

## Chemically Crosslinked Polyurethane Hydrogels Based on PEG and PCL

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### Abstract

Chemically crosslinked polyurethanes (PU) were synthesized using poly(ethylene glycol) – PEG, poly( $\epsilon$ -caprolactone)diol - PCL-diol, as hydrophilic and hydrophobic polyols, and PCL-triol, as crosslinking agent, and hexamethylene diisocyanate (HMDI). The water swelling capability of the PU depends on the composition and temperature. The hydrogels present a typical elastomeric behavior and mechanic synergism under load and unload cycles. Moreover, the increase of the temperatures result in hydrogel shrinkage, as consequence of the LCST phase behavior.

### Introduction

Polymeric hydrogels have been extensively studied for biomedical applications mainly due to high hydrophilicity and potential biocompatibility or biodegradability<sup>1</sup>. Polyurethanes (PU) composition can be designed by combining hydrophilic and hydrophobic polyols, potentially biocompatible or biodegradable, in different mass ratio aiming the production of hydrogels. The water swelling capability, mechanical properties and responsiveness against temperature and pH of the medium are some desired properties that can be controlled by PU composition and its crosslinking density<sup>2</sup>. In this work we synthesized polyurethanes based on poly(ethylene glycol) – PEG and poly( $\epsilon$ -caprolactone)diol – PCL-diol, hydrophilic and hydrophobic segments, respectively, using poly( $\epsilon$ -caprolactone)triol – PCL-triol as crosslinking agent and hexamethylene diisocyanate (HMDI). The PU were characterized in both conditions: dry and as hydrogel.

### Results and Discussion

The compositions of PU and the reaction medium are close, as determined by NMR C<sup>13</sup>, making easy the modulation of the hydrophilic-hydrophobic balance of the hydrogels. Dry PU are stiff and semicrystalline materials. The crystalline phase is due to PEG or PCL segments, depending on the composition, while the amorphous phase is a homogeneous mixture, as determined by DRX and DSC, respectively. The water uptake capability of the PU is directly related to the PEG content, crosslinking density and temperature, as can be seen in Figure 1a. The water uptake increases with increasing PEG content. On the other hand, increasing the temperature results in water desorption, a typical LCST phase behavior, as verified by swelling measurements and thermodilatometry. This effect is more pronounced in PEG richer PU. Stress-strain compression tests were conducted with hydrogels at 25 °C under a rate of 0.01 N/min. All

hydrogels present an elastomeric behavior and mechanical hysteresis when subjected to a load and unload cycle. The compression strain ( $\epsilon$ ) at 6.3 kPa for the hydrogels increases with increasing water uptake, Figure 1b. DSC analyses of the hydrogels revealed lower crystallization temperatures of the water into the hydrogels (highlighted as  $T_c$  in Figure 1b) in comparison with neat water. This phenomenon is associated to the porous structure of the hydrogels, in which the water crystallization occurs<sup>3</sup>. This hypothesis was reinforced by the SEM images of dry PU.

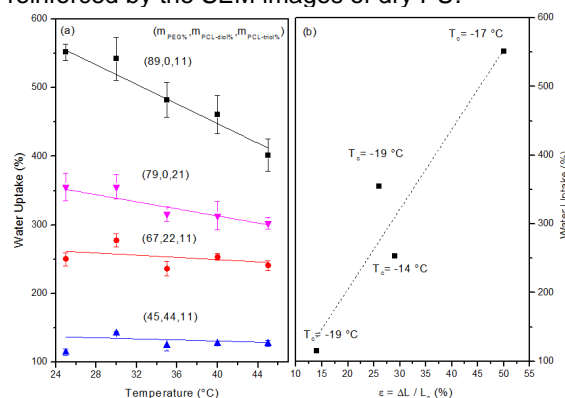


Figure 1. (a) Water uptake as a function of composition and temperature; (b) Water uptake vs compression strain ( $\epsilon$ ).

### Conclusions

The properties of the PU hydrogels can be tailored by the composition and crosslinking density. In general, the hydrogels are resilient, elastomeric and present LCST phase behavior.

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