

# Solid-state $^1\text{H}$ NMR Study of Cornstarch Plasticized with Urea and Glycerol during Ageing

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## Introduction

Thermoplastic starch (TPS) is a moldable material that can be used as low cost bioplastics in many applications. It is prepared from native starch with addition of plasticizers (e.g. glycerol, urea) at high temperature under shear stress (Fig. 1).

During this process called **plasticization**, native starch crystallinity is disrupted and hydrogen bonds between hydroxyl groups of starch chains are replaced by hydrogen bonds between plasticizers and starch whereby urea forms stronger and more stable bonds with starch than glycerol.

Starch-based materials are **sensitive to ageing**. TPS plasticized with glycerol was shown to recrystallize resulting in TPS embrittlement. Urea is thought to prevent starch retrogradation. However it is solid and does not add much flexibility to plasticized starch. Therefore, a combination of the two could suppress the TPS retrogradation and besides makes TPS flexible.

## MAS $^1\text{H}$ NMR

The measurements were performed on a Varian solid-state NMR spectrometer (VNMRS 400, Palo Alto, CA, USA) working at the  $^1\text{H}$  resonance frequency of 400 MHz. Duration of  $^1\text{H}$   $\pi/2$  pulse was 2.9  $\mu\text{s}$ . A recycle delay of 10 s and acquisition times of 20-80 ms were applied. A probe-head equipped with 4-mm rotor spinning at 10 kHz was used. The chemical shifts were referenced to tetramethylsilane using adamantane as an external standard.

## Results

Signal assignment (Fig. 2):  
**U** ...  $^1\text{H}$  nuclei of urea  
**W** ...  $^1\text{H}$  nuclei of water  
**G(OH)** ...  $^1\text{H}$  nuclei of OH glycerol groups  
**G(CH)** ...  $^1\text{H}$  nuclei of CH and  $\text{CH}_2$  glycerol groups

**U signal** is well resolved in the MAS  $^1\text{H}$  NMR spectra (Fig. 2a) and its width does not change significantly during sample ageing. Thus, hydrogen nuclei of urea are mobile and are probably not involved in H-bonds with starch. We propose that **H-bond is formed between carbonyl oxygen in urea and hydroxyl hydrogen in starch**.

**G(CH)** signal is the narrowest (width  $\sim$  120 Hz) compared to other signals because hydrogens in CH and  $\text{CH}_2$  glycerol groups do not form H-bonds.

Widths of **G(OH)** and **W** signals decreased to approximately half (Fig. 3) after 52 weeks. This could be explained by breaking of glycerol-starch H-bonds during sample ageing which were replaced by stronger urea-starch hydrogen bonds. As a consequence, more mobile glycerol molecules along with water molecules could form **glycerol-rich domains** with new network of hydrogen bonds between glycerol and/or water molecules.

