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Molybdenum disulphide—A traditional external lubricant that shows interesting interphase properties in pulp-based composites

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Abstract
Compression molded composites were prepared through a water-assisted mixing of an aqueous suspension of poly(ethylene-co-acrylic acid), additive, and pulp fibers [thermomechanical pulp (TMP) or dissolving pulp (DP)]. The lubricating additives used were magnesium stearate (MgSt) and molybdenum disulphide (MoS2). The composite materials had dry pulp contents ranging from 30 to 70 wt% and 5 wt% additive relative to the weight of the pulp. The adsorption of the additives onto the fibers was confirmed by scanning electron microscopy and energy dispersive X-ray analysis. DMA showed that MgSt and MoS2 gave similar interphase properties for the TMP samples at all loading contents, but the combination of MgSt and MoS2 improved the overall properties of the DP-based composites. The tensile modulus, at 70 wt% fiber content (TMP or DP), increased compared to the matrix by a factor of 6.3 and 8.1, without lubricants, and by a factor of 8 and 10.7, with lubricants, respectively. The increase in melt viscosity observed for the lubricated samples was greater for the TMP-based samples containing MoS2. At a lubricant content of 5 wt%, in 30 wt% TMP, the MoS2 behaved as both a lubricant and compatibilizer.

KEYWORDS
interphase, mechanical properties, molybdenum disulphide, thermomechanical pulp

1 | INTRODUCTION

Many efforts have been made to reduce the use of fossil-based plastics and one suggestion has been to use renewable reinforcing fibers in the plastics, preferably with a high content of this renewable source.[1,2] Although wood-polymer composites (WPCs) have been commercially available since the 1960s, they are mostly reinforced with a high loading contents of sawdust or wood powder that behave as a filler and lacks the reinforcement ability of fibers.[3] However, in the case of the fiber-reinforced composites referred to in the literature, the fiber content is usually about 30% or lower due to their higher aspect ratio.[4] Polypropylene composites with refined wood fibers are stronger than the same type of composite with wood...
In the preparation of fiber-reinforced composites, the dispersion of the lignocellulosic wood fibers in the matrix is a challenging task as the hydrophilic wood material does not disperse well in the hydrophobic polymer matrix.\cite{6} The wood fibers also have a strong tendency to self-aggregate during melt-processing, which has a negative effect on the properties of the compounded material. The higher the fiber content, the higher is the melt viscosity of the compound and increasing the fiber length increases the tendency for aggregation. Another challenge is that interfacial shear stresses can be expected to occur due to the non-uniform distribution of residual stresses because of large differences in the coefficient of thermal expansion (CTE), melt and phase transition properties and improper adhesion between the matrix and the fiber.\cite{7,8} These residual stresses can also lead to stress concentrations, inefficient load transfer, matrix cracking, and delamination. To improve the compatibility between lignocellulosic fibers and matrix, and also to improve the fiber dispersion, additives such as compatibilizers, lubricants and chemically modified fibers are used.\cite{9,10,11} To reduce the residual stresses particles of an appropriate size, nano-sized, micro-sized, can be added as spacers to improve the sliding between fiber-fiber and fiber-matrix.\cite{12,13} Lubricants can also be used; internal lubricants, often containing groups that interact with the alcohol groups in the fiber or external lubricants that primarily reduce friction between the composite and metal surfaces.\cite{14} Among the common external lubricants, molybdenum disulphide (MoS2), which has a lamellar structure, has become popular and it has been shown to interact with the aromatic structure in lignin.\cite{15,16} Among the internal lubricants, long chain carboxylic acids such as stearates that can improve the flow properties by reducing the viscosity are very common.\cite{10,17,18}

