

Water absorption and plasticization in non-isocyanate polyurethanes with POSS inclusions

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Introduction

While polyurethanes are considered a very versatile family of polymeric materials, and they have been employed in a wide range of applications, they suffer from a significant drawback, namely the use of diisocyanates in their synthesis. Diisocyanate components raise health concerns because on one hand they are themselves very toxic, and on the other, their synthesis involves phosgene which is an explosive and toxic gas [1]. Several approaches have been undertaken for the greener synthesis of polyurethanes, without isocyanates [2].

A popular route is the polyaddition reaction between cyclic carbonate and amine groups which results in a hydroxy-urethane group i.e. a urethane group with an adjacent hydroxyl.

On the other hand, in order to tune mechanical properties, improve heat-resistance, and decrease flammability of polymers, large molecules commonly known as POSS are introduced in the structure. POSS, an abbreviation of Polyhedral Oligomeric Silsesquioxane, are based on a siliceous cage, usually cubic, with Si on the vertices and O on the edges, being essentially molecular silica. On each of the vertex Si atoms, an organic group can be attached. Interestingly these groups can be chosen virtually without limitations regarding their physicochemical properties and most notably their reactivity resulting in a variety of chain architectures [3].

In this poster, we present our first results on an isocyanate-free polyhydroxyurethane system including POSS moieties. One of the first observations after synthesis of these materials was that the resulting materials are considerably hydrophilic, absorbing large amounts of water in ambient conditions. In this poster we show a detailed study of the water uptake with varying environmental humidity in the range 0-97%, as well as the effects of the absorbed water on the glass transition of the polymers.

Experimental

The matrix is a network prepared on the basis of a trifunctional cyclic carbonate (W3), an oligomeric diamine (polypropylene diamine, PPD, molar mass ~400), and a short diamine (putrescine) (Figure 1). Equimolar amounts of cyclic carbonate groups and amine groups are used. The molar ratio of PPD and putrescine is 1:1. I.e. in the matrix the molar ratio of the components W3:PPD:putrescine is 4:3:3.

Two types of POSS molecules are incorporated (Figure 1). Their reactive group is an epoxy ring, which can react via standard epoxy reaction with the amine groups of the diamines. One of the moieties is mono-functional (1-epoxy POSS) which is expected to interrupt the formation of the network, while the

second is tri-functional, and expected to lead to similar networking as the matrix. Up to 15 wt% of POSS was introduced in the matrix with substitution of equally reactive amounts of the cyclic carbonate.

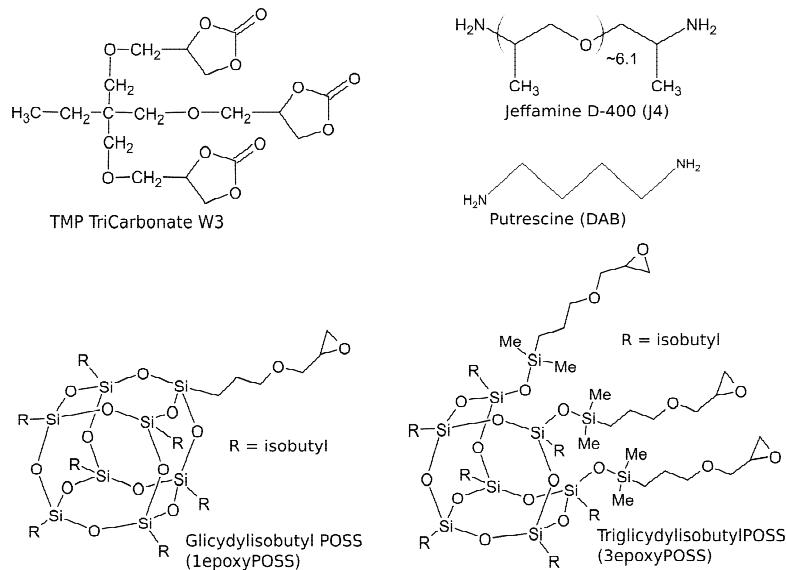


Figure 1 Chemical structures of components used in the synthesis of the materials.

In order to study the water uptake, samples of ~400 mg were exposed to environments of varying relative humidity, and upon equilibration, their mass was recorded and the water uptake determined as fraction of the dry mass. The dry mass was determined by equilibration over P_2O_5 . Humidity was controlled by equilibration of the samples over saturated solutions of selected salts [4].

Differential scanning calorimetry was used to study the glass transition. Samples of 5-8 mg in perforated pans were equilibrated at the same environments, and at each level, DSC curves were recorded in the range -80 to 50 °C at 10 K/min, with a Mettler Toledo 823 calorimeter.

Results and Discussion

The equilibrium sorption isotherms of Figure 2 show that the amount of absorbed water is considerable, reaching 5-10 % at relative humidity 70 % and 30-60% at relative humidity 98%. These values are an order of magnitude higher than those typically observed for conventional polyurethanes [5,6]. The result is even more striking taking into account that the main polymeric component (i.e. polypropylene glycol) is quite hydrophobic. Hence this considerable hydrophilicity should be attributed to the effects of the hydroxyl accompanying the urethane bond formed by the reaction of the cyclic carbonate and the amine group. It should be noted also that the water absorption curves cannot be described by standard models like the Guggenheim-Anderson-deBoer, indicating some level of complexity in the water absorption mechanism in this class of materials.

Incorporation of POSS suppresses the water uptake capacity of the matrix, but the effect depends on the topology of the system. The 1-epoxy POSS initially decreases the water uptake considerably at 5 wt% loading but then the effect is counteracted, possibly due to aggregation of the moieties. The hybrids with 3-epoxy POSS show a more monotonic trend, which could be attributed to a more compact structure of the network with increasing POSS content.

