MODIFIED BIOMEDICAL POLY(URETHANE) BLOCK COPOLYMERS: NANOCOMPOSITES AND POLYISOBUTYLENE COMB POLYMERS

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Introduction

Poly(urethane urea) multiblock copolymers [PUU] are used in variety of biomedical applications, including as blood-contacting components in ventricular assist systems. One of the drawbacks of these materials (particularly when used in completely implantable devices) is their relatively high permeability to air and moisture. Conventional biomedical PUU elastomers are generally composed of ~80 wt% soft segment, most often poly(tetramethylene oxide) [PTMO]. It is penetrant diffusion through the continuous, low T_g polyether phase that gives rise to the high permeability.

One approach to resolving this problem is to synthesize a polymer architecture that has backbone chemistry nearly identical to a typical biomedical PUU, and possesses polymeric combs of a material with superior barrier properties.[1] The PUU backbone would render the comb polymer 'compatible' with existing PUU multiblock copolymers, while the combs, which are anticipated to microphase separate, would be expected to reduce the transport of air and water vapor. Polyisobutylene (PIB) was chosen for the combs due to the combination of its good barrier properties and its controllable (living cationic) polymerization.

A second approach involves dispersing organically-modified layered silicates (OMS) in typical biomedical PUUs.[2] As a result of their high aspect ratio, the introduction of modest amounts of intercalated or exfoliated OMS inorganic layers in PUUs can dramatically enhance the barrier properties. We describe our initial experiments on polymer/inorganic hybrids based on a PUU having a composition comparable to typical biomedical PUUs and an alkyl-ammonium modified montmorillonite, a biocompatible layered silicate frequently used in cosmetics and food supplements.

Experimental

Amphiphilic PUU – PIB Comb Polymers[1]

A series of unique, relatively narrow molecular weight distribution PIB macromonomers were synthesized containing two hydroxyl sites on the initiating ends of the molecules using pseudo-living cationic polymerization. Characterization of the macromonomers (and their precursors) was accomplished using GPC, ^{1}H NMR, and FTIR. Amphiphilic comb polymers were synthesized via a condensation reaction from methylene bis(phenyl isocyanate), ethylene diamine, Terathane (a 2,000 g/mol telechelic poly(tetramethylene oxide) [PTMO] diol) and the desired dihydroxyl-polyisobutylene. This reaction resulted in a polyurethaneurea - polyether multiblock backbone and polyisobutylene combs. PIB incorporation ranged from ~3 – 33 wt% (as determined by CPMAS and TOSS-CPMAS ^{13}C NMR), with comb lengths ranging from ~3,000 to 29,000 g/mole. The hard segment concentrations of all copolymers were in the range of 20 wt%.

PUU Nanocomposites[2]

The PUU used in this part of the study was synthesized in a two-step condensation reaction in DMAc. It was prepared using the same 2,000 g/mol PTMO as above, end-capped with MDI and chain extended by a mixture of EDA and 1,4 diamino cyclohexane, DACH (EDA:DACH = 75:25 by mole). The copolymer hard segment concentration was ~22 wt%. The OMS used in these experiments was Cloisette 15A (Southern Clay Products, TX). It was prepared by the supplier through ion-exchanging Na^+ montmorillonite (with a reported cation exchange capacity of 0.95 meq/g) with dimethyl ditallow ammonium. The tallow used was composed of about 65% C_{18}, 30% C_{16} and 5% C_{14} units, and is introduced in excess of the CEC to approximately 1.25 meq/g.

3 wt% solutions of the OMS in toluene was prepared then added drop-wise to a 3 wt% solution of the PUU in DMAc, and stirred for 3 h at 80 ˚C. Cast films were prepared containing 1, 3, 7, 13 and 20 wt% OMS (correspond to 0.3, 0.8, 2.0, 3.8 and 5.9 vol% layered silicate).

Characterization

Microphase separation in the PUU – PIB comb polymers was investigated using a Digital Instruments MultiMode AFM using TappingMode and PhaseImaging. The images were acquired under ambient conditions using light to moderate tapping. Water vapor permeability was determined at 27 ˚C using ASTM E96-95 and oxygen transmission rate following ASTM F1927-98. X-ray diffraction experiments were performed on nanocomposite films using a Rigaku x-ray diffractometer operating in a theta-theta geometry and Cu K_α ($\lambda = 0.154$ nm) radiation.

