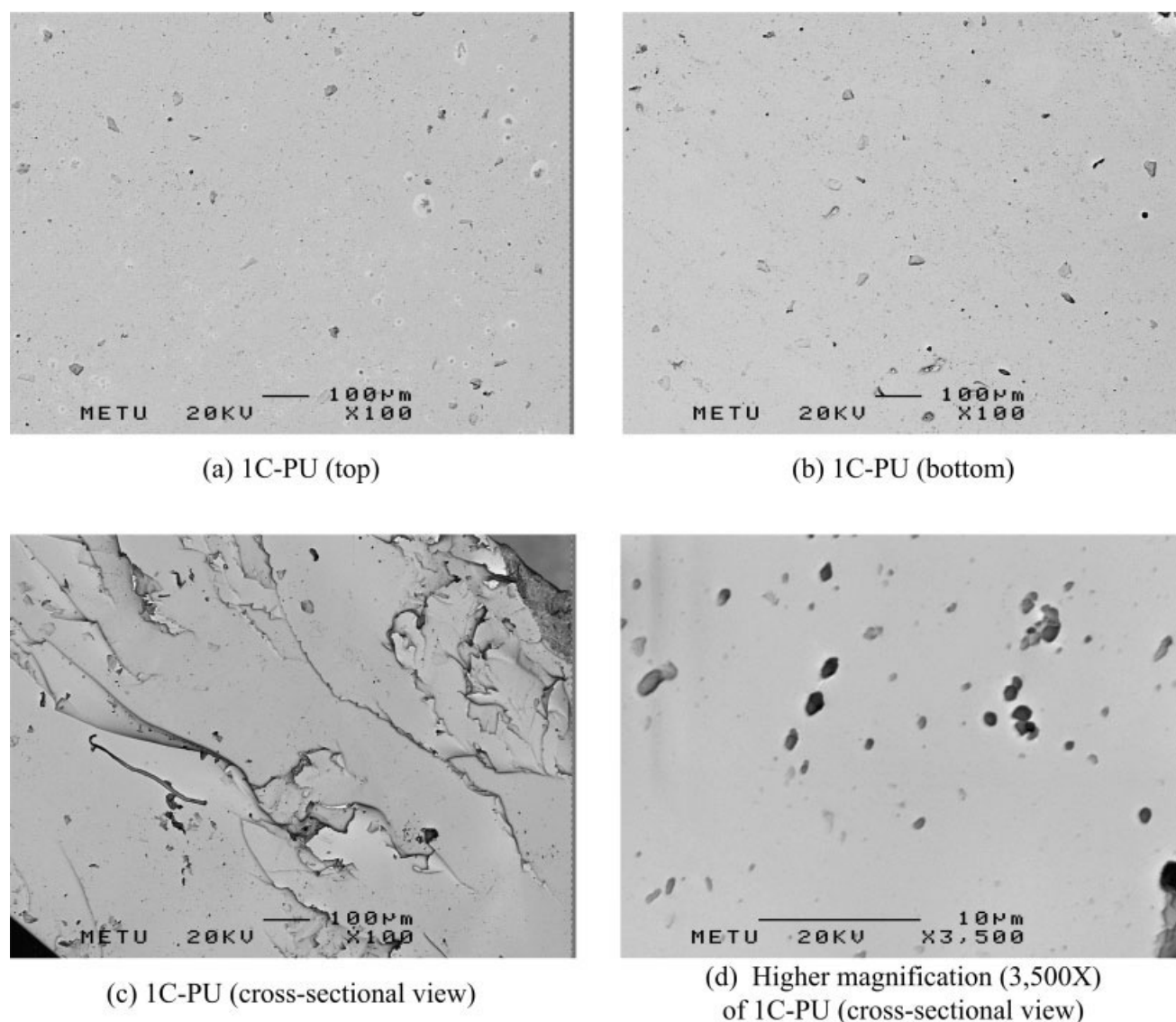


Figure 5 SEM images of 1C-PU composite membranes.

Figure 5(c,d). Thus, it was observed that agglomeration of the calcined zeolite beta crystals were significantly less in the 1C-PU composite membranes than that of the 1AS-PU composite membranes.

The lower loading content of 0.1 wt % seemed to result in somewhat less precipitation of the as-synthesized zeolite beta crystals in 0.1AS-PU composite membrane. For 0.1C-PU composite membranes, where calcined zeolite beta crystals were loaded, the result was a more homogeneous dispersion and almost no precipitation of the zeolite crystals (not shown). The loading content seemed to be more important in the as-synthesized zeolite beta-PU composite membranes to obtain a more homogeneous structure. These results further suggest that if as-synthesized zeolite beta crystals are required for any particular purpose, a low amount of zeolite beta loading should be more desirable.