## References

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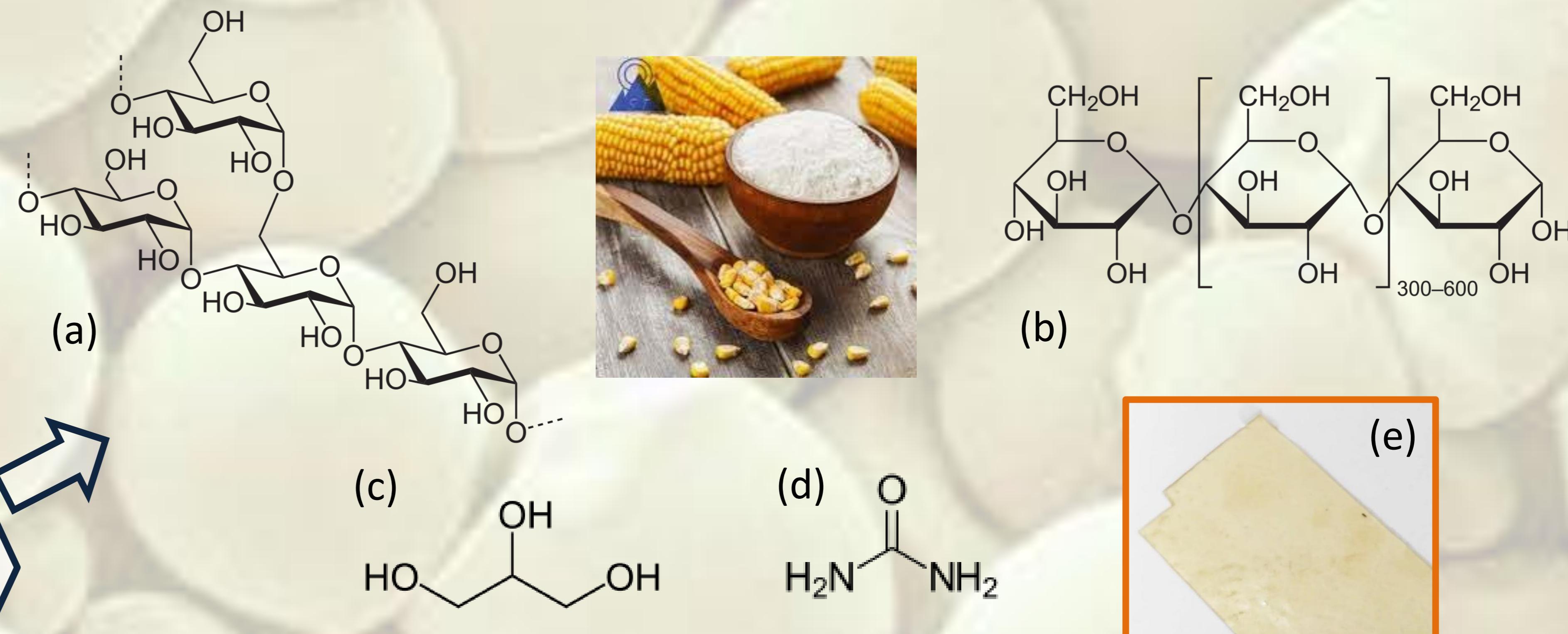


Figure 1. Native starch composes of highly branched amylopectin (a) and mostly linear amylose (b). After plasticization for example with glycerol (c) and urea (d), a TPS material is obtained (e).

## Sample preparation

Native cornstarch Meritena® 100 (Brenntag, Slovakia), glycerol, urea and water at weight ratio of 1:0.35:0.35:2.3 were used for preparation of TPS. Suspension was stirred at 70°C and then dried at 100°C for 5 hours. The plasticized material was kneaded in a laboratory mixer Plastograph Brabender PLE 331 for 10 min at 130°C and 100 rpm. One-millimeter-thick slab was prepared by compression moulding at 130°C under a pressure of 100 kPa and then was stored in a plastic bag at 22°C. The sample was prepared at the Polymer Institute of the Slovak Academy of Sciences, Bratislava.

