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Diffusion and Mechanical Properties of Polyether-Polyurethanes Reinforced with Silica

by James M Sloan and Henry Feuer

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14. ABSTRACT In this work, we consider the effect of adding functionalized silica particles to a poly (tetramethylene oxide)-based polyurethane that is a candidate to be used as flexible storage containment for a variety military fuels. We have synthesized urethanes with silica concentrations varying from 0% to 40% by weight and evaluated the diffusion of commercial gasoline and their mechanical properties.					
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1. Introduction

Polyurethanes are used as coatings, adhesives, thermal insulation, and more recently as polymer binders. These thermoplastic polyurethane materials are typically phase segregated and consist of a combination of hard, rigid, organized segments and soft, flexible, rubbery segments. Typically, the hard segments contain diisocyanate groups with a chain extender, a diol, or a diamine, and the soft segment is usually a polyether or polyester. Their structure and morphology have been studied extensively¹⁻⁷ because of their excellent elastomeric and thermal properties.

The elastomeric properties of polyurethanes can be attributed to phase segregation. Many studies³⁻⁵ have shown that microphase segregation occurs in polyurethanes due to the thermodynamic incompatibility of the hard and soft segments and physical crosslinking among hard segments. Phase segregation leads to a variety of morphologies depending on the content of hard or soft segment in the polymer. Usually, at phase ratios greater than 2:1, the minority phase is dispersed in a matrix of the majority phase, while at near 1:1 phase ratios, lamellae structures are observed.⁶ The extent of segregation varies depending on the amount of physical crosslinking that takes place, usually through hydrogen bonding. Hydrogen bonding can occur between the urethane groups of different hard segments or between the urethane group in a hard segment and the oxygen in a polyether or polyester soft segment.⁷ Increased crosslinking between hard segments leads to a higher degree of phase segregation, while hydrogen bonding between hard and soft segments leads to phase mixing.^{8,9}

The benefits of incorporating fillers into polymer systems is a tried and true method for improving many physical properties and transport properties.^{10,11} This report details the effect of the addition of functionalized silica to improve the diffusion of commercial gasoline through these materials and considers the effect of the addition of silica has on the chemical structure, thermal, and mechanical properties.

2. Experiment

2.1 Materials

Poly (tetramethylene oxide) (PTMO) (0.04 mol) was placed in 600 mL of tetrahydrofuran contained under dry nitrogen gas within a flame-dried 1-L 3-neck round-bottom flask equipped with a water cool condenser and a heating mantle/magnetic stirring plate. When it completely dissolved, 0.088 mol of

4,4'-Methylenebis (cyclohexyl isocyanate, H₁₂MDI) and 5 drops of catalyst (dibutyltin dilaurate) were added to the flask. The mixture was heated to gentle reflux (66 °C) and allowed to react for 5 h while being stirred. Then 0.04 mol of 1,4 butanediol was added to link together PTMO/H₁₂MDI oligomers, and refluxing continued for an additional 16 h. The reaction was cooled down below 40 °C and 20 mL of methanol was added to cap-off remaining isocyanates. Polymer was isolated by pouring tetrahydrofuran (THF)/polymer solution into water and collecting the solids, which subsequently were soaked in additional water to remove residual THF and then dried in the vacuum oven at 50 °C.

The functionalized silica particles used was Angstromsphere, which is a high purity, amorphous silica powder available from Fiber Optic Center (New Bedford, MA). The particle size was 500 nm.

Polyurethane composites containing 0%, 5%, 10%, 20%, 30%, and 40% silica filler were created. The urethane was dissolved in THF. Functionalized silica particles were dispersed in THF by the use of a sonicator and then added to the dissolved polyurethane mixture. The solutions were then stirred for 4 h before solution casting in an oven at 60 °C. Once formed, samples were further dried under vacuum for 48 h at 60 °C and were then characterized. Molecular weights varied from 38,000 to 49,000 as measures by GPC for all urethanes synthesized.