In fiber-reinforced composite materials, wet-mixing techniques have shown promising results in achieving a homogenous distribution of the fibers in the matrix,\cite{19,20} and aqueous slurries of magnesium stearate (MgSt) have been used with textile fibers.\cite{18} The mixing of fibers, matrix and additives could thus be a way to obtain homogenous mixtures for compression molding processing. A polymer with polar protic groups, such as a copolymer of poly(ethylene acrylic acid) (EAA), can form such stable dispersions, without emulsifiers, in slightly basic water.\cite{21,22} In the present study, the effect of lubricating additives on the homogeneity, viscosity and mechanical properties of fiber-containing polymer composites has been investigated. Two types of cellulose fibers were employed, dissolving pulp, DP, consisting mainly of cellulose, and thermomechanical pulp, TMP, with a high content of lignin on the surface of the fibers. As additives, MgSt, which is known to have an affinity towards cellulose, and MoS2, that has been shown to interact with aromatics, were used. It was assumed that MgSt would have a stronger affinity towards DP fibers whereas MoS2 would exhibit a stronger interaction with TMP due to lignin-MoS2 interactions. Since MoS2 is known to be an excellent solid lubricating additive, due to its two-dimensional layer structure, and since it has been shown to improve tribological properties, it has earlier been used as an additive in composites.\cite{23} An ethylene-acrylic acid copolymer, with a 15% content of acrylic acid (EAA), was used as the polymer matrix in this case. The EAA has previously been used in composites and has been shown to be compatible with cellulosic materials.\cite{19,20,24} MoS2 has, to our knowledge, not previously been used as a lubricant in lignocellulose fiber-polymer composites.

## MATERIALS AND METHODS

Thermomechanical pulp (TMP) was obtained from StoraEnso, Hyltebruk, and bleached dissolving pulp from eucalyptus, with an average degree of polymerization (DPw) of 1340, was provided by Bahia Pulp S.A., Camacari, Brazil. According to the literature, TMP has ca. 50% of polysaccharides and ca. 30%–35% lignin.\cite{25,26} According to the fiber analysis, the mean fiber length, fiber width and fines content were 3.2 mm, 35 μm and 33%, respectively, for the TMP, and 0.8 mm, 11 μm and 24%, respectively, for the DP. The poly (ethylene-co-acrylic acid) (EAA) copolymer was obtained from BIM Kemi AB, Sweden in the form of an aqueous dispersion with a pH of 9.7 and a solids content of 20 wt%. The poly(ethylene-co-acrylic acid) dispersion contained Na+ as a result of the dispersion preparation process\cite{27} and according to the supplier, the acrylic acid content of the polymer was 15% and it had a melting point of 88°C, a density of 0.994 g/cm³ and a melt flow rate of 36 g/10 min (ISO 1133, 190°C, 2.16 kg). Molybdenum disulphide (MoS2) and magnesium stearate (MgSt) were obtained from Sigma Aldrich. According to the supplier, MoS2 was not exfoliated and had a density of 5.06 g/ml and the particle size was less than 2 μm and the Mg stearate had a density of 1.026 g/cm³ and a melting point of 200°C.

### 2.1 Manufacture of the composites

The composites were produced as described by Venkatesh et al.\cite{19} The pulp (TMP or DP), the EAA dispersion and an additive (MgSt or MoS2) were mixed in different proportions as indicated in Table 1. The amount of lubricating additive added to the composite was 1.5, 2.5, and 3.5 wt% for 30, 50, and 70 wt% pulp samples, respectively (5% lubricant with respect to the total pulp content). Samples reinforced with 30 wt% TMP and DP containing a lubricant
content equivalent to 5 wt% (16% lubricant with respect to the total pulp content), were also manufactured. The mixtures had a solids content of 3–4 wt% in deionized water and were mixed at room temperature in a L&W pulp disintegrator (Lorentzen & Wettre) for 60,000 revolutions at 2900 rpm. After mixing, the samples were dried at room temperature and 12 g of the dried material was compression molded at 105°C into square plates of 100 × 100 mm² in size with a thickness of about 1 mm using a Bucher-Guyer KHL 100, Switzerland. A pressure of 40 bar was applied initially, allowing for pre-heating, until the distance between the mold halves had stabilized, which took about 2 min. The pressure was then raised to 500 bar for 1 min and the sample was then cooled under high pressure to 28°C, which took 5 min. The pressure was then released, and the sample removed from the mold.