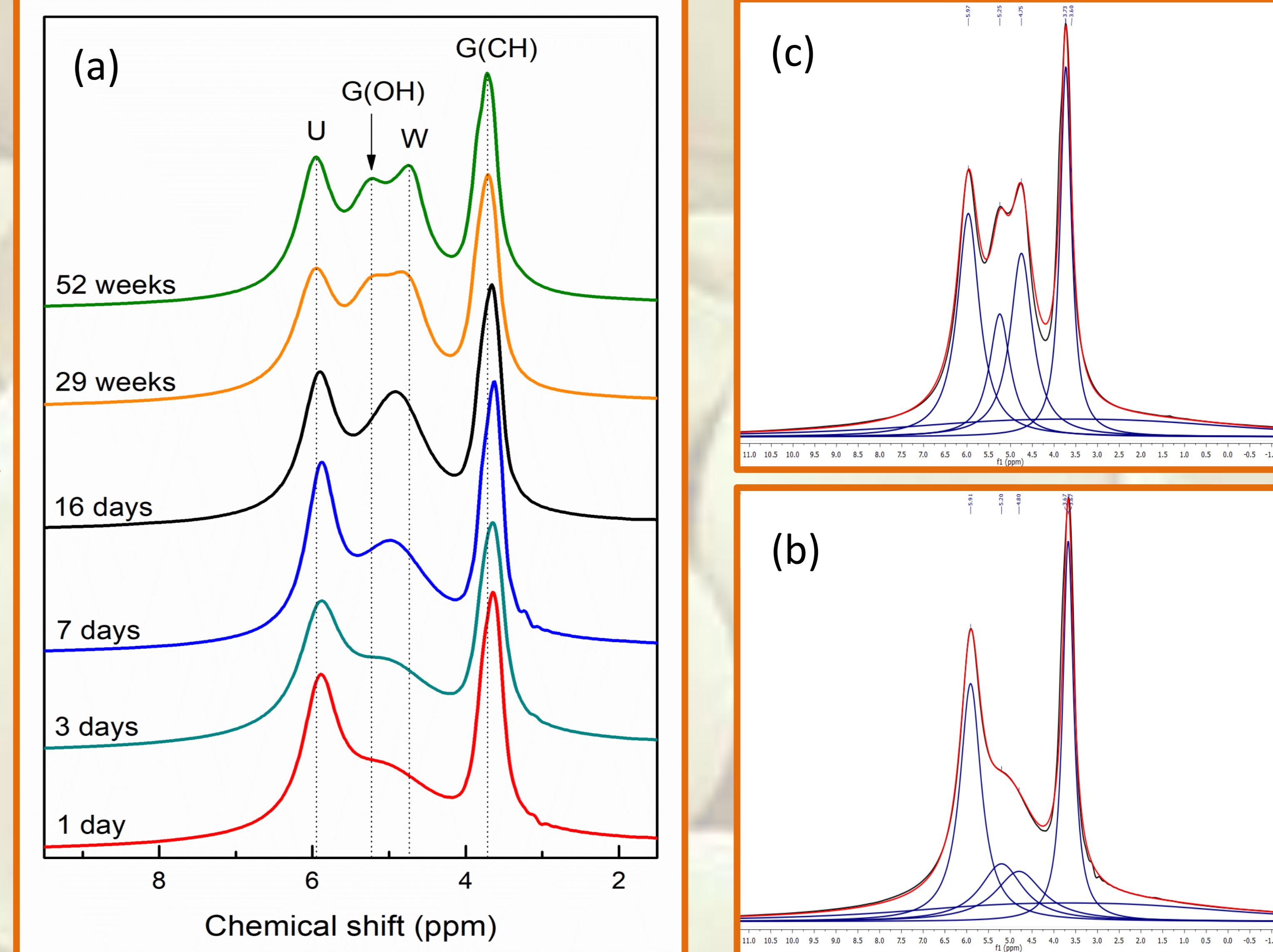


Figure 2. MAS  $^1\text{H}$  NMR spectra of the TPS sample aged as indicated (a). Deconvolution of the spectra of the TPS sample aged 1 day (b) and 52 weeks (c).

## Conclusions

In our sample with urea content 35 wt.% of native starch urea-starch H-bonds established during plasticization preferentially involve carbonyl oxygen in urea and are stable during sample ageing.

Phase separation of glycerol, i.e. formation of glycerol-rich domains took place in the sample after 29 weeks of storage. This process was accompanied by slight water content increase causing higher mobility of glycerol molecules.

Retrogradation of the sample did not occur as was found through XRD measurements (not shown) and thus, urea effectively prevented starch recrystallization.

