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New hybrid Siloxane / Polysaccharides Based Sol-Gel Matrices : Synthesis and Properties.

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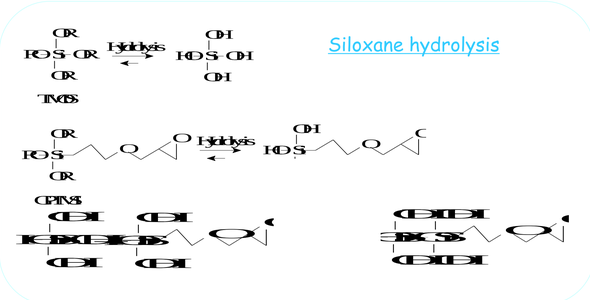
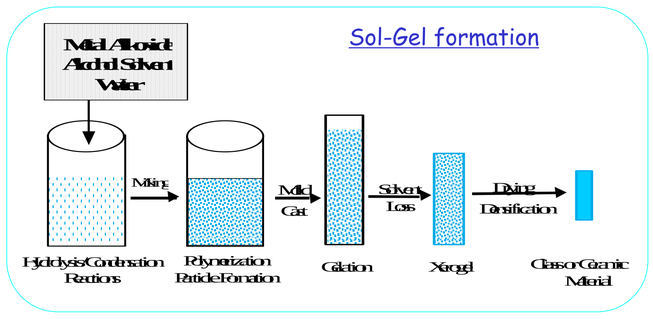
Abstract :

In this poster we present the synthesis of new hybrid materials constituted of a dual siloxane-polysaccharidic based materials by inter intertwining/cross-linking two polymeric epoxy-silane/polysaccharide based networks in aqueous solution ; using the carbohydrate framework as the building template for the siloxane polymerization.
The advantage of cross-linkable sol-gel matrices over traditional sol-gel chemistry methods are primarily the use of low temperature processing to prepare the material, the opportunity to incorporate useful organic functionality into the final matrix, modified mechanical properties and partial and adjustable biodegradability.
Depending on the starting silanes and polysaccharides these gels are cross-linked in a number of ways, to produce materials with unique, innovative and potentially valuable properties.

Aim and Scope :

The aim of this project was to demonstrate the feasibility of hybrid Polysaccharide-Siloxane sol-gel materials and study their properties and characteristics.





Introduction:

The Inorganic Materials Research Laboratory of the Department of Chemistry & Material Science Program at Trent University Ontario Canada is specialized in the synthesis of silicon -based polymeric matrices from binary or ternary combinations of alkylalkoxysilanes. After hydrolysis and condensation, these species produce water stable colloids with molecular weights of approximately 9000 to 13000 amu. Depending on the starting silane, these colloids can be crosslinked in a number of ways, as free radical or cationic cross-linking or using epoxy-diamine crosslinking, to produce materials with unique, innovative and potentially valuable properties.
The most completely explored family of materials makes use of polyamine crosslinking agents with epoxy decorated silane colloids (1,2). Other systems include a self-crosslinking two part silane system and UV curing of vinyl functionalized silanes using both free radical and cationic polymerization. The choice of crosslinking system is dependent on the conditions in which the material will be used and the type of molecular activity to be exploited within the material (3).

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The "Oligo & Polysaccharide" team of the "Polymère Fonctionnels et Réseaux" group of the "Institut de Chimie Moléculaire de Reims" has developed several unique processes for polysaccharide modification and cross-linking leading to hydrogels and material possessing innovative properties, such as gels and materials from amylaceous polysaccharides (4,5,6).

The methodology consists of selecting linear or branched polysaccharidic families according to the targeted properties and adapting the targeted properties by selective chemical or photochemical modification.

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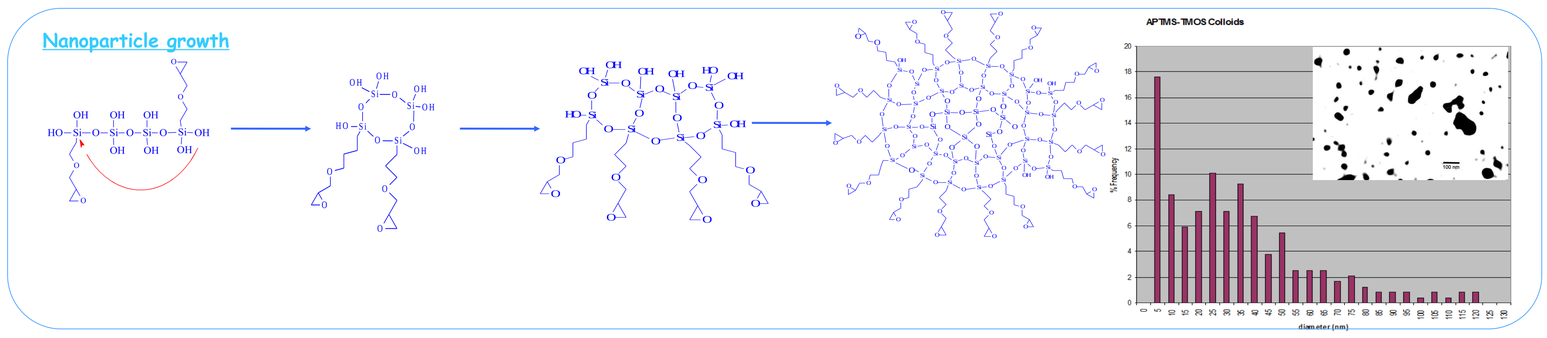