2.2 Characterization

Dynamic mechanical analysis (DMA) was completed using a TA Instruments Q800 Series DMA in tension film mode. Rectangular specimens with dimensions of 4-mm width and 15-mm gauge length were used. The thicknesses were recorded by taking the average across the length of the film. The samples were tested from -100 °C to 250 °C at a heating rate of 3 °C/min, a frequency of 1 Hz, and amplitude of 20 µm.

Infrared (IR) spectra were recorded with a Nicolet Magna 560 ATR-FTIR spectrometer using films placed on a ZnSe (Zinc Selenide) crystal. Spectra were recorded in the mid-IR region (4,000–400 cm⁻¹). Each spectrum was obtained by accumulating 64 scans at a resolution of 4 cm⁻¹. Data collection and processing were completed using OMNIC series software.

Tensile testing of samples was performed on a MTS Synergie tensile testing machine with a 500-N load cell. A self-tightening clamp was used to prevent slippage of the sample. All tests were carried out following ASTM Standard D412.¹²

Tests were performed on samples that were 4 mm in width and 25 in gauge length at a displacement rate of 300 mm/min. Strain was estimated based on grip displacement. Three samples per material were tested.

Diffusion experiments were carried out by immersing a 10-mm-wide disk with a thickness of 1 mm into a commercial gasoline (Shell 87 octane). Samples were tested at 25 °C. The samples were removed at selected time intervals, blotted dry, and weighed.

If we assume that the diffusion process is Fickian, a plot of the weight gain with time will be linear for the most of the curve before levelling to equilibrium.

$$D = \frac{.0492L^2}{t_{1/2}} \quad (1)$$

where $t_{1/2}$ is the half time to max sorption value, L is the thickness in centimeters, and D has the dimensions of square centimeters per second.

3. Results and Discussion

3.1 Mechanical Testing

Figure 1 shows the effect of silica filler on the tensile properties of the PTMO 2,000 composite. The unfilled urethane shows typical elastomer behavior with a low modulus and high elongation at break, at approximately 2,400%. As the concentration of filler increases, a number of changes become apparent. The yield point for the 0%, 5%, and 10% are very similar, showing little change with silica addition. However, when the loading is increased to 20% and subsequently 40% we observe a significant increase in the yield point. This can be interpreted as a percolation threshold. The unfilled urethane yields around 100 psi, while the 40% filled urethane shows a 10-fold increase to 1,000 psi. The elongation at break decreases significantly, going from 2,400% in the unfilled urethane to a respectable 800% in the 40% urethane. Similar to the yield point results, the 0%, 5%, and 10% samples show very similar behavior in the shape and magnitude of their tensile properties. Table 1 summarizes these results.