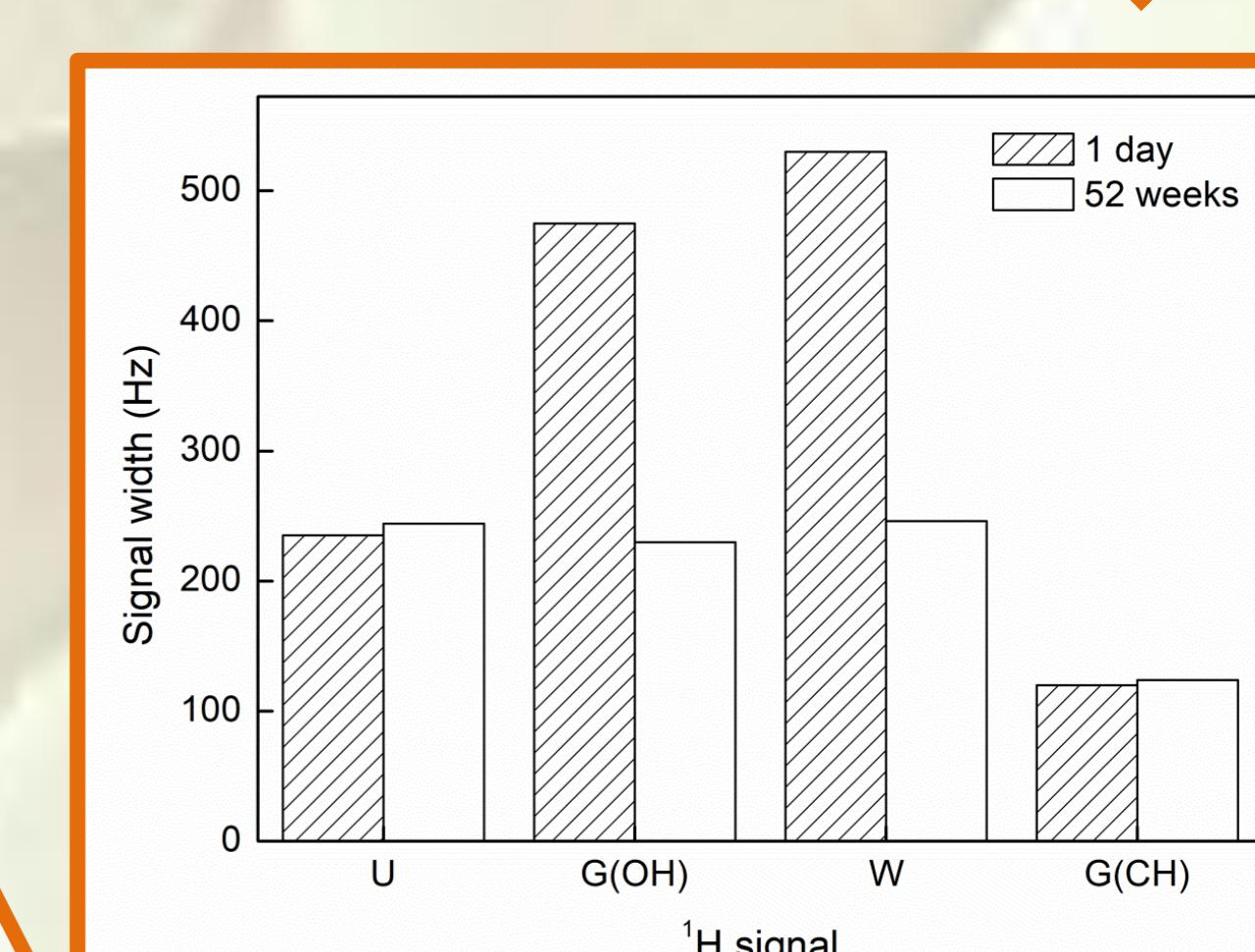


Figure 3. Widths of the signals related to hydrogen nuclei in urea (U), glycerol (G(OH), G(CH)) and water (W) determined from deconvolution of MAS  $^1\text{H}$  NMR spectra.