### Table 1 Composition of the composite samples with different weight percentages of pulp, additive and EAA

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Pulp (wt%)</th>
<th>Additive (wt%)</th>
<th>EAA (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMP, DP</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>EAA</td>
<td>0</td>
<td>0.5</td>
<td>99.5</td>
</tr>
<tr>
<td>EAA-MoS₂</td>
<td>0</td>
<td>1.5</td>
<td>98.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>EAA-MgSt</td>
<td>0</td>
<td>0.5</td>
<td>99.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>98.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>TMP30, DP30</td>
<td>30</td>
<td>0</td>
<td>70</td>
</tr>
<tr>
<td>TMP50, DP50</td>
<td>50</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>TMP70, DP70</td>
<td>70</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>TMP30-MgSt, DP30-MgSt</td>
<td>30</td>
<td>1.5</td>
<td>68.5</td>
</tr>
<tr>
<td>TMP30-MgSt</td>
<td>30</td>
<td>5</td>
<td>65</td>
</tr>
<tr>
<td>TMP50-MgSt, DP50-MgSt</td>
<td>50</td>
<td>2.5</td>
<td>47.5</td>
</tr>
<tr>
<td>TMP70-MgSt, DP70-MgSt</td>
<td>70</td>
<td>3.5</td>
<td>26.5</td>
</tr>
<tr>
<td>TMP30-MoS₂, DP30-MoS₂</td>
<td>30</td>
<td>1.5</td>
<td>68.5</td>
</tr>
<tr>
<td>TMP30-MoS₂</td>
<td>30</td>
<td>5</td>
<td>65</td>
</tr>
<tr>
<td>TMP50-MoS₂, DP50-MoS₂</td>
<td>50</td>
<td>2.5</td>
<td>47.5</td>
</tr>
<tr>
<td>TMP70-MoS₂, DP70-MoS₂</td>
<td>70</td>
<td>3.5</td>
<td>26.5</td>
</tr>
<tr>
<td>DP30-MgSt + MoS₂, TMP30-MgSt + MoS₂</td>
<td>30</td>
<td>0.75 + 0.75</td>
<td>68.5</td>
</tr>
<tr>
<td>TMP30-2.5 (MgSt + MoS₂)</td>
<td>2.5 + 2.5</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>DP50-MgSt + MoS₂, TMP50-MgSt + MoS₂</td>
<td>50</td>
<td>1.25 + 1.25</td>
<td>47.5</td>
</tr>
</tbody>
</table>

2.2 | Fiber analysis

The fiber length and width were determined as the mean values of approximately 25,000 to 30,000 fibers, according to the Tappi standard T271 using a Kajaani FS300 fiber analyzer (Metso Automation, Finland), based on the centerline length. No significant changes of the fiber dimensions are expected due to the processing method used.[19]

2.3 | Thermal gravimetric analysis (TGA)

The onset of thermal degradation of EAA and of the composites was determined using a TGA/DSC 3 + Star system (Mettler Toledo, Switzerland). The specimens (about 6 mg) were subjected to a heating ramp of 10°C/min between 25 and 500°C under nitrogen at a flow rate of 20 ml/min.

2.4 | Differential scanning calorimetry (DSC)

The thermal transitions and the crystallinity of the materials were assessed using a Mettler Toledo DSC2 calorimeter equipped with a HSS7 sensor and a TC-125MT intercooler. The endotherms were recorded while the temperature was increased from 25 to 160°C at a scan
rate of 10°C/min with a nitrogen flow of 50 mL/min. The degree of crystallinity (X_c) was calculated as

\[ X_c = \frac{\Delta H_c}{w_{EAA} \Delta H_o} \]

where \( \Delta H_c \) is the specific heat of fusion of the composite, \( w_{EAA} \) the weight fraction of the matrix and \( \Delta H_o \) the specific heat of fusion of 100% crystalline polyethylene; 277.1 J/g.[28]

2.5 | Field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX)

The surface morphology of pulp fibers was imaged using a Field Emission Scanning Electron Microscope (SEM—FEI Quanta 200 FEG ESEM) using an acceleration voltage of 10 kV. Since the samples were not conductive, each sample was attached to a carbon tape and a low pressure, 0.2–1 bar, was applied in the chamber. Micrographs were taken before and after the compression molding. After the compression molding, the samples were cryo-fractured to examine the fracture surfaces and to identify the elemental composition using energy dispersive X-ray analysis.