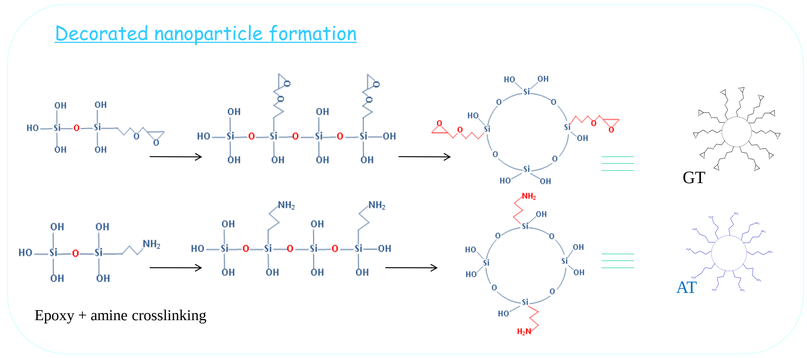

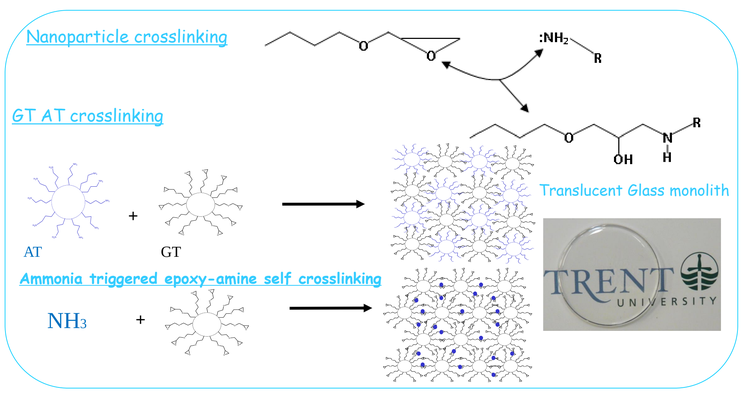

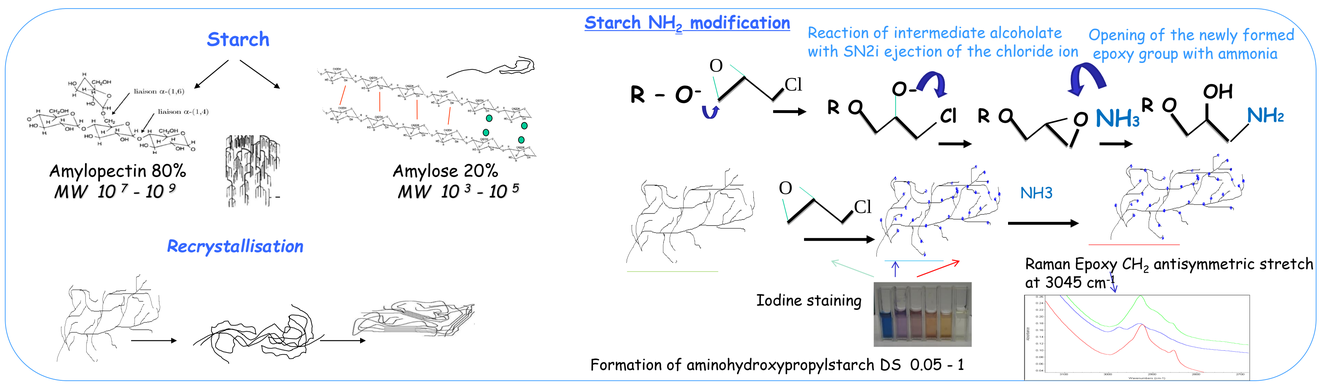

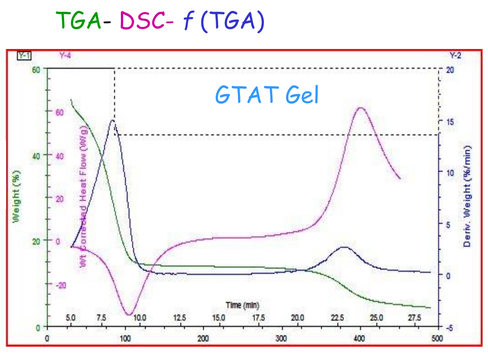

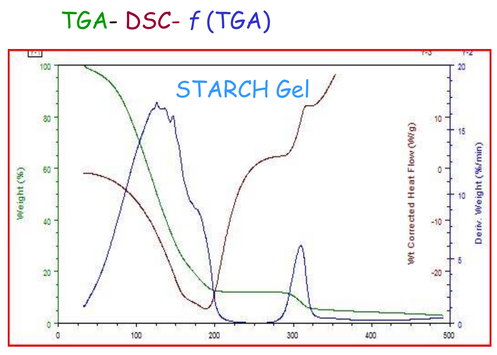

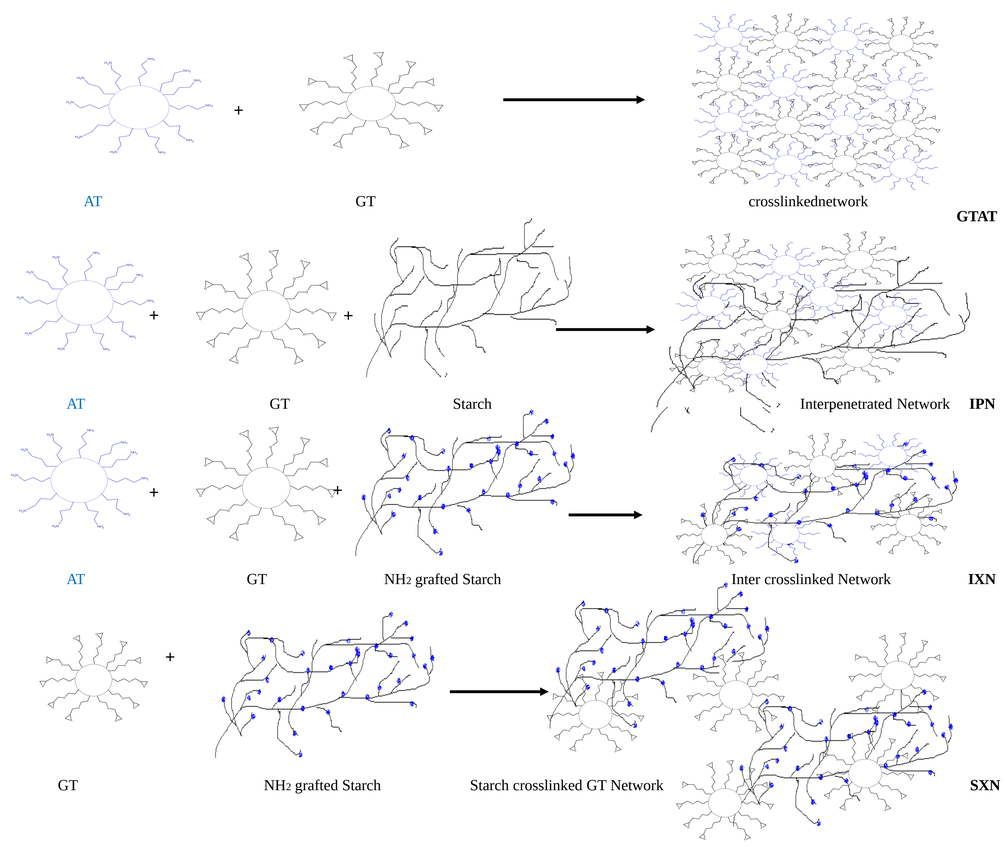

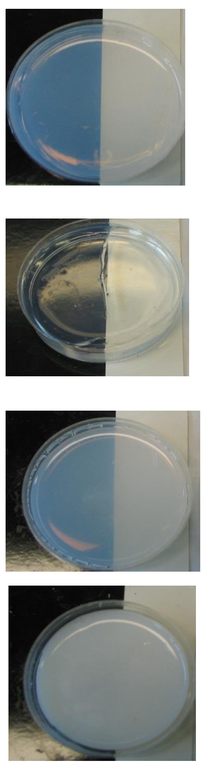

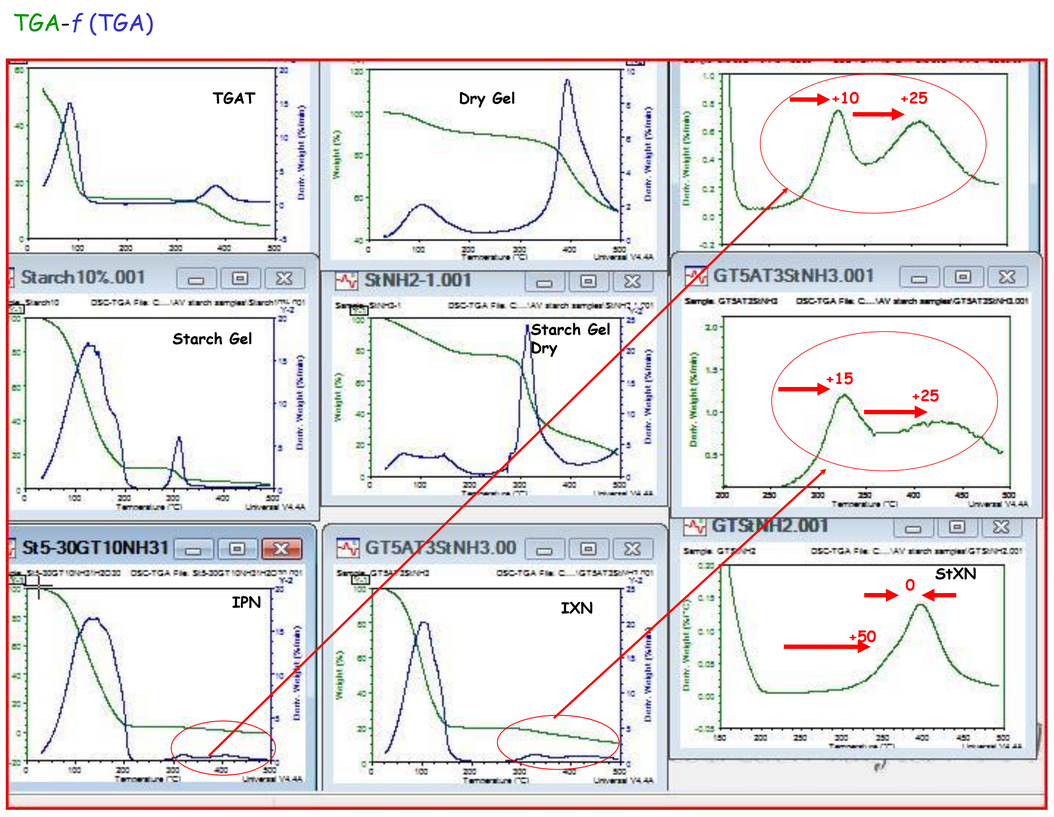

Cross-linking Results

Cross linking experiments involving simple 1-2 % soluble starch aqueous solutions combined with the silane based matrix (GT + AT) have produced some interesting changes to the mechanical properties of the resulting hybrid gel material as compared to the reference GTAT materials.
The obtained gels are from perfectly translucent to slightly turbid. In particular the starch effectively softened the material and significantly decreased the extent of shrinkage and cracking exhibited by typical sol-gel materials when drying. In this case, no particular efforts were made to chemically