# Effect of Added Silver Ions on Physiochemical Properties of Polyurethane

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**ABSTRACT:** The influence of incorporated silver on the properties of polyurethane based on poly(tetramethylene glycol) 1010, methylenebis(*p*-cyclohexyl isocyanate), and butanediol was investigated. The influence of the incorporated metal ions was reflected in the form of a reduction in the stress–strain parameters as well as an alteration in the thermal behavior. The water uptake of the material was increased severalfold by the incorporation of the silver ions. The induced hydrophilicity together with the variation in mechanical and thermal properties was assigned to the considerable alteration in the morphological features of the polyurethane that resulted from the incorporation of silver ions. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2081–2084, 1997

**Key words:** silver ions; physicochemical properties; polyurethane

## INTRODUCTION

Polyurethanes (PUs) are derived from a unique phase separated morphology and possess interesting properties. Additionally, the materials can be tailored to various requisites by a judicious choice of ingredients. The excellent mechanical and related properties together with a comparatively better biocompatibility make PUs an important class of materials in contemporary health care applications.[1,2]

Synthetic materials in contact with blood often act as loci for infection.[3] Efforts to reduce material associated infection have been made largely by adding antimicrobial agents into polymeric devices.[4,5] Silver and its compounds are traditionally known for their antimicrobial action.[6,7] Silver in a suitable form has been added as an active agent in several drug formulations. Recently silver compounds have been incorporated in polymeric materials intended for medical applications to check the polymer associated infections.[8–10] In addition to these reports, Huang et al.[11] reported the modification of polymers with metal ions including silver to induce conductivity. However, it is not known to what extent the added metal ions or metal compounds influence the properties of the polymers like PUs. We feel that it is worthwhile to study the influence of added silver salt on the properties of PUs, particularly considering their importance as biomaterials.

## EXPERIMENTAL

The PU used in this study was based on poly(tetramethylene glycol) (molecular weight of 1010), methylenebis(*p*-cyclohexyl isocyanate), and butanediol. The PU had a hard segment content of 43% and a weight average molecular weight of 115,000 and was synthesized as reported elsewhere.[12]

One gram of silver nitrate (Merck, Bombay, India) and 5 g of PU were dissolved in 25 mL dimethyl acetamide by heating (50–60°C) and stirring. A dark brown solution was obtained. The solution was transferred into a petri dish and vac-

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**Table I Influence of Added Silver on Major Absorption Bonds of PU**

| Peak Position ($cm^{-1}$) | Assignment | Nature of Peak[a] |
|---|---|---|
| 3320 | —NH stretching | Broadened |
| 1715 | Urethane, amide I | Broadened |
| 1092 | C—O—C, aliphatic ether stretching | Broadened |

[a] Compared to the control PU.

uum dried to get a dark brown colored film. The film was washed with water several times and vacuum dried. In a similar fashion, films containing other ions like ferric iron and copper were prepared.

A Perkin–Elmer model 597 IR spectrophotometer was used for recording the IR spectra. A Dupont 990 thermal analyzer system in conjunction with a model 910 DSC cell was used for the thermal study. Samples (10–20 mg) were encapsulated in aluminum pans and heated from 30 to 350°C under a dynamic nitrogen atmosphere with a heating rate of 10°C/min.

A colorimetric procedure was used to detect the presence of silver in the polymer as reported elsewhere.[13] A known weight of polymer was dissolved in tetrahydrofuran. The residue left was collected and dissolved in nitric acid. The solution was treated with dithizone to form a complex having an absorption maximum at 620 nm. A Hitachi model 220 UV-visible spectrophotometer was used for measuring the absorption.

A model 1193 Instron Universal Testing machine (Instron Co., U.K.) was used to assess the mechanical parameters of the polymers as per ASTM D-882.

Samples (100–150 mg) were placed in triple distilled water. Samples were periodically taken out, blotted gently with filter paper strips, and weighed. The equilibrium water absorption was estimated from $(W - W_o)/W_o \times 100$, where $W$ and $W_o$ are the final initial weights of the samples.

## RESULTS AND DISCUSSION

Table I summarizes the results of the IR spectroscopic studies. It can be seen that —NH stretching, amide, and —O—C— stretching modes are broadened, indicating the influence of added silver ions. We could not observe any drastic spectral changes like a substantial shift in the peak positions or the creation of any new peaks, etc. The perturbation of the above mentioned bands indicates the possibility of the association of silver ions with —N— and —O— atoms that could be expected because these entities have higher electronegativities.

Huang et al.,[11] in their studies on polyvinyl alcohol containing silver compounds, made more or less similar observations. These researchers observed a minor shift or broadening in the peaks corresponding to —NH and —OH and concluded that silver acts as a chelating agent.

