NOVEL POLYMERIC MATERIALS AND SUSTAINABLE TECHNOLOGIES BASED ON THE USE OF RENEWABLE RESOURCES FROM THE CENTRAL REGION OF ARGENTINA

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Outline

1. Introduction and main objectives

2. Work in progress

3. Nanocellulose as additive in drilling fluids
   3.1 Introduction
   3.2 Objectives
   3.2 Experimental and theoretical work
   3.3 Conclusions
1. Introduction
Polymeric Materials

**Challenges**

- Expand industrial activity
- Respond to market demand (quality, cost)
- Environmental regulation

**Strategies**

Use of Renewable Sources

- **Byproducts**
  - Proteins
  - Glycerol

- **Raw Materials**
  - Vegetable Oils
  - Proteins
  - Nanocelulosa

- **Industrial waste**
  - Whey
  - Furfural
  - Lignins
General objective:

✓ To develop innovative strategies for the synthesis of polymeric materials that increase the industrial/commercial value of renewable resources from economic activities in the Central Region.

Specific objectives:

✓ Chemical modification and characterization of the renewable resources.
✓ Synthesis of the materials and post-processing.
✓ Structural characterization of monomers, prepolymer and polymers.
✓ Characterization of application properties.
✓ Evaluation of the environmental impact and biodegradation.
✓ Economical analysis
3. Work in progress
Work in progress

Polyurethanes from vegetable oils

- Characterization and chemical modification of castor oil
  - Synthesis
  - Characterization
  - Environmental impact
  - Economical analysis
  - TPUs
  - Foams
  - Mechanical properties, FTIR, SEM, NMR, SEC
  - Biodegradation by different microorganisms

Lignins in phenolic resins: Production of laminates

- Activation of lignins
  - Synthesis
  - Characterization
  - Environmental impact
  - Economical analysis
  - Base resin and production of laminates
  - Mechanical properties, FTIR, SEM, water absorption
  - Replacement of phenol

Lignins in agriculture area: Controlled release applications

- Lignin characterization
  - Synthesis
  - Characterization
  - Environmental impact
  - Economical analysis
  - Microparticles
  - Size, morphology, encapsulation efficiency, release behavior
  - Leaching experiments in soil
Work in progress

Synthesis of PLA from whey

Charact. – Chem. Mod. → Synthesis → Characterization → Environmental impact → Economical analysis

→ Fermentation, extraction, purification and characterization of lactic acid from whey
→ Poly(lactic acid) → SEC, NMR, GC

Hybrid Latexes for coatings and adhesives

Charact. – Chem. Mod. → Synthesis → Characterization → Environmental impact → Economical analysis

→ Characterization and chemical modification of proteins
→ Obtention of the latexes by emulsion and miniemulsion
→ Morphol., thermal, mechanical, and optical characterization of latexes and films
→ Degradation under composting conditions

Hyaluronic acid microgels for enzymatic-triggered release of hydrophobic drugs

Charact. – Chem. Mod. → Synthesis → Characterization → Environmental impact → Economical analysis

→ Methacrylation and characterization of hyaluronic acid
→ Microgels
→ Size, morphology, encapsulation efficiency, release behavior
→ Enzymatic degradation
Work in progress

Drug release systems based on regional proteins

Charact. – Chem. Mod. → Characterization and chemical modification of casein and collagen
Synthesis → Obtention of the films and nanoformulation for medical treatments
Characterization → Morphol., thermal, mechanical, and surface charact. Load and release behavior
Environmental impact → Degradation under composting conditions
Economical analysis

Nanocellulose as additive in drilling fluids

Charact. – Chem. Mod. → Manufacturing process for production of nanocellulose
Synthesis → Preparation of water-based drilling fluids
Characterization → Rheometric, filtration, thermal and structural assays
Environmental impact → Additives from renewable and biodgradable source
Economical analysis → Additives with low cost of production
3. Nanocelululose as additive in drilling fluids
Hydrocarbon Exploitation

Conventional Reserves
Unconventional Reserves

Energy Deficit

High consumption:
- Energy
- Materials derived from petroleum

The hydrocarbons are trapped within the formation

Shale resources are globally abundant
Operation – Stages – Drilling Fluids

✓ Exploration
✓ Drilling
✓ Termination
✓ Production

Drilling Fluids

✓ Transport the cuttings to surface
✓ Control pressures
✓ Preserve wellbore stability
✓ Cool and lubricate tools
✓ Transmit hydraulic energy