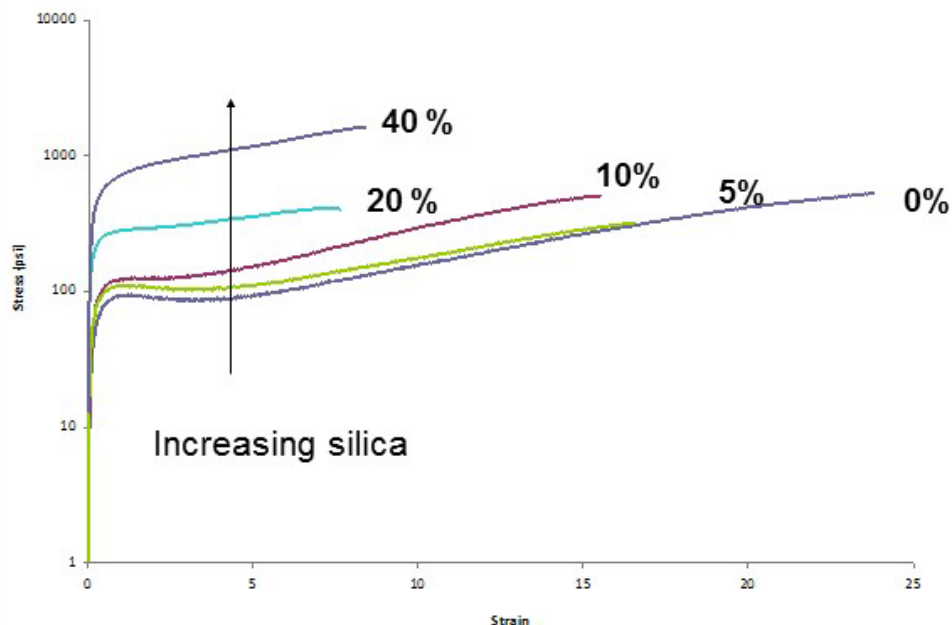


Fig. 1 Tensile testing data for the PTMO 2,000 urethane filled with 0%, 5%, 10%, 20%, and 40% silica

Table 1 Results of tensile testing

Silica level (%)	Stress, psi 100% elongation	Stress, psi 300% elongation	Tensile (psi)	Elongation at break (%)
0	94	87	535	2,375
5	123	129	505	1,794
10	122	113	520	1,489
20	282	310	614	764
40	722	977	1,634	809

The DMA results are shown in Fig. 2. The lower curve represents the unfilled urethane. A significant reinforcing effect is observed as the silica content is increased. The overall increase from 0% to 40% is approximately an order of magnitude increase. Additionally, the rubbery plateau between -25°C through $+50^{\circ}\text{C}$ is not flat but has an appreciable slope throughout the range. Generally, this suggest a considerable amount of phase mixing between the rubbery PTMO chains and the rigid isocyanate clusters.

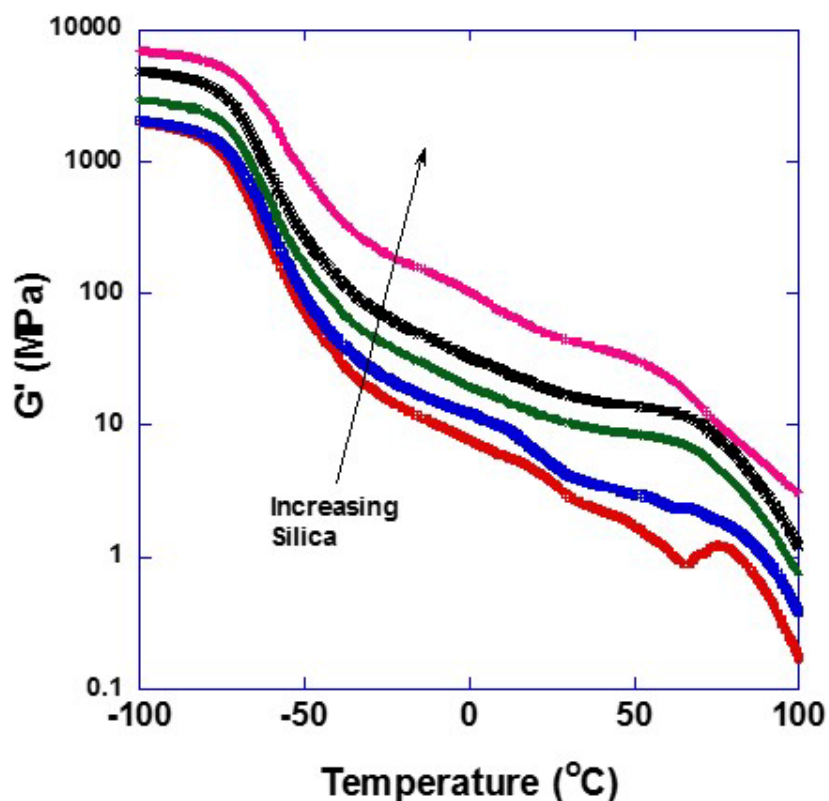


Fig. 2 DMA results for urethane with 0%, 5%, 10%, 20%, and 40% silica filler

The other notable feature of the DMA is the position of the glass transition temperature, T_g , of the PTMO soft segment. The dramatic decrease in G' in the low temperature region is a result of the softening of the PTMO chains.

