Packaging materials provide a barrier against water, air, grease, microbes and odor. Currently used packaging materials are petroleum-based plastic materials coated with wax and aluminum, glass, and paper. These materials have various disadvantages, they are unsustainable (metal), fragile (glass), increase cost of transportation (glass) and are not renewable (metals, coated papers).

The packaging industry is valued at around $4.6 billion currently and is projected to grow at 3% a year. Therefore there is a need to replace conventionally used, unsustainable packaging materials with completely renewable, recyclable, biodegradable packaging materials which can provide the same properties as conventionally used packaging materials.

Pure cellulose-based packaging material is unheard of since they do not have good barrier properties in the native form. All IPST there have been recent developments in the field of Nanocellulosic barrier materials. Nanocellulosic materials are composed of cellulose fibers of diameter 10-50nm and lengths up to 1000nm. These materials can be easily modified chemically and can be cast into dense coatings. Materials that offer excellent gas barrier properties while being completely renewable, biodegradable, non-toxic and stable have been developed. Additionally, they are lightweight and can help reduce transportation costs and are easily stored.

Here we present a novel method to improve the oxygen and water barrier properties of membranes made from nano cellulose fibers (MCF) via thermal annealing of the material. We report that controlled thermal exposure resulted in improvement in the barrier properties of the membranes and could be further tuned to get to extremely high barrier materials made from nano cellulose materials.

### Experimental

Nano cellulose pulp (MCF) was produced by homogenizing softwood pulp for 12 hours at a consistency of ~2.5%.

Membranes were produced by the following procedure:
1. The MCF pulp was diluted to 1%.
2. The diluted pulp was heated and stirred on a hot plate until a boil was achieved to ensure proper mixing and uniform consistency of the solution.
3. The films were then annealed in the oven for 3 hours each at temperatures, 100°C, 125°C, 150°C, 175°C.
4. After annealing the films were cut into desired shapes for testing.
5. The cut films were then placed in a 23°C/50% RH conditioning chamber for 24 hours.
6. The samples were then characterized and tested.

### Oxygen and Water Barrier

It was found that with increasing temperature, the barrier properties increased as well. The films annealed at 175°C were ca.96% less permeable for oxygen and ca.50% less permeable for water.

### Crystallinity

It was found that with increasing temperature of treatment, the crystalline structure showed marked changes indicating a gradual increase in crystallinity with increasing temperature. It was found that the size of crystallites increased by 46% in the extreme case.

### Discussion

The structure of the films shows marked changes with increase in annealing temperature. Clearly from the SEM images, it can be observed that the porous structure changes. It is also observed that the fibers which were “fibrilated” display shrinking and “zipping” or closing down of the pores and densification.

Shown above are the widely known phenomena that also occur in paper during recycling which is the shrinking of the fibers and “zipping” or closing up of pores due to thermal exposure. The reason for this phenomenon is the formation of internal hydrogen bonding between the surface –OH groups on the cellulose fibrils due to the absence of water, which these – OH groups were previously hydrogen bonding with. This causes the material to become increasingly hydrophilic as well, well indicated by both increasing contact angle and decreasing water retention value. This though is a disadvantage in the recycling industry, here is an advantage as it help reduce permeation of both oxygen and water.

Furthermore, the increasing crystallinity enhances the barrier properties. It is well known that amorphous parts of the membrane mainly contribute to permeation of fluid, while the highly ordered crystalline part contributes to prohibiting permeation. The increased crystallinity also helps with reducing both water permeation and retention since it is a hydrophobic cellulosic structure.