Physical properties of fluids

• Rheological
  Shear thinning
  Viscosity range (40-50mPa.s)

• Filtration
  Filtrate volume
  Permeability
  Thickness of filter cake

• Others..
  Density
  Environmental behavior

Input: Drill string
Output: Drill bit
Drilling Fluids - Types

Drilling Fluids

- OBM (Oil based mud)
  - Continuous phase: oil
  - Shale inhibition
  - Thermal stability
  - Lubricity
  - Fluid-Clay interaction (wellbore instability)
  - High environmental impact

- WBM (Water based mud)
  - Continuous phase: water
  - Low environmental impact

Additional additives: polymers (PAC, XGD) and inorganics
To propose a more sustainable alternative for the design of WBMs for a shale formation with environmental and economic advantages.

To study the use of cellulose nanofibrils (CNF) from eucalyptus and birch pulps as replacement of xanthan gum (XGD) in WBMs.

- Low environmental impact
- Similar structural and physical characteristics to XGD
- Cost of XGD
### Preparation of Fluid - Base Mud Design

#### Base mud composition

<table>
<thead>
<tr>
<th>Order of Addition</th>
<th>Component</th>
<th>Dosage</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na-Bentonite</td>
<td></td>
<td>Base</td>
</tr>
<tr>
<td>2</td>
<td>Polyanionic cellulose (PAC)</td>
<td>8.00 g/L</td>
<td>Viscosifier and filtration control agent</td>
</tr>
<tr>
<td></td>
<td>Xanthan gum (XGD)</td>
<td>1.50 g/L</td>
<td>Viscosifier</td>
</tr>
<tr>
<td>3</td>
<td>D</td>
<td></td>
<td>Lubricant</td>
</tr>
<tr>
<td>4</td>
<td>E</td>
<td></td>
<td>Filtration control agent</td>
</tr>
<tr>
<td>5</td>
<td>H</td>
<td></td>
<td>pH control</td>
</tr>
<tr>
<td>6</td>
<td>I</td>
<td></td>
<td>Cuttings</td>
</tr>
</tbody>
</table>

#### Polymer Characterization

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC</td>
<td>692.000</td>
<td>1.146.000</td>
</tr>
<tr>
<td>XGD</td>
<td>881.000</td>
<td>1.622.000</td>
</tr>
</tbody>
</table>

XRD Characterization of Shale (Vaca Muerta)

\[ \text{WBM with similar rheological properties to OBM} \]
CNFs Characterization

- **Surface characterization**
  - | Sample       | ζ Potential (mV) |
  - | CNF1 (pH:7.0) | -24.7           |
  - | CNF2 (pH:7.0) | -34.7           |

- Surface charge: washing treatment (sodium form)

- **Thermal Characterization**
  - CNF2: Fully bleached pulps (0% Lignin)
  - CNF1: Unbleached pulps (5.6% Lignin)
  - Higher thermal stability of CNF2

- **Rheological Characterization**
  - CNF2: more stabilized suspension
  - CNF2: more shear-thinning behavior
CNFs Characterization

- **Morphological Characterization**
  
  - **SEM**
    
    - CNF1
    
    - CNF2
    
    - Higher degree of fibrillation in the structure for CNF2
  
  - **AFM**
    
    - CNF1
    
    - CNF2
    
    - Smaller fibril width, coarser fibrils and smaller roughness for CNF2
### Preparation of Systems: BT/CNFs/PAC/H₂O – BT/XGD/PAC/H₂O

<table>
<thead>
<tr>
<th>System: SCNF1 (BT/CNF1/PAC/H₂O)</th>
<th>System: SCNF2 (BT/CNF2/PAC/H₂O)</th>
<th>System: SXGD (BT/XGD/PAC/H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fluid</strong></td>
<td><strong>BT(%wt)</strong></td>
<td><strong>CNF1(%wt)</strong></td>
</tr>
<tr>
<td>1CNF1</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td>2CNF1</td>
<td>1.00</td>
<td>0.50</td>
</tr>
<tr>
<td>3CNF1</td>
<td>3.00</td>
<td>0.50</td>
</tr>
<tr>
<td>4CNF1</td>
<td>4.50</td>
<td>0.50</td>
</tr>
<tr>
<td>5CNF1</td>
<td>6.00</td>
<td>0.50</td>
</tr>
<tr>
<td>6CNF1</td>
<td>4.50</td>
<td>0.00</td>
</tr>
<tr>
<td>7CNF1</td>
<td>4.50</td>
<td>0.10</td>
</tr>
<tr>
<td>8CNF1</td>
<td>4.50</td>
<td>0.25</td>
</tr>
<tr>
<td>9CNF1</td>
<td>4.50</td>
<td>0.50</td>
</tr>
<tr>
<td>10CNF1</td>
<td>4.50</td>
<td>0.50</td>
</tr>
<tr>
<td>11CNF1</td>
<td>4.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Rheological Properties

