Low Permeability Biomedical Polyurethane Nanocomposites for Cardiac Assist Devices

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Introduction

Biomedical polyurethanes generally possess good biocompatibility and mechanical properties but, due to the low T_g and relatively high concentration of soft segments, are relatively permeable to air and water vapor. The 'traditional' approach to the permeability problem is to modify the chemistry of the copolymer, particularly that of the soft segment. For example, replacement of polytetramethylene oxide (PTMO) soft segments with aliphatic polycarbonate segments results in about a factor of two reduction in water vapor transmission rate.[1] Recently, a more efficient approach for reducing the permeability of elastomers has received widespread attention. The basic idea is to disperse an organically-modified layered silicate (OMS) in the polymer, creating a more tortuous path for diffusion of gas molecules through the resulting composite. In a recent publication[2] we demonstrated the utility of this approach for a generic poly(urethane urea) [PUU], resulting in as much as a 5× reduction in water vapor permeability at modest OMS loadings. The current paper represents an extension of this work to commercial PUUs that are used in cardiac assist devices.

Materials and Methods

Two PUUs were used in this study: BioSpan and BioSpan MS/0.4, obtained from the Polymer Technology Group. Although the precise compositions of these segmented block copolymers are proprietary, BioSpan is prepared from MDI, ~2000 molecular weight PTMO and mixed diamine chain extenders (EDA and 1,3- cyclohexanediamine).[3] The hard segment concentration of this copolymer is ~20 wt%. The chemistry of BioSpan MS/0.4 is similar, except that a portion of the chain ends are capped with ~2000 molecular weight poly(dimethylsiloxane) to a level of 0.4 wt% of the copolymer. The two organically modified layered silicates used in our experiments were Cloisite 15A (Southern Clay Products) and Nanomer I.30TC (Nanocor). The former material was prepared by the supplier by ion-exchanging Na^+ montmorillonite (MMT) with dimethyl ditallow ammonium. Nanomer I.30TC was also prepared by the supplier, by ion-exchanging Na^+ MMT with octadecylammonium. The average aspect ratios of Cloisite 15A and Nanomer I.30TC have been reported by the manufacturers to be about 200 – 500.

Composites containing 1, 3, 7, 13 and 20 wt% OMS were prepared from each copolymer by solution casting from N, N-dimethylacetamide. X-ray diffraction experiments were performed on film samples on a Rigaku x-ray diffractometer. Evaluation of the mechanical properties was carried out in tension (crosshead speed = 100 mm/min) using specimens cut using a microtensile die. Water vapor permeability was determined at 27 °C according to ASTM E96-95. Selected Fourier transform infrared (FTIR) spectra were acquired in transmission using a Biorad FTS 45 spectrometer.

Results and Discussion

From x-ray diffraction experiments, the spacing between silicate layers (d_{001}) of an unmodified Cloisite Na^+ MMT was determined to be 1.2 nm. The layer spacing increases to 2.8 nm for Cloisite 15A due to the presence of the hydrocarbon brushes in the silicate galleries. This increases to about 3.4 nm for all BioSpan – Cloisite 15A composites. Similar behavior was observed for the BioSpan MS/0.4 – Nanomer I.30TC mixtures. These results demonstrate that some of the PUU chains are intercalated between silicate layers, which readopt a parallel registry after solvent evaporation.

The role of the non-polar alkyl ammonium cations in an OMS is generally to lower the surface energy of the native MMT and improve wetting with selected polymers. If the change in interlayer spacing in the nanocomposite is modest, as is usually the case, the change in system enthalpy is expected to determine if intercalation is possible from a thermodynamic prospective.[4] Like the present case in which the polymer and OMS layers are originally in solution and films are formed by casting, kinetic trapping of the polymer chains in interlayer regions is also a possibility.

Favorable enthalpy for silicate – PUU mixing could arise from polar or hydrogen bonding interactions between C=O and N-H in the PUU chains and polar sites on the silicate surface. FTIR spectra of polyurethanes are well known to be sensitive to hard domain organization and urea and urethane hydrogen bonding. Consequently, FTIR spectra of BioSpan – Cloisite 15A nanocomposites were compared with those of the neat components. However, even at 30 wt% OMS content, no changes in the spectra of the nanocomposites compared to that of BioSpan were observed. Consequently, the evidence at this stage supports the likelihood that the PUU chains in silicate galleries are kinetically trapped.

The nanodispersed silicates result in a significant increase in modulus (by a factor of 2 –3 at 20 wt% OMS) and possess an ultimate strength comparable to the neat PUU. Remarkably, these changes are accompanied by retention of the neat PUU ductility. Although silicates in the bulk state behave as relatively rigid materials, transmission electron micrographs of nanocomposite morphology show that individual silicate layers, due to their high aspect ratio and namometer thickness, exhibit a measure of flexibility.[5]

There is a very significant reduction in water vapor permeability in the nanocomposites, reaching about five-fold at the highest OMS contents. The reduction is similar for the two series of materials, with the I.30TC OMS perhaps a bit more effective at lower OMS concentrations.

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