Figure 1 shows the DSC scans of PU and the PU-silver system (PU-Ag). The PUs were subjected to extensive thermal studies, and generally showed three endothermic transitions.[14] The first endotherm centered around 70°C was attributed to the dissociation of domains with limited short-range order. The peak around 120–190°C represented the disruption of domains with long-range

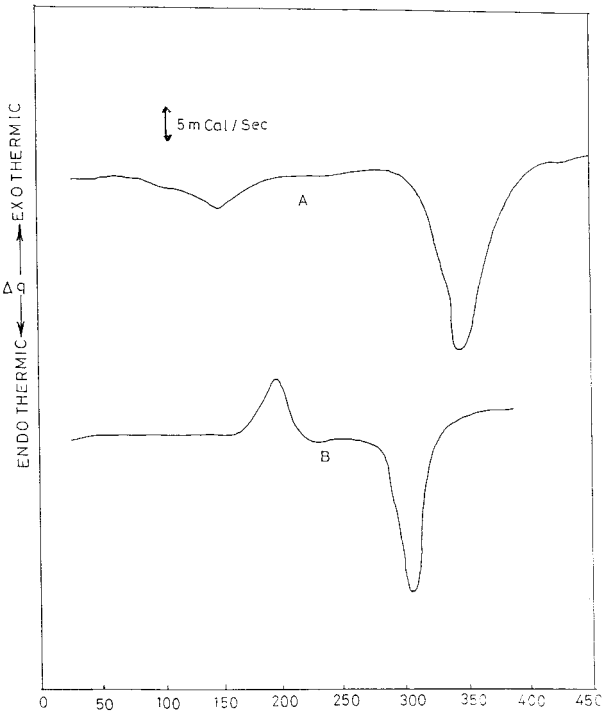


**Figure 1** Differential scanning calorimetric scans of (A) polyurethane and (B) polyurethane–silver system.

**Table II Extent of Water Uptake by Polymer**

| Polymer | Equilibrium Water Absorption (%) |
|---|---|
| PU | 0.6 ± 0.07 |
| PU-Ag | 95 ± 0.8 |

order. Often the first transition can be shifted upward to merge with the higher transition, depending upon the morphological features. PUs with crystalline domains normally show another endothermic transition beyond 190°C.

The PU used in this study showed an endotherm [Fig. 1(A)] centered around 145°C that could be assigned to the dissociation of the long-range order as per the previous discussion. The PU used in this study was a typical amorphous material and, indeed, peaks associated with melting of the crystalline regions were not seen. The strong endothermic transition around 340°C was due to the degradation of the polymer. The PU-Ag system showed an exothermic peak [Fig. 1(B)] around 190°C, which may be assigned to the dissociation of the silver oxide formed during the preparation of the polymer film.[15] The typical transition associated with the long-range order was absent in the modified material, which may be a reflection of the alteration in structural architecture of the PU induced by the incorporated silver ions. Another notable observation was the reduced thermal stability of PU-Ag compared to PU. The degradation temperature of PU was centered around 340°C while that of PU-Ag was around 305°C. The thermal and spectral data point to the disturbance of the typical structural features of PU by silver ions. The presence of silver in the polymers was detected by the colorimetric method discussed in the Experimental section.

Table II shows the equilibrium water absorption of PU and PU-Ag. The PU used here was highly hydrophobic and the water absorption was just 0.68%. The addition of silver dramatically altered the water uptake of PU, and the equilibrium water absorption was remarkably as high as 95%. Silver can disturb the charge distribution in the polymer and the charged species such as $—NH^{\delta-}\cdots Ag^{\delta+}$ may be created. An increase in conductivity in polymers, including PU, was reported by Yen et al.[16] The creation of ionic centers may be responsible for the enhanced hydrophilicity of PU. After attaining the equilibrium water absorption, the PU-Ag polymers experienced a dimensional change of 9–11%. The considerable amount of water uptake by the modified PU may improve its blood contacting properties. PU samples containing ferric chloride and copper chloride also showed a similar tendency toward water absorption, although the amount of water absorption was considerably less than the PU-Ag system. The interesting aspect noticed in the PU-Ag system was the reduction of water uptake with the age of the samples. The equilibrium water absorption of a 4-month-old PU-Ag sample was 22%, which is much less compared to the 95% water uptake of a freshly prepared sample. We presume that the time dependent variation in water absorption capacity of the samples was due to the further structural changes in the PU-Ag samples with age.

Table III summarizes the stress–strain parameters of PU and PU-Ag samples. It is apparent that the ultimate mechanical parameters of PU are reduced as a result of the addition of silver ions. Researchers have made substantial efforts to understand the mechanical properties of PUs in terms of their morphological and structural parameters.[17,18] The ultimate mechanical properties are largely governed by the feasibility of stress induced chain ordering and induced morphological changes like strain induced crystallinity, etc. The presence of silver ions in the PU-Ag material could affect the chain ordering, and these ions could also act as interlocks or stress concentrating points leading to the premature failure of the material. The alteration in the morphological features of PU induced by silver ions are reflected in the reduced ultimate mechanical parameters. The stress–strain parameters of PU-Ag are less compared to PU; the material has adequate strength for most of the intended biomedical applications.

This study showed that the presence of silver discourages the adhesion of bacteria on polyethylene terephthalate for suture application.[10] Our recent studies demonstrated that the added silver prevents the adhesion of several strains of microorganisms on various polymers.[19]

We feel that the acquired hydrophilicity to-

**Table III Stress–Strain Parameters of Polymers**

| Polymer | Stress (kg/cm$^2$) | Strain (%) |
|---|---|---|
| PU | 455 ± 5 | 482 ± 7 |
| PU-Ag | 165 ± 9 | 285 ± 6 |

gether with the induced antimicrobial properties of PU from the incorporation of silver would be advantageous in improving the blood contacting properties of PU. Our future efforts will be directed toward evaluating the blood contacting properties of PU-Ag.

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