Dynamic mechanical behaviors

DMA was carried out to determine the changes in the dynamic properties ($\tan \delta$, storage modulus E' , and loss modulus E'') of the PU membranes upon the incorporation of as-synthesized or calcined zeolite beta at two different loadings. All materials were observed to exhibit a typical elastomeric polymer behavior with respect to the E' versus temperature curves (Figs. 6 and 7). The glassy state is observed at low temperatures (approximately -100°C) where the E' stays at a high modulus plateau and a rubbery plateau is reached with a lower E' at a temperature range of approximately 10 – 120°C .

Figure 6 compares the elastic behaviors (storage modulus, E') of the control PU membranes with the 0.1AS-PU and 0.1C-PU composite membranes as a function of temperature. According to Figure 6, no

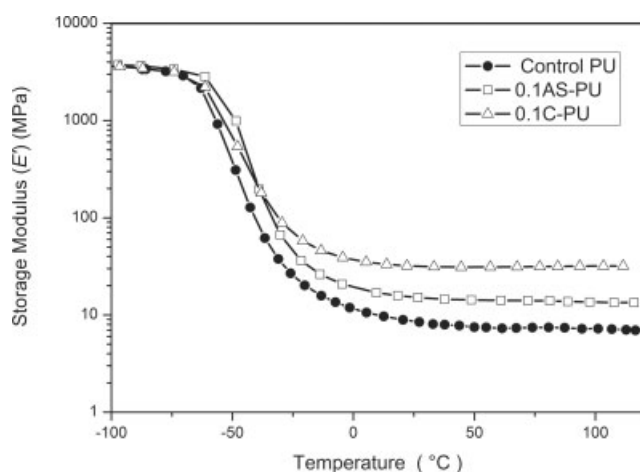


Figure 6 Logarithm of storage modulus (E') versus temperature curves for 0.1AS-PU and 0.1C-PU.

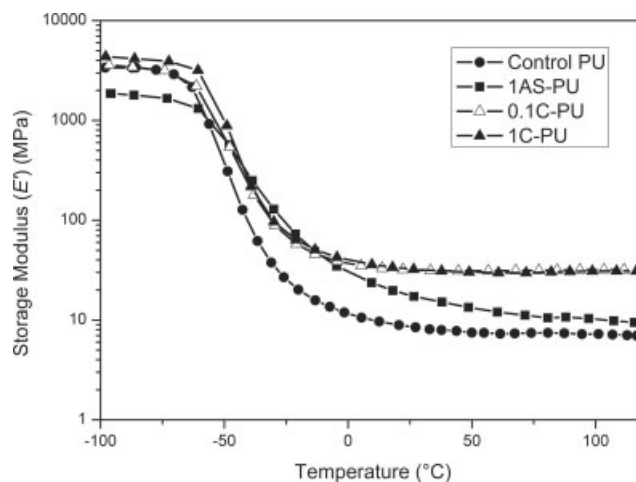


Figure 7 Logarithm of storage modulus (E') versus temperature curves for 1AS-PU, 1C-PU, and 0.1C-PU.

significant increase in E' upon incorporation of 0.1 wt % zeolite beta was observed in the glassy state and it was found to be 3740 MPa. On the other hand, in the rubbery plateau region the incorporation of 0.1 wt % zeolite beta lead to a significant increase in the E' of the composite membranes with respect to the control PU. Among the three samples, it was also seen that the 0.1C-PU exhibited the highest values for E' (31 MPa) followed by the 0.1AS-PU (15 MPa) and control PU (8 MPa) in the rubbery plateau region of the curves.

E' is known to be a measure of the material stiffness.²⁶ Accordingly, the effect of inorganic reinforcement was higher upon the incorporation of the calcined zeolite beta with respect to its as-synthesized form in the rubbery state. Furthermore, the existence of a region in the rubbery state where the storage modulus remains constant (i.e., 31, 15, and 8 MPa for 0.1C-PU, 0.1AS-PU, and control PU, respectively) indicates that a stable elastomeric network existed not only in the control PU membranes but also in the 0.1 wt % zeolite incorporated PU composite membranes.