The incorporation of silica filler increases the soft segment glass transition temperature. Figure 3 shows the loss modulus, which we use to estimate the T_g of the soft segment. The PTMO 2,000 urethane exhibits an extra transition at -25°C , where an increase in modulus is observed after the initial drop in storage modulus. This is likely due to a crystallization occurring at the low temperature, a known effect for higher molecular weight PTMO-based urethane materials.

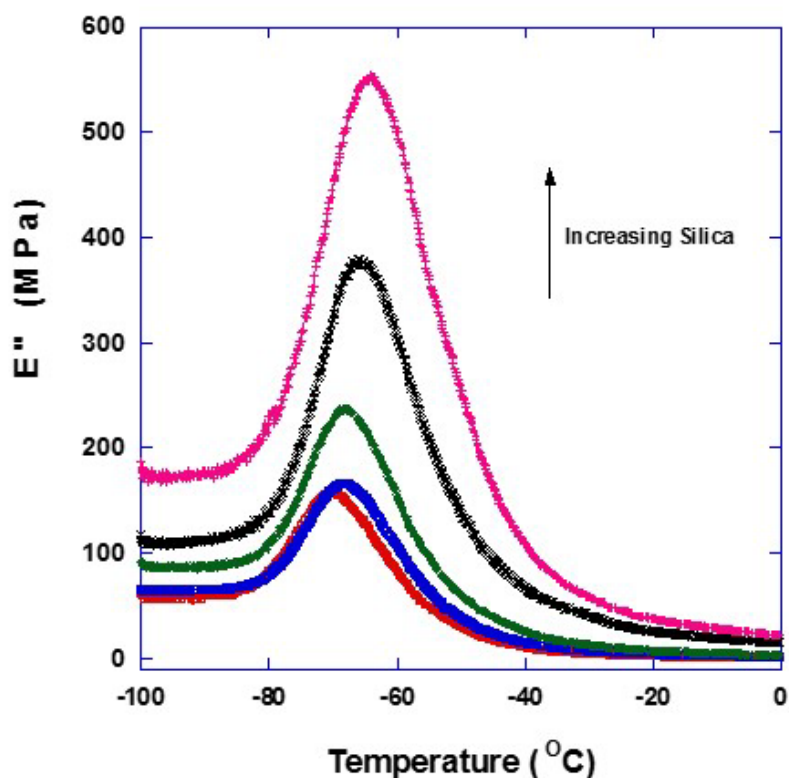


Fig. 3 The loss modulus results for urethane with 0%, 5%, 10%, 20%, and 40% silica filler

Table 2 shows the DMA results for the shifts in T_g with silica addition. Here it can be seen that a reinforcing effect occurs at larger silica filler levels.

Table 2 T_g shifts with silica loading

Silica (%)	T_g (°C)
0	-71
5	-70
10	-68
30	-66
40	-63
PTMO	-76

3.2 Fourier Transform-IR (FT-IR)

Since urethanes are phase-segregated polymers, they have hard crosslinks that can be investigated by FT-IR spectroscopy. Figure 4 shows the carbonyl region for the PTMO 2,000 soft segment polyurethane material. The figure overlays the carbonyl

peaks for urethane with varying silica content. The silica content varied from 0% to 40% by weight. These overlaid spectra consist of 2 critical peaks: the one centered at $1,720\text{ cm}^{-1}$ is assigned to the unassociated carbonyl of the urethane linkage, and the one centered at $1,700\text{ cm}^{-1}$ is attributed to a carbonyl group that is hydrogen bonded to a nearby N-H group. These 2 IR bands give insight as to the amount of phase mixing occurring within the urethane matrix. The more hydrogen bonding that is present (increase in the $1,700\text{ cm}^{-1}$), the more the urethane is phase separated. The IR spectra for the 0%, 5%, and 10% are virtually identical; no band intensity changes or peak shifts can be observed. This is direct evidence that the silica is residing completely in the PTMO and not impinging upon the isocyanate hard segments.

