THE POLY(URETHANE)-CALCIUM ION INTERACTION. I. EFFECT ON THE MECHANICAL
AND THERMAL PROPERTIES

R. S. Benson, C. A. Warner and R. P. Wong

Department of Material Science and Engineering
and
Center for Materials Processing
University of Tennessee
Knoxville, Tennessee 37996-2200

Understanding the effects of blood on poly(urethanes) requires a knowledge of the interactions between the polymer and individual blood components. This study examines the calcium-poly(urethane) interaction. Calcification has been associated with a loss of mechanical properties leading to premature failure of polymer implants. Using tensile testing, dynamic mechanical testing, differential scanning calorimetry and infrared spectroscopy, this study observed the changes in structure and properties of a poly(ether urethane) when calcium is blended with it. It is shown that the polyether soft segment may serve as an initiation site for calcification, leading to premature failure.

INTRODUCTION

Linear elastomeric poly(urethanes) are the materials of choice for many biomedical applications involving blood contact because of their physiological stability in the body. These poly(urethanes) have been used in a variety of medical implants including the total artificial heart, artificial blood vessels and cardiac pacemakers.1-5

Recent evidence indicates that poly(urethanes) undergo calcification when implanted in certain cases with a subsequent loss of mechanical properties.6-9 Calcification may either be a cause or a result of the degradation observed in the poly(urethane). Calcification within a poly-(urethane) implant appears most likely to result from one of the following mechanisms:

1. Calcification originating in fragments of devitalized cells.10

2. Calcification of proteins and lipids at accumulation sites at calcification.11

3. Calcification at sites of stress concentration due to alteration
of the local domain structure secondary to increases in local polymer structure.\textsuperscript{11}

4. Accumulation of calcium within the bulk of the polymer by metal ion chelation with the polyether "soft segment" of the poly(urethanes).\textsuperscript{6}

Earlier studies of calcification centered on the physical nature of the surfaces.\textsuperscript{12-14} Recently the emphasis has been on the effects of the chemical nature of the material, however, the role of the polymer in the calcification of biomedical implants remains unclear. The metal chelation (MIC) hypothesis has served as the basis for many studies. The principle embodied in the MIC hypothesis is the demonstrated ability of poly(urethanes) to absorb metal ions from organic and inorganic solutions.\textsuperscript{15,16}

Poly(urethanes) have moderately strong selectivity in their ability to extract cations.\textsuperscript{11} The absorption of metal ions appears to be dependent on the structure and molecular weight of the polyether segment. The binding of cations to poly(urethanes) is also strongly dependent on the ions present: large polarizable anions have been shown to be most effective in increasing sorption of cations.

The flexibility of the polyether segment allows structures to form which can accommodate metal ions. These structures are similar to those formed by crown ethers and metal ions. Complexes of crown ethers with molecular guests have been studied extensively, especially the formation of inclusion compounds by the unsubstituted 1,4,7,10,13,16-hexaoxacyclo-octadecane, also known as 18-crown-6-ether.\textsuperscript{17} The mechanism of metal extraction by the poly(urethane) is referred to as cation-chelation.\textsuperscript{13} It suggests that the cation forms a complex with a helical polyether segment with the selectivity based on the size of the cation. The chemical structure of the polyether determines the shape and size of the helical conformation. The selectivity of the cation complex is affected by the extraction of the anion which must allow for charge balance. Infrared measurements have been used to support the cation-chelation mechanism of ion extraction. Shifts of about 30 cm\textsuperscript{-1} in the ether vibrational modes near 1100 cm\textsuperscript{-1} were observed when Co(II) was absorbed from sodium thiocyanate solution.\textsuperscript{13}

Killis, et al.\textsuperscript{18} used dynamic mechanical properties to study the effects of sodium tetraphenylborate on the mechanical properties of crosslinked poly(ether-urethane). The crosslinked structure was synthesized from poly(ethylene oxide) or poly(propylene oxide) salt blend with a triisocyanate. For poly(ethylene oxide) systems, a decrease in $T_g$ was observed at low salt concentrations followed by an increase at higher salt concentrations. The poly(propylene oxide) networks displayed increases in $T_g$ for all salt concentrations. These shifts in the glass transition indicate the presence of significant cation-polyether interactions.

Benson et al.\textsuperscript{16} studied the effects of lithium chloride on the morphology of a poly(ether-urethane-urea) copolymer synthesized from poly(propylene oxide), methylene-bis(phenyl isocyanate) and ethylene diamine. In this study, the salt was blended into polymer solutions. The addition of LiCl to the poly(urethane) resulted in an altered morphology which demonstrated a significant increase in water absorption. While this may not seem unusual upon the addition of hygroscopic material, the persistence of the absorption upon removal of the LiCl suggested that a lasting alteration of morphology had occurred. Infrared studies of the hydrogen bonded and non-hydrogen bonded urethane and urea carbonyls showed