Figure 7 compares E' among 1AS-PU, 1C-PU, and the control PU at a higher loading content (1 wt %) as a function of temperature. The same control plots were used in Figures 6 and 7. It can be seen that the incorporation of 1 wt % of all zeolite beta samples lead to an increase of the E' in the rubbery state with respect to the control PU membrane. Similar to what was observed upon the incorporation of 0.1 wt % zeolite beta samples (Fig. 6), the incorporation of 1 wt % calcined zeolite beta (1C-PU) also possessed the maximum E' (32 MPa) in the rubbery plateau region. In the glassy region, the 1 wt % calcined zeolite beta (1C-PU) incorporated composite membranes lead to the maximum E' as 4365 MPa (Fig. 7), in con-

trary to the identical elastic moduli observed among different composite membranes with 0.1 wt % zeolite beta incorporation (Fig. 6). Furthermore, the E' of the 1AS-PU composite membrane in the glassy region was observed to be 1861 MPa, which was lower than the control PU (3740 MPa) and the 1C-PU (4365 MPa) membranes, indicating a lower stiffness. The observed decrease in the E' of the 1AS-PU composite in the glassy region can be due to a decrease in the density of the material. The decreased densities can be attributed to an increased external porosity, which can be interpreted as the increase in the free volume of the composites caused by a decreased interaction between the polymer and the zeolite as a result of a higher loading content. It seems that the incorporation of calcined zeolite beta leads to a more elastic and stiffer composite material once they are integrated into the PU membranes. Furthermore, the membranes formed by adding the calcined zeolite beta were observed to form a more homogeneous (well dispersed) composite membrane. These results are in agreement with the observed morphologies of the composite membranes by SEM (Figs. 4 and 5).

As shown in Figure 7, the decline of the E' curve for the 1AS-PU sample did not reach a constant and stable value ($T > 0^\circ\text{C}$) upon increasing the filler content to 1 wt %. E' decreased from 24 to 9.5 MPa as the temperature varied from 10 to 120°C . This shows that the 1AS-PU did not show an ideal elastomeric behavior as was the case for a loading content of 0.1 wt % (Fig. 6, 0.1AS-PU). The fact that such a behavior was not observed at low loading content implies that there might be an upper limit to the amount of filler that can be used and the desired elastic properties of polymers are still maintained. If the weight percent of filler is too high in reinforced composites, there may not be enough polymer matrix to hold the composite together. On the other hand, calcined zeolite beta-PU composite membranes showed stable behaviors in both glassy (~ 4365 and 3740 MPa for 1C-PU and 0.1C-PU, respectively) and rubbery (~ 32 MPa) states at the loadings that were studied. In the current study, the unstable behavior of 1AS-PU as a function of temperature can be a result of the ongoing process of the removal of the template from the zeolite structure with an increase in the temperature. On the other hand, the calcined zeolite beta incorporated PU composite membranes showed a more significant stability, which again is a result of the fact that the zeolite was calcined at 500°C before it was incorporated into the polymer (precalcination), and thus has a more stable structure. Furthermore, an increase in the filler content from 0.1 to 1 wt % did not seem to make a significant difference in the storage moduli of the C-PU composite membranes and it was found to be 32 MPa in the rubbery region as shown in Figure 7. This may also

be a result of precalcination, where the zeolite beta-PU network was better formed with a more uniform dispersion, and thus the polymer could bear a higher loading of the calcined zeolite beta.

Calcination at high temperatures (e.g., 500°C) removes the template molecules from the pores of the zeolite. Furthermore, an enhanced thermal stability, and increased hydrophobicity are known to be among the major reasons for considering calcination of zeolites. Increased hydrophobicity is usually related with the lowered number of Brønsted and increased number of Lewis sites. This trend in the decrease and increase in the Brønsted (tetrahedral Al sites) and Lewis sites (distorted Al sites), respectively, upon calcination were shown in our previous studies.¹⁵ The polymer used in the current study, PU, is not only hydrophilic but also has hydrophobic properties. For the organic-inorganic segments to be compatible, the added inorganic material should match the organic segment of the composite. Hydrophilic particles and hydrophobic polymers are not compatible, which results in poor interfacial bonding. Usually organic modifiers are used to impart hydrophobicity of the inorganic material in such cases.²⁷ Zeolites also possess both hydrophilic and hydrophobic properties, which can be controlled by changing the Si/Al ratio or by calcining the zeolite crystals. In the current study, it was observed that calcination lead to a better match and miscibility between the organic-inorganic composites forming more homogeneously dispersed crystals within the polymer matrix. The reasons for this can be the better compatibility of the hydrophilic/hydrophobic properties of zeolite particles and PU upon calcination of zeolite particles, which results in less agglomeration and better dispersion of calcined zeolite particles within the polymer matrix.