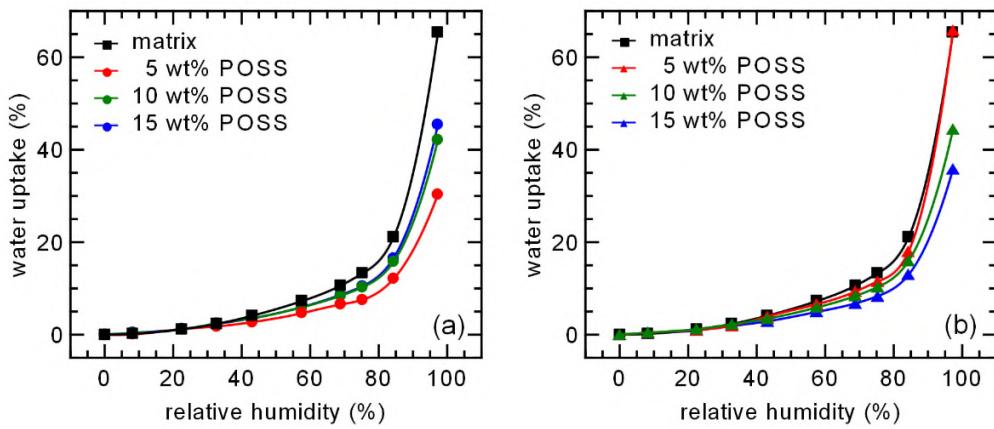


Figure 2 water uptake as a function of environmental humidity for all materials under investigation. (a) with 1-epoxy POSS (b) with 3 epoxy POSS.

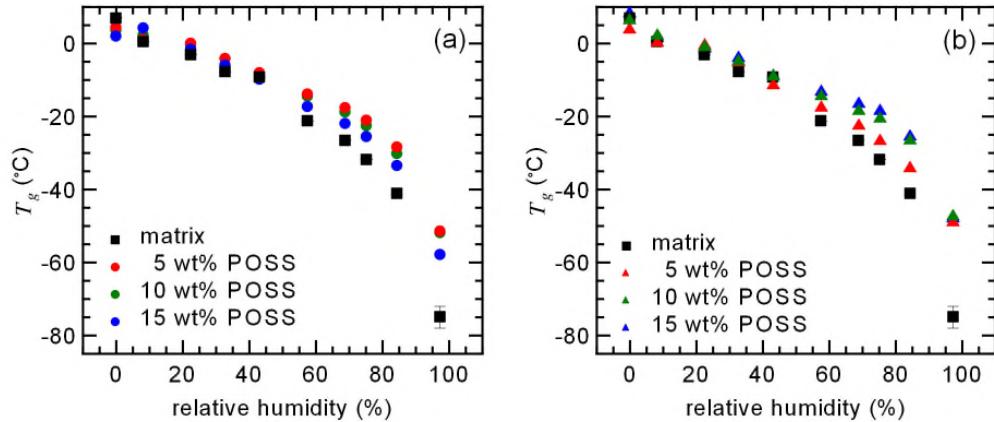


Figure 3 Glass transition temperature as a function of environmental humidity for all materials under investigation. (a) with 1-epoxy POSS (b) with 3 epoxy POSS

For the dry materials, the calorimetric glass transition temperature T_g drops by a few degrees with increasing 1-epoxy POSS content, presumably due to acceleration of dynamics in the looser network (Figure 3). The 3-epoxy POSS hybrids on the other hand show a less monotonic behaviour, with an initial drop of T_g followed by an increase, presumably due to slowing of dynamics in the stiffer polymer network.

As expected, T_g drops considerably with relative humidity, due to plasticization by the large amounts of absorbed water. At relatively low water contents the degree of plasticization is well correlated with the amount of absorbed water (Figure 4). However, at larger water contents, of 3-epoxy POSS the correlation collapses, and glass transition temperature deviates to higher values, presumably because despite the presence of water, molecular mobility is determined by the stiffness of the network.

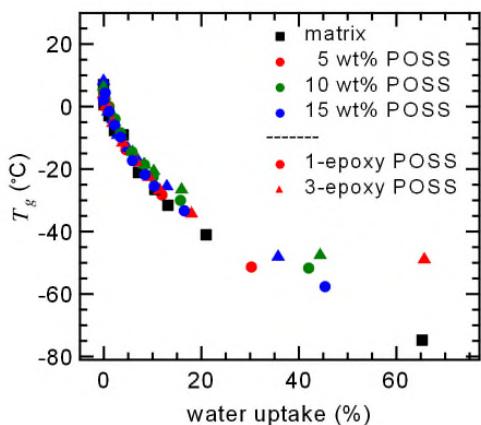


Figure 4 Glass transition temperature as a function of absorbed water.

Conclusions

Isocyanate-free Polyhydroxyurethanes synthesized by polyaddition reaction between cyclic carbonates are very hydrophilic, absorbing up to 65% of water at relative humidity 97%. Incorporation of POSS with reactive epoxy groups and inert isobutyl ones in the structure causes a marked decrease in the hydrophilicity, which however is dependent on the architecture of the incorporation (i.e. the number of the reactive groups in the POSS molecule).

Monofunctional POSS cause a drop of T_g by a few degrees, presumably due to loosening the density of the network. The opposite effect is observed for the tri-functional POSS which reinforce the network. As expected, with increasing hydration, glass transition temperature drops markedly with absorbed water. This plasticization however is interrupted by the trifunctional POSS.

Acknowledgment

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