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New Biomedical Poly(urethane urea)–Layered Silicate Nanocomposites

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Introduction

Poly(urethane urea) segmented block copolymers [PUU] are used in a variety of biomedical applications,¹ most prominently as blood sacs in ventricular assist devices and total artificial hearts. However, one of the principal drawbacks of these elastomers (particularly when used in completely implantable devices) is their relatively high permeability to air and water vapor. Conventional biomedical PUUs are comprised of ca. 80 wt % poly(tetramethylene oxide) [PTMO] soft segments, and it is the penetrant diffusion through this continuous polyether soft phase that gives rise to the high permeability. Several chemical approaches have been taken in an attempt to reduce PUU permeability, while maintaining the desirable biocompatibility and mechanical properties. One such approach has been to replace the PTMO with aliphatic polycarbonate soft segments.² Alternatively, we recently described the synthesis and characterization of a series of polymers that have backbones chemically identical to the multiblock PUU, but which also possess polymeric combs of a material with superior barrier properties.³ Polyisobutylene (PIB) was chosen as the comb material due to the combination of its good barrier properties and its controllable (living cationic) polymerization. PIB incorporation varied between 2 and 30 wt %, with comb lengths ranging from ~3000 to 29 000 g/mol. Water vapor and oxygen permeability were reduced by about a factor of 2 at the highest PIB contents,⁴ in line with what is expected from models assuming dispersed, spherical PIB microphases.⁵ The lack of precise control of the morphology of the PIB domains of these comb polymers limits further significant improvement in the permeability.

In the past 5 years there has been intense interest in dispersing organically modified layered silicates (OMS) in polymers, particularly as mechanical reinforcement at low silicate loading levels.^{6–8} As a result of their high aspect ratio (often approaching 1000), the introduction of intercalated or exfoliated OMS inorganic layers in the polymer matrix can dramatically enhance the barrier properties at very low concentrations.^{9–11} In a natural

extension of our earlier work on polyether-based PUUs, we have applied this nanocomposite approach to biomedical poly(urethane urea)s. In this note we describe our initial experiments on polymer/inorganic hybrids based on a generic PUU and an alkylammonium-modified montmorillonite, a biocompatible layered filler frequently used in cosmetics, food supplements, and stomach acid-reducing medicines.

Experimental Section

Materials and Composite Preparation. The poly(urethane urea) used in this study was synthesized using a procedure described in a previous publication.¹² The composition was chosen to be similar to that of PUUs used in biomedical applications. The copolymer was synthesized via a two-step condensation reaction in *N,N*-dimethylacetamide (DMAc). It was prepared using 2000 g/mol poly(tetramethylene oxide) (PTMO), end-capped with 4,4'-methylene di(*p*-phenyl isocyanate) (MDI) and chain-extended by a mixture of ethylenediamine (EDA) and 1,4-diaminocyclohexane, DACH (EDA:DACH = 75:25 by mole). All of the above were purchased from Aldrich Chemical, Co. The hard segment concentration of the final copolymer was ~22 wt % (by reaction stoichiometry), assuming all MDI and EDA contribute to the hard segments. The weight-average molecular weight was determined by gel permeation chromatography (using dimethylformamide/0.05 M lithium bromide as the mobile phase) to be 40 600 g/mol ($PDI \sim 2.1$), relative to poly(ethylene oxide) standards.

The OMS used in our experiments was Cloisette 15A (Southern Clay Products, TX). This material was prepared by the supplier through ion-exchanging Na^+ montmorillonite (with a reported cation exchange capacity of 0.95 mequiv/g) with dimethyl ditallow ammonium. The tallow used was composed of ca. 65% C_{18} , 30% C_{16} , and 5% C_{14} units and is introduced in excess of the CEC to approximately 1.25 mequiv/g.

A 3 wt % transparent solution of the OMS in toluene was prepared,¹³ then added dropwise to a 3 wt % solution of the PUU in DMAc, and stirred for 3 h at 80 °C. The mixture was then stirred overnight at room temperature. The solution was degassed, and then films were cast onto round glass Petri dishes. The films were air-dried for 24 h and subsequently dried under vacuum at 50 °C for 24 h. Composites containing final concentrations of 1, 3, 7, 13, and 20 wt % OMS were prepared. Assuming that the hydrocarbon surfactant and neat silicate have densities of 0.8 and 2.5 g/cm³, respectively, these OMS weight fractions correspond to 0.3, 0.8, 2.0, 3.8, and 5.9 vol % inorganic layered silicate.