Table II summarizes the E' at 25°C of the control PU and the zeolite beta incorporated composite membranes. Table II and Figures 6 and 7 show that the composite membranes lead to the highest stiffness and elasticity with the highest E' upon incorporation of calcined zeolite beta when compared with AS-PU and control PU membranes in the rubbery

TABLE II
Dynamic Mechanical Properties of Control PU and Zeolite Beta-PU Composite Membranes

Name	T_g ($^\circ\text{C}$)	E' (MPa) at 25°C	Normalized $\tan \delta$ values
Control PU	-43	8 ± 0.3	1.00 ± 0.1
0.1AS-PU	-40	15 ± 0.3	0.95 ± 0.1
1AS-PU	-44	16 ± 1.2	0.57 ± 0.1
0.1C-PU	-44	31 ± 0.3	0.77 ± 0.1
1C-PU	-44	32 ± 0.3	0.75 ± 0.1

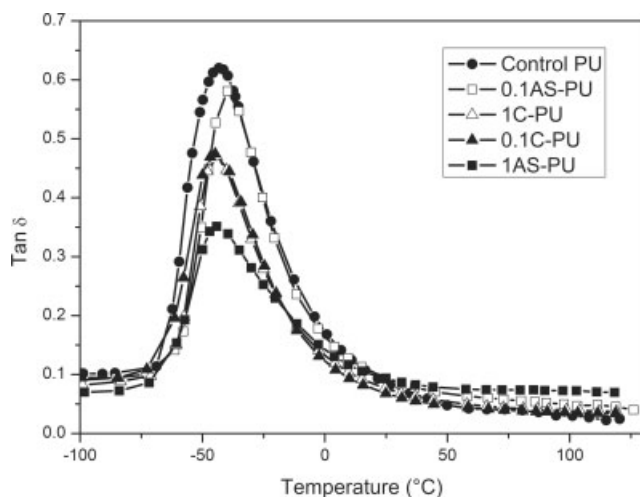


Figure 8 $\tan \delta$ versus temperature curves for 0.1AS-PU, 1AS-PU, 0.1C-PU, and 1C-PU.

state and particularly around room temperature. It was found that as-synthesized zeolite beta incorporation resulted in a twofold, while calcined zeolite beta incorporation resulted in a fourfold increase in the E' of the control PU. Thus, in the current study, it was found that calcination had a major influence on the dispersion, stiffness, mechanical stability, and the elastomeric behavior of the zeolite beta-PU composite membranes with respect to the AS-PU and control PU membranes.

The fact that larger agglomerates were formed in the as-synthesized zeolite incorporated composites may or may not affect the mechanical properties of the composites. It was found that the mechanical and viscoelastic properties of the polymer composites are particle size independent; however, contradictions do exist in the literature for submicron crystals.²⁸ In the current study, the aim is not to study the effect of particle size on the mechanical properties; however, it can be speculated that it did not have a significant effect for the samples prepared in this study. First of all, the zeolite crystals used were in the micron range. Furthermore, the formation of agglomerates was found to strongly increase the modulus of the composites, especially at low frequencies.²⁸ This was the case in the current study (1 Hz) and the calcined zeolite incorporated composites still exhibits higher modulus. Thus, it is believed that the results observed are not solely due to less agglomeration of calcined particles in the polymer matrix, but due to better compatibility of the organic polymer-inorganic calcined zeolite particles.

Figure 8 compares the changes in the $\tan \delta$ curves of the composite membranes prepared with incorporation of calcined or as-synthesized zeolite beta at high (1 wt %) and low (0.1 wt %) loadings as a function of temperature. The temperature corresponding

to the maximum of $\tan \delta$ curve is considered as the glass transition temperature (T_g). As shown in Figure 8, only one major α relaxation (single T_g) is observed in each composite membrane indicating a single homogeneous phase. T_g and the relative differences in the normalized $\tan \delta$ values of the control PU and the composite PU membranes are summarized in Table II.