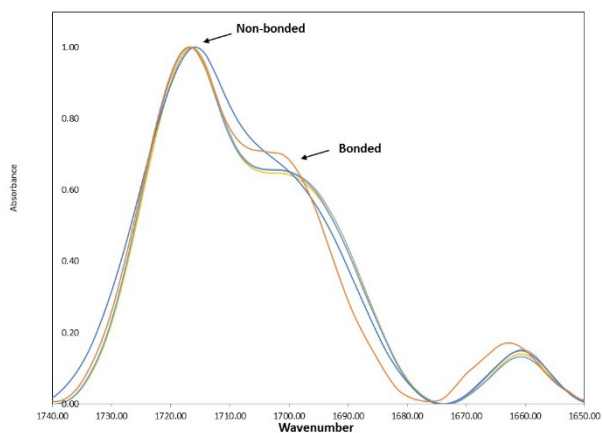


Fig. 4 FT-IR spectra compare filled and unfilled urethane composites

For the 20% material, you begin to see some band broadening occurring as the silica has saturated the PTMO rubbery phase and begins to compete for the free carbonyl dispersed in the PTMO phase. At this level, it is likely that the silica is forming associations with a portion of the non-bonded carbonyls that are dispersed throughout the PTMO soft segment. At the 40% level, a more prominent increase in the $1,700\text{ cm}^{-1}$ band begins to occur.

The $1,700\text{ cm}^{-1}$ is attributed to a carbonyl group that is hydrogen bonded to a nearby N-H group. These interactions form the basis for the crosslinking network. The increase in this band is direct evidence that the silica particles are beginning to become attached to any “non-bonded carbonyls” but does not appear to disturb the already formed hydrogen bond of the urethane network.

Figure 5 shows the results from a curve fit analysis of the ratio of the $1,700\text{ cm}^{-1}$ and $1,716\text{ cm}^{-1}$ peaks and confirms, quantitatively, that the bonded IR band at $1,700\text{ cm}^{-1}$ begins to increase at 20% silica content.

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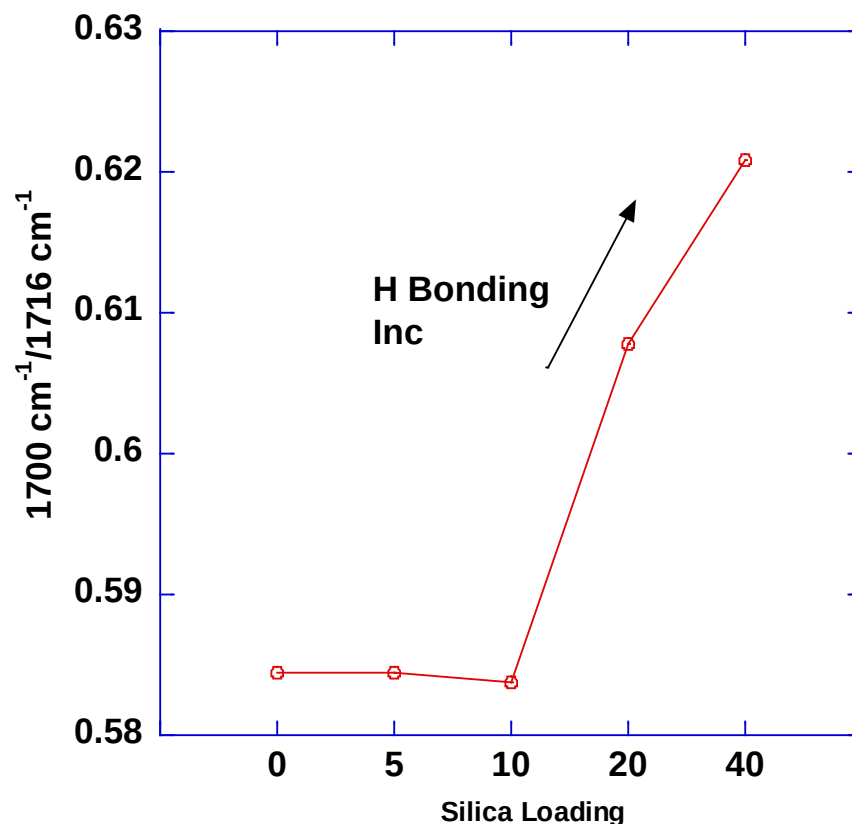