Results and Discussion

Amphiphilic PIB – PUU Comb Polymers

Assuming only dispersive interactions and treating PTMO soft segments and PIB combs as a simple mixture, to a first approximation, we estimated the critical interaction parameter for phase separation, using solubilities parameters derived from group contributions and from 'experiments'.[3] These calculations support PIB/PTMO phase separation at even modest PIB molecular weights. This prediction is in line with the observation that 2,000 molecular weight PTMO and 1,500 molecular weight PIB are phase separated at room temperature.[4] Thus the prediction is that the PUU – PIB comb polymers should exhibit a three phase microdomain morphology. Tapping mode AFM experiments were conducted on both free surface of cast films and microtomed cross-sections. A soft phase(s) overlayer was detected on free surfaces but not on the surfaces of the cross-sections, similar to our observations on neat PUUs[5]. On the surface, hard domains are in the form of randomly oriented cylinders with additional spherical domains. **Figure 1** is a phase image of the surface of the comb polymer containing 15% 29K molecular weight PIB combs. The hard domains are visible as the bright regions in the 500 nm × 500 nm image. Hard domains are on the order of 5 – 10 nm in width, independent of PIB content. This compares to an interdomain spacing for the base PUU of 13 nm determined from small-angle x-ray scattering. We were unable to image higher PIB content comb polymers due to high adhesive forces. For lower PIB content materials, we were not able to resolve PIB microdomains, presumably due to insufficient contrast between PTMO- and PIB-rich regions.
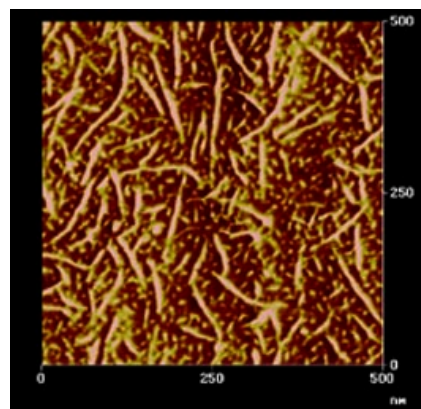

Figure 1. Tapping mode phase image of free surface of PUU-PIB comb polymer containing 15% 29K PIB

Water vapor and oxygen permeability were reduced by about a factor of two at the highest PIB contents, in line with what is expected from models[6] assuming dispersed, spherical PIB microphases. The lack of precise control of the PIB microdomain morphology limits further significant improvement in the permeability with these materials.

PUU Nanocomposites

The x-ray diffraction pattern of the neat PUU exhibits an amorphous halo at 20° 2θ and is observed at the same location for all nanocomposites. The gallery spacing (d_{001}) of the alkyl-modified montmorillonite is 2.9 nm. This increases to 3.4 – 3.5 nm for all of the composites. These results indicate that some of the PUU chains are intercalated between the silicate
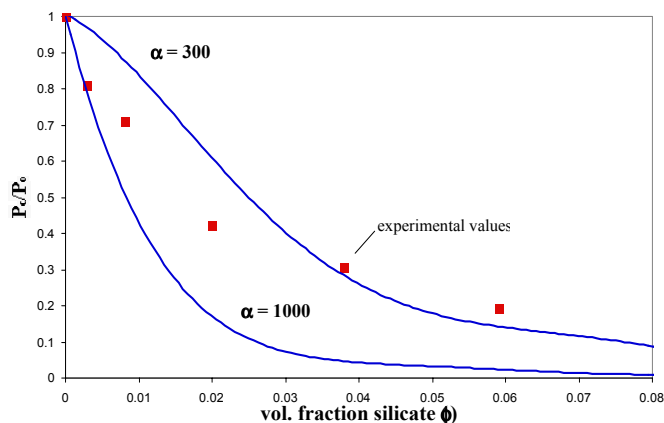
layers, which readopt a parallel registry.

Figure 2. Relative water vapor permeabilities for the nanocomposites.

The water vapor permeabilities for the PUU - OMS composites are presented in **Figure 2** 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 for these non-optimized materials, there is a dramatic reduction in permeability, reaching 5× at the highest OMS content. This is a consequence of the more tortuous path that gas molecules must traverse to penetrate the membrane. The solid lines in the figure represent predictions[7] for the permeability through the thickness of a composite film that has dispersed (impenetrable), completely oriented filler layers with aspect ratios (α) = 300 and 1000. A comparison between the experimental values and the model predictions suggests a gradual change in the effective aspect ratio of the filler; i.e., a change from high aspect ratio exfoliated layers, to lower α intercalated multi-layer stacks.

Summary

We describe 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. PIB was used as the comb material due to the combination of its good barrier properties and controllable polymerization. The modest reduction in water vapor and oxygen permeability observed in PUU-PIB comb polymers is comparable to that observed in PUUs containing polycarbonate soft segments.[8] We also described a nanocomposite approach for biomedical PUUs, that resulted in a significant reduction in gas permeability, with simultaneous improvement in mechanical properties.[2] These concurrent property enhancements are well beyond what can be generally be achieved through chemical modification of PUU polymers.

References

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