According to Figure 8 and Table II, the control PU exhibits a well-defined relaxation peak centered at -43°C , which is ascribed to the T_g of the PU. 0.1AS-PU showed a slight shift in T_g to a higher value of -40°C . This indicates that low concentrations of as-synthesized zeolite beta restricted the segmental motion of PU chains. With an increase in the loading content of as-synthesized zeolite beta in the PU (1AS-PU), a decrease in the T_g from -40 to -44°C was observed. Such a change in the T_g as a function of loading content was not observed for the C-PU composite membranes. The final T_g values for 0.1C-PU, 1C-PU, and 1AS-PU composite membranes are not significantly different from the control PU as shown in Table II. However, the fact that an initial increase followed by a decrease in the T_g of the AS-PU composite membranes can be an indication of the formation of an inhomogeneous composite structure (i.e., agglomeration of zeolite particles within the membrane). Another reason may be the presence of organic templating agent in the overall structure of the composite membrane, which may become more significant at higher loading of 1 wt %. A decreasing T_g was observed by other researchers as a function of temperature and was suggested that the modification agent used in the nano-silica particles were acting as softeners in the macromolecular chains of the polymers.⁵ The fact that the similar T_g values for 1C-PU and 0.1C-PU composite membranes with the control PU, indicates that the addition of calcined zeolite beta in the corresponding amounts to the PU membranes did not have a significant role in the motion of the macromolecular chains in these particular cases. In general, the low T_g values ($<0^\circ\text{C}$) are more favorable with respect to the ones with higher T_g if elastomeric behavior is desired at room temperatures for any specific purposes.⁶

The relative heights of the $\tan \delta$, ratios of loss modulus (E'') to storage modulus (E'), are known to be an indicator of capability of energy dissipation within the microstructures.⁵ According to Figure 8 and Table II, $\tan \delta$ intensities of the composite membranes showed a decrease in the peak heights, which suggests lower dissipation of energy as heat with the incorporation of zeolite beta into the PU. These results suggest a higher mechanical stability against the degradation of the zeolite beta-PU composite membranes. Furthermore, the $\tan \delta$ intensities were essentially the same for the 0.1C-PU and 1C-PU

TABLE III
Mechanical Properties of Control PU and Zeolite
Beta-PU Composite Membranes

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Control PU	5	1.9	68.8
0.1AS-PU	8	2.3	87.1
1AS-PU	8.1	2.5	75.13
0.1C-PU	13.9	4.7	148.5
1C-PU	12.1	4.1	137.1

composite membranes (~ 0.75), while the $\tan \delta$ intensity decreased from 0.95 to 0.57 when the loading content was increased from 0.1 to 1 wt % for the AS-PU composite membranes. Thus, the loading content did not have a significant effect on the $\tan \delta$ intensities of the C-PU composite membranes as it did for the AS-PU composite membranes.

Mechanical properties

Mechanical properties of zeolite beta-PU composites membranes are shown in Table III. The composite membranes showed higher Young's modulus, tensile strength, and elongation at break in comparison with the control PU sample. For 0.1C-PU samples, these values demonstrated a change from 5 to 13.9 MPa, from 1.9 to 4.7 MPa, and from 68.8% to 148.5%, respectively. Among all membranes, calcined zeolite-PU composites showed the highest mechanical properties and this is most probably due to better dispersion of these particles in the polymer matrix.

Mechanical improvements of the composites in general can be due to the nature of zeolites that already possess OH groups in their nature. There are various studies with montmorillonite where surface modifications were made to increase the number of surface OH groups to achieve better dispersion in PUs.²⁹ It is well known that H-bond formation among urethane groups greatly contributes to the strength and modulus of PU's. This interaction can form between —NCO groups of PU and especially the —OH groups of calcined zeolite leading to a better interaction between these two components. These results in general are in agreement with the dynamic mechanical behaviors, SEM, and ATR-FTIR results that again suggest that calcination had a major influence on the dispersion and mechanical properties of the composite membranes.²⁹

CONCLUSIONS

In this work, zeolite beta-PU composite membranes were prepared and investigated. The effect of incor-

poration of as-synthesized (AS) and calcined (C) zeolite beta into PU was studied at two different loadings. In general, the incorporation of zeolite beta into the PU improved the mechanical properties of the PU against deformation, which was more significantly observed for the calcined zeolite beta crystals. The C-PU composite membranes lead to the highest stiffness, elasticity with a highest E' , tensile strength, and elongation at break when compared with AS-PU and control PU membranes in the rubbery state. The mechanical properties of the C-PU were also maintained at a higher loading content. However, if as-synthesized zeolite beta is desired to be used for any particular purpose, higher loading contents may not be practical, since there may be an upper limit to the amount of filler that can be used while the properties of the polymer are still maintained. Taken together, these results suggest that the mechanical properties of the PU was changed and improved upon the incorporation of zeolite beta without altering the chemical structure of the PU membranes. The incorporation of the calcined zeolite beta lead to more homogeneous, well dispersed, stiffer, and mechanically stronger composite membranes. Further studies on PU composite membranes using modified zeolite beta crystals for desired purposes are currently under investigation.