reinforce the starch-silane interaction and the material was largely an interpenetrating network material (IPN). Control over the explicit chemical interactions between the two components is expected to provide access to a highly tunable range of material properties and chemical environments within the system.
When starch, chemically modified with pending NH2 groups, was used in combination with GT and AT the obtained gel materials (IXN) where consistently less translucent showing a slightly larger level of visible light diffraction. When NH2 modified starch was used alone as a crosslinking substrate for GT the obtained gels where very opaque(SXN) showing a very large diffraction of visible light.

Conclusion:

We have shown that hybrid inorganic siloxane - polysaccharide gels can be readily obtained in aqueous solution ; using the polysaccharidic framework as the building pattern for the siloxane polymerization and as the crosslinker. The obtained hybrid gels display a unique behavior as far as their mechanical, thermal and physicochemical properties.

TGA Results:

Wet or dried GTAT gels undergo rapid endothermic water loss at 100° followed by an exothermic decomposition near 400° C, whereas wet or dried starch gels show a very efficient water retention until 200° C then a decomposition near 300° C. Interpenatrated GTAT- Starch hybrid networks (IPN) display the starch water retention behavior and the two decomposition peaks for GTAT and Starch with a 10° and 25° *thermoprotecting effect respectively.A similar result was obtained with intercrosslinked hybrid networks with a 15+ and 25 ° thermoprotecting effect. Interestingly in starch crosslinked GT hybrid networks (StXN) the termoprotecting effect was much larger for the starch component but negligible for GT.

Aknowledgements:

Trent Centre for Materials Research
CNRS URCA ICMR UMR6229
BSR Fdt Ontario