Fig. 5 Influence of silica loading on the urethane carbonyl

3.3 Diffusion

Figure 6 shows the diffusion results for 0%, 5%, 20%, and 40% silica-loaded urethanes. The addition of silica has a significant slowing of the diffusion process. Table 3 is a summary of these results. The diffusion coefficient decreases from $24.6 \times 10^6 \text{ cm}^2/\text{s}$ for the unfilled urethane to $8.9 \times 10^6 \text{ cm}^2/\text{s}$ at the 40% level. In addition to the reduction in the diffusion coefficient, a significant decrease in the solubility of these materials is observed. The unfilled silica urethane shows a solubility of 15.5 wt% that decrease to 7.3 wt% for the 40% silica filled material. The diffusion results differ from those of the mechanical in that the decrease in the diffusion coefficient is a continuous process nearly linear, where the mechanical show a percolation threshold effect.

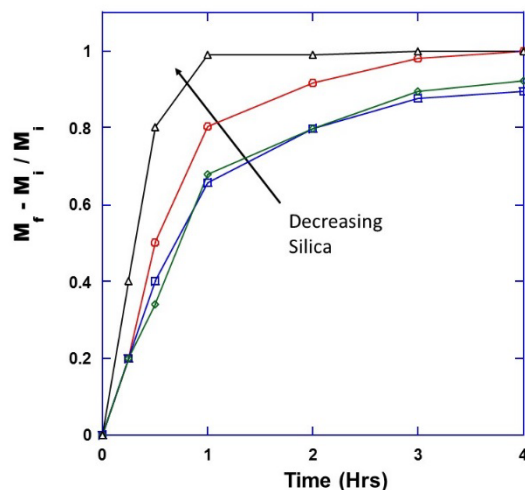


Fig. 6 Sorption curves for 0%, 5%, 20%, and 40% silica-loaded urethanes

Table 3 Effect of silica on the diffusion coefficient

Silica	D (cm ² /s) X 10 ⁶	Solubility (wt%)
0	24.6	15.5
5	16.4	14.7
10	12.3	10.2
20	9.4	9.6
40	8.9	7.3

4. Conclusions

In this study, we evaluated the effect of incorporating functionalized silica into a series of polyurethanes on their structural, diffusion, and mechanical properties. The tensile properties of the unfilled urethanes exhibited a lower yield stress than that of the filled urethane materials. They also showed that ultimate tensile strength increases and the elongation at break decreases with silica incorporation. The DMA demonstrated that a reinforcement effect occurs with silica incorporation. In addition, the T_g of the soft segment gradually increased. The real benefit of the addition of silica is the significant decrease in diffusion coefficient that results. The diffusion coefficient decreased from 24.6×10^6 cm²/s for the unfilled urethane to 8.9×10^6 cm²/s at the 40% level. Finally, the FT-IR results showed that when silica is added, it resides in the PTMO soft segment and at elevated silica levels will bond to the non-associated carbonyls residing in the soft segment phase.

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