Comparison of *Parthenium argentatum* and *Hevea brasiliensis* rubber: Effect of non-rubber constituents on rubber intrinsic properties.

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**ABSTRACT**
Natural rubber (NR) is an indispensable polymer used to manufacture industrial products and has many exceptional features that make it as yet irreplaceable by synthetic rubber. Currently, almost all NR used in commerce comes from the hevea tree (*Hevea brasiliensis*). However, to meet the increasing demand for NR, guayule (*Parthenium argentatum*) has emerged on the market as a sustainable commercial source of high quality rubber. Guayule rubber (GR) has similarities to hevea rubber but also has unique properties. For example, it was found to be malleable at extremely cold temperatures. We aim to understand causes of this malleability to tap this potential for aerospace, cryogenic sealing, and other low temperature applications.

Non-rubber constituents play an important role in NR intrinsic properties. We conducted research on GR malleability by comparing the effect of non rubber constituents, such as protein, lipid and resin. Firstly, a film casting method was developed to obtain rubber films with a uniform thickness. Second, the physical properties were tested by dynamic mechanical analysis (DMA). Acetone solubles (lipids and resin) were found to soften the rubber and behave as plasticizers. Furthermore, removal of the rubber particle membrane (proteins and lipids) was found to affect the tensile properties of the films.

**RESULTS AND DISCUSSION**

- **GR** and **MRGNR** were found to have similar glass transition temperatures ($T_g$). These materials contain rubber and non-rubber constituents which must be contributing to the $T_g$ because the $T_g$ of the GR particle core is clearly much lower than seen here (Fig.1). The stress-strain plot of rubber films (Fig. 5) shows a stiffness decreasing sequence of NR < LMwNR < GNR < MRGNR. The weight average molar mass ($M_w$) is estimated at 1.7 x 10<sup>5</sup> g mol<sup>-1</sup> for NR, at 0.3 x 10<sup>7</sup>-2.2 x 10<sup>7</sup> g mol<sup>-1</sup> for LMwNR and at 1.33 x 10<sup>8</sup> g mol<sup>-1</sup> for GNR.

- It is well known that the longer and more branched a polymer chain is, the more entanglement can occur and, consequently, the stiffer and stronger the native polymer is (Fig.2). Thus, it is not surprising that NR is stiffer than LMwNR.

- LMwNR still appears to have higher modulus than GNR. Even assuming that GNR and LMwNR have the similar $M_w$ still LMwNR is a stronger material. This difference can be assigned to the higher amount of branch points in LMwNR than in GNR.

- MRGNR films appear to be softer than GNR films: the removal of proteins and phospholipids destroys the naturally occurring network (Fig.2), resulting in a decrease in tensile properties.

- An overall increase in the modulus is observed for all acetone-extracted (AE) samples. Acetone soluble compounds include resin, a complex mixture of terpenoids, glycerides, lipids, and pigments. Since lipids behave like plasticizers, their removal enhances the strength of the material. Still GNR-AE is softer than LMwNR-AE and NR-AE. This can be explained by the higher amount of proteins in HR compared to GNR, which participate in the branch point formation.

- MRGNR rubber contains a higher amount of acetone soluble compounds than LMwNR and NR (Table 1).

- After removal of the membrane of GNR particles, lipids and resins still appear to be present in the rubber core, and may play a role in the cryomalleable property observed (Fig. 1).

**METHODS**

MRGNR was prepared with chemical and enzymatic treatments of GNR latex. LMwNR was obtained from the soluble fraction of NR in hexane after 3h of mixing. Rubbers with acetone-soluble constituents were removed by washing 3.5 g of rubber sample with 2 x 30 ml acetone for 48h at room temperature.

**Film casting method:** 3.5 g of rubber was dissolved in ~50 ml CHCl<sub>3</sub>. The mixture was shaken for 24h, centrifuged at 3800 rpm for 10 min at 20°C. Then the films were cast in glass petri dishes (Fig.3). The thickness of the films obtained was ~0.4 mm. Films of 7 x 5.3 x 0.4 mm dimension were analyzed by DMA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acetone extract weight</th>
<th>Resin % in the sample</th>
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</thead>
<tbody>
<tr>
<td>GNR</td>
<td>0.42 g</td>
<td>12%</td>
</tr>
<tr>
<td>MRGNR</td>
<td>0.27 g</td>
<td>7.7%</td>
</tr>
<tr>
<td>NR</td>
<td>0.10 g</td>
<td>2.9%</td>
</tr>
<tr>
<td>LMwNR</td>
<td>0.23 g</td>
<td>6.5%</td>
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</tbody>
</table>

**Table 1: amount of acetone soluble recovery after extraction. acetone fraction is mainly composed of resin.**

**CONCLUSION**

The higher amount of acetone soluble compounds in MRGNR than in NR and LMwNR seems to be responsible of the softness and the malleability of MRGNR films. This result also indicates that there is still ~7.7% of lipids, resin and other acetone soluble compounds remaining in the guayule rubber core. Further experiments have to be conducted at low temperature to verify there role in cryomalleability.

**BIBLIOGRAPHY**