- Bentonite variation
- CNF1, CNF2 or XGD variation
- PAC variation

- Shear thinning behavior
- Increase of yield stress and viscosity with composition (more noticeable for SCNF1 and SXGD)
Bentonite variation

CNF1, CNF2 or XGD variation

PAC variation

- Lower viscosity and yield stress for SNCF2
- A higher viscosifier effect of XGD
- No significant effect of PAC

- Very good predictions of Sisko Model

\[ \eta = \eta_\infty + k\dot{\gamma}^{n-1} \]
Filtration Properties

- API Filtration

Bentonite variation

CNF1, CNF2 or XGD variation

PAC variation

✓ Higher BT and PAC effect on filtering properties
✓ Better filtering properties for SCNF2
• Filter Cake

Smaller fluid loss for cakes with CNF2

Important effect of lignin (sealing the filter cake)
**Filter Cakes**

<table>
<thead>
<tr>
<th>System</th>
<th>Tc (cm)</th>
<th>q x 10^{-3} (cm³/s)</th>
<th>Kc x 10^{-3} (mD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCNF1</td>
<td>0.08 - 0.11</td>
<td>3.25 - 4.93</td>
<td>1.27 - 1.92</td>
</tr>
<tr>
<td>SCNF2</td>
<td>0.09 - 0.14</td>
<td>3.08 - 4.91</td>
<td>1.07 - 1.47</td>
</tr>
<tr>
<td>SXGD</td>
<td>0.09 - 1.13</td>
<td>3.09 - 3.73</td>
<td>0.91 - 1.13</td>
</tr>
</tbody>
</table>

✓ Increase of thickness and decrease of filtration rate with composition

✓ Similar properties for **SCNF2** and **SXGD**

✓ Filter cakes: more compact in **SCNF2**
Replacement of XGD by CNF2 in WBMs for Argentina Shale

- Rheological Properties

<table>
<thead>
<tr>
<th>Fluid</th>
<th>CXGD (%wt)</th>
<th>CPAC (%wt)</th>
<th>CNF2 (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Mud</td>
<td>0.15</td>
<td>0.80</td>
<td>----</td>
</tr>
<tr>
<td>A</td>
<td>-----</td>
<td>0.80</td>
<td>0.15</td>
</tr>
<tr>
<td>B</td>
<td>-----</td>
<td>0.80</td>
<td>0.30</td>
</tr>
<tr>
<td>C</td>
<td>-----</td>
<td>0.80</td>
<td>0.45</td>
</tr>
</tbody>
</table>

✓ Fluid with $C_{\text{CNF2}} = 2 C_{\text{XGD}}$ (Base Mud) exhibits a similar rheological behavior
Fluid with CNF2 (B) showed better thermal stability.
The system with CNF2 (BT/CNF2/PAC/H₂O) has both rheological and filtering properties similar to the XGD system (BT/XGD/PAC).

Suspensions containing CNF1 exhibited more viscosifier characteristics in WBMs, and suspensions containing CNF2 improved filtration properties.

Rheological parameters were obtained by following the Sisko model. The adjusted model can be used to obtain a better optimization of the drilling fluid composition.

Rheological properties very similar to the base mud were obtained by duplicating the composition of CNF2 in WBMs for Argentina shale. In addition, the WBMs for Argentina shale with CNF2 presented a better thermal stability.

CNF2 seems to be a viable additive in WBMs for Argentina shale.

The structural differences in dimension, shape, surfaces characteristics, rheological behavior and lignin content, between CNF1 and CNF2 produced different effects on the rheological and filtration properties of the studied fluids.
¡Thank you very much for your attention!