Characterization. X-ray diffraction experiments were performed on film samples on a Rigaku X-ray diffractometer operating in a θ – θ geometry using $Cu\ K\alpha$ ($\lambda = 0.154\text{ nm}$) radiation. Samples were scanned at a rate of 1 deg/min from ca. 2° to 40° in 2θ .

Evaluation of the mechanical properties was carried out on a table model Instron tensile testing machine on specimens cut with a microtensile die (ASTM D1708-93). A crosshead speed of 100 mm/min was used for all experiments. Ultimate strength (σ_b) and elongation (ϵ_b) as well as the modulus at 50% extension (E_{50}) were determined from five specimens taken from each of the composites.

Water vapor permeability of the nanocomposite films was determined at 27 °C according to ASTM E96-95, for film in

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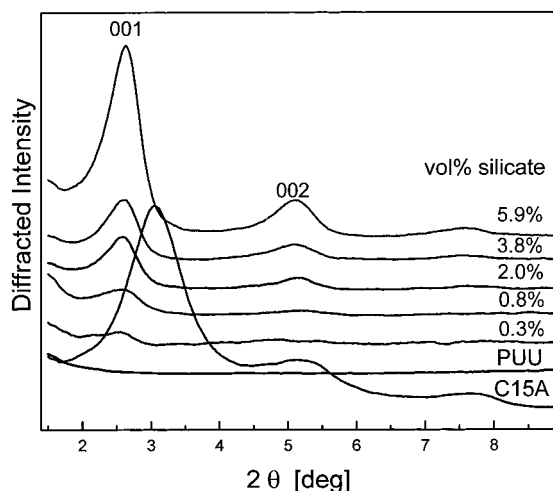


Figure 1. X-ray diffraction patterns of the neat poly(urethane urea), the neat OMS, and selected PUU–OMS nanocomposites.

thicknesses on the order of 0.25 mm. Dry films were sealed to the open mouths of test bottles containing desiccant (anhydrous calcium sulfate) and placed in a chamber controlled at 90% relative humidity. Periodic weighings of the assembly allow for the water vapor transmission rate determination, from which the permeability is calculated.

Results and Discussion

The X-ray diffraction patterns of the OMS, the neat PUU, and selected composites are presented in Figure 1. The neat PUU exhibits an amorphous halo at $20^\circ 2\theta$ and is found at the same location for all of the composites (not shown in Figure 1). The gallery spacing (d_{001}) of the alkyl-modified silicate is 2.9 nm. This increases to about 3.4–3.5 nm for all of the composites. These results clearly indicate that some of the PUU chains are intercalated between the silicate layers, which readopt a parallel registry.

Relative to the surfactant used (i.e., aliphatic), our PUU chains have very strong favorable enthalpic interactions with the silicate surface, through polar and hydrogen-bonding interactions. This enthalpic gain apparently prevails over the loss of conformational entropy, which the PUU macromolecules experience when confined in the 2.5 nm galleries, and leads to the formation of intercalated nanocomposites.¹⁴ Considering the presence of strong specific interactions between the intercalated chains and the silicate surfaces, casting from solution at very low inorganic concentrations can result in layer exfoliation. This inorganic delamination originates from the kinetic trapping of layers by the polymer, as is the case with other hydrogen-bonding polymers,¹¹ or polymers with strong intermolecular interactions.¹⁵

Tensile force–extension curves measured for the neat PUU and several nanocomposite films are presented in Figure 2, and the average mechanical properties are summarized in Table 1. The nanodispersed silicates result in a significant increase in modulus and strength: e.g., for the 20 wt % composite, by more than 300% and 30%, respectively. However, in contrast to conventional filled polymer systems, the increase in strength and stiffness does not come at the expense of the ductility. In fact, the elongation to break of the 20 wt % nanocomposite increases by 50% over that of the neat PUU. There has been some speculation about the