References

- Chen, T. K.; Tien, Y. I.; Wei, K. H. *Polymer* 2000, 41, 1345.
- Ma, X.; Lu, H.; Lian, G.; Zhao, J.; Lu, T. *J Appl Polym Sci* 2005, 96, 1165.
- Gall, K.; Dunn, M. L.; Liu, Y.; Finch, D.; Lake, M.; Munshi, N. A. *Acta Mater* 2002, 50, 5115.
- Liu, H.; Zheng, S. *Macromol Rapid Commun* 2005, 26, 196.
- Chuang, T. H.; Yang, T. C. K.; Chang, A. H. *Int J Polym Mater* 2004, 53, 465.
- Xu, J.; Shi, W.; Pang, W. *Polymer* 2006, 47, 457.
- Petrovic, Z. S.; Javni, I.; Waddon, A.; Banhegyi, G. *J Appl Polym Sci* 2000, 76, 133.
- Chen, Y.; Shuxue, Z.; Yang, H.; Gu, G.; Wu, L. *J Colloid Interface Sci* 2004, 279, 370.
- Wang, H.; Holmberg, B. A.; Yan, Y. *J Mater Chem* 2002, 12, 3640.
- Zimmerman, C. M.; Singh, A.; Koros, W. J. *J Membr Sci* 1997, 137, 145.
- Suer, M. G.; Bac, N.; Yilmaz, L. *J Membr Sci* 1994, 91, 77.
- Berry, M. B.; Libby, B. E.; Rose, K.; Haas, K. E. *Microporous Mesoporous Mater* 2000, 39, 205.
- Jia, M.; Peinemann, K. V.; Behling, R. D. *J Membr Sci* 1992, 73, 119.
- Akata, B.; Yilmaz, B.; Jiranpongphan, S. S.; Warzywoda, J.; Sacco, A., Jr. *Microporous Mesoporous Mater* 2004, 71, 1.
- Akata, B.; Warzywoda, J.; Sacco, A., Jr. *J Catal* 2004, 222, 397.
- Van Bokhoven, J. A.; Koningsberger, D. C.; Kunkeler, P.; van Bekkum, H.; Kentgens, A. P. M. *J Am Chem Soc* 2000, 122, 12842.
- Bourgeat-Lami, E.; Massiani, P.; Di Renzo, F.; Espiau, P.; Fajula, F. *J Appl Catal* 1991, 72, 139.

18. Burke, A.; Hasirci, N. In *Biomaterials: From Molecules to Engineered Tissues*; Hasirci, N.; Hasirci, V., Eds.; Kluwer Academic/Plenum: New York, 2004; p 83.
19. Hasirci, N.; In *Polyurethanes: High Performance Biomaterials*; Szycher, M., Ed.; Technomic: Lancaster, 1991; p 71.
20. Yang, C.; Xu, Q. *Zeolites* 1997, 19, 404.
21. Kiricsi, I.; Flego, C.; Pazzuconi, G.; Parker, W. O., Jr.; Millini, R.; Perego, C.; Belussi, G. *J Phys Chem* 1994, 98, 4627.
22. Marques, J. P.; Gener, I.; Ayrault, P.; Bordado, J. C.; Lopes, J. M.; Ribeiro, F. R.; Guisnet, M. *Microporous Mesoporous Mater* 2003, 60, 251.
23. Ozdemir, Y.; Serbetci, K.; Hasirci, N. *J Mater Sci Mater Med* 2002, 13, 1147.
24. Ulubayram, K.; Hasirci, N. *Colloids Surf B* 1993, 1, 261.
25. Ulubayram, K.; Hasirci, N. *Polymer* 1992, 33, 2084.
26. Crawford, D. M.; Escarsega, J. A. *Thermochim Acta* 2000, 161, 357.
27. Zhou, H. J.; Rong, M. Z.; Zhang, M. Q. Friedrich, K. *J Mater Sci* 2006, 41, 5767.
28. Osman, M. A.; Atallah, A. *Polymer* 2006, 47, 2357.
29. Cao, X.; Lee, L. J.; Widya, T.; Macosko, C. *Polymer* 2005, 46, 775.