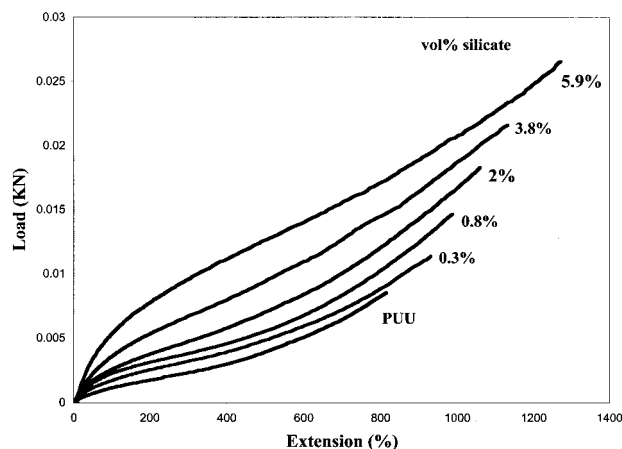


Figure 2. Representative force–extension curves for the neat PUU and the nanocomposites.

Table 1. Mechanical Properties of PUU and PUU/Layered Silicate Nanocomposites

composite (wt % modified silicate)	modulus E_{50} (MPa)	tensile strength (MPa)	elongation to break (%)
neat PUU	3.38 ± 0.21	27.4 ± 2.9	800 ± 50
1 wt %	3.93 ± 0.34	31.4 ± 2.3	890 ± 60
3 wt %	4.34 ± 0.48	31.4 ± 3.2	950 ± 40
7 wt %	4.96 ± 0.34	32.1 ± 1.4	1040 ± 60
13 wt %	8.83 ± 0.48	34.8 ± 1.9	1150 ± 50
20 wt %	11.51 ± 0.55	37.4 ± 1.7	1230 ± 70

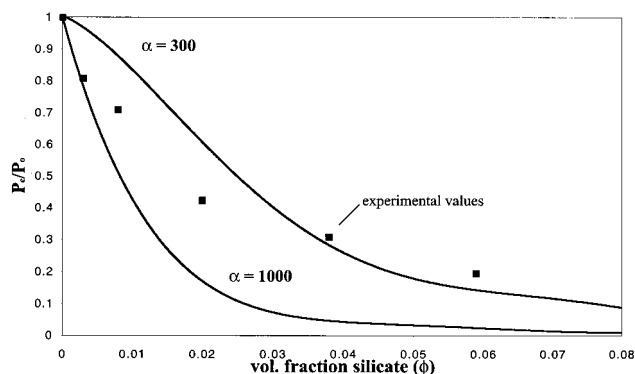


Figure 3. Relative water vapor permeability for the nanocomposites. The nanocomposite formation results in a dramatic decrease in water vapor transmission through the PUU membrane. The solid lines represent the predictions from eq 1 for aspect ratios = 300 and 1000. A comparison between the experimental measurements and the theoretical model predictions suggests a gradual change in the effective aspect ratio of the filler. This suggests a change from high aspect ratio exfoliated layers to lower α intercalated multilayer stacks.

origin of similar behavior in other nanocomposites,^{8,16,17} but a clear picture of the micromechanics of the silicate–polymer “interaction” that leads to this remarkable behavior has not yet emerged.

The water vapor permeabilities for the PUU–OMS nanocomposites are presented in Figure 3 in terms of P_c/P_0 , i.e., the permeability of the composite (P_c) relative to that of the neat PUU (P_0). Even in these nonoptimized materials, there is a strong reduction in permeability: reaching 5-fold at the highest silicate content. This is a consequence of the more tortuous path required for gas molecules to penetrate the membrane, and the magnitude of the reduction is considerably larger than what is observed upon typical chemical modification.³ The solid lines in Figure 3 represent predictions for the permeability through the thickness of a composite film

that has dispersed (impenetrable), completely oriented filler layers. In the dilute and semidilute regime^{18,19}

$$P_C/P_0 = (1 + \mu\alpha^2\phi^2)^{-1} \quad (1)$$

where α is the particle aspect ratio, ϕ the silicate volume fraction, and μ a "geometric factor",¹⁹ $\mu = \pi^2/16 \ln^2 \alpha$. Note that at the highest volume fractions the relative permeabilities are better fit with smaller particle aspect ratios, consistent with greater layer aggregation at higher OMS loadings.

In summary, we describe a novel nanocomposite approach for biomedical poly(urethane ureas) that results in a significant reduction in gas permeability, with a simultaneous improvement in mechanical properties. These concurrent property enhancements are well beyond what can be generally be achieved through painstaking chemical modification of PUU polymers.

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