2.6 | Rheological properties

The shear viscosity of the 30 wt% composite melts was determined as a function of shear rate using an Anton Paar MCR 702 rheometer (Graz, Austria) with parallel plate geometry (15 mm plate diameter) at 170°C. The disk-shaped samples, with a thickness of 1.0–1.5 mm, were gradually squeezed to set a plate gap of 1 mm. A shear rate range of 0.01–10 s⁻¹ was achieved using this geometry due to the high melt viscosity.

2.7 | Tensile testing

Tensile test bars with a gauge length of 20 mm were cut from the compression molded plates and kept in a conditioned environment at 25°C and 55% relative humidity for at least 3 days prior to the tensile tests. The tensile properties (Young’s modulus, stress at break and elongation at break) were measured at room temperature with a strain rate of 2.5 × 10⁻³ s⁻¹ (6 mm/min) using a Zwick/ Z2.5 tensile tester with a grip-to-grip separation of 40 mm and a load cell of 2 kN. The reported values are the averages of five independent measurements.

2.8 | Dynamic-mechanical analysis (DMA)

The dynamic-mechanical properties of the TMP- and DP-reinforced composites were assessed in order to evaluate the effect of the lubricants on the composites and to obtain a qualitative understanding of the properties of the interphase region between the matrix and the reinforcement. The variation of the mechanical loss factor (\( \tan \delta \)) relative to the loss factor of the matrix with increasing strain amplitude can be used to assess the adhesion between matrix and reinforcement in terms of the presence of an interphase.[29] The dynamic-mechanical properties were measured using a Rheometrics RSA II at room temperature (25°C) at a frequency of 1 Hz, using a procedure similar to that used by Forsgren et al.[30] where the samples were pre-strained in tension by about 0.15% which was kept constant during the measurements and subjected to a sinusoidal deformation with a strain amplitude which was increased from about 0.009% to 0.14%.

2.9 | Impact strength of notched Izod specimens

The impact strength of notched Izod specimens was measured according to ISO 180 in a Testing Machines Tinius Olsen, model 92T plastics impact tester with a 0.936 kg pendulum. Results are the averages for six specimens of each data set.

3 | RESULTS

3.1 | Thermal and mechanical properties of the composites

Table 2 shows, the average onset temperatures and crystallinity of each of the samples. The addition of reinforcements and additives reduced the onset temperatures of the composites. As expected, the DP-based composites, which mainly contained cellulose, showed a higher thermal stability when compared to the TMP-based composites.[31] Additionally, the presence of additives in the samples reduced the thermal stability of the samples more than that of the un lubricated samples and this has been observed in other polyolefin based systems too.[32] Interestingly, only the TMP based samples containing MoS₂, at lower concentrations, (5% of total pulp fraction) exhibited a thermal stability similar to that of the additive free samples and this could probably be related to its
interaction with the aromatic structures of lignin in the TMP. However, with increasing lubricant content (16 wt % of total pulp fraction), the first onset temperature reduced to 266°C for the TMP based samples. For most of the samples, the extent of changes between the reinforced samples were not significant due to the heterogeneity of the samples and the overlapping standard deviations. The DSC analysis of the matrix in the composites do not show any significant difference in the crystallinity of the samples and this result is typical of EAA-based samples reinforced with cellulose reinforcements.[19,33]

The addition of the cellulose fibers increased the tensile modulus of the composite by a factor of 8.1 with TMP and by a factor of 6.3 for the DP at the highest loading content of 70 wt%, the addition of lubricant further increased the tensile modulus by a factor of 10.7 for the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus (GPa)</th>
<th>Stress at break (MPa)</th>
<th>Elongation at break (%)</th>
<th>Izod impact strength (kJ/m²)</th>
<th>T_onset (°C)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMP</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>290 (3)</td>
<td>—</td>
</tr>
<tr>
<td>DP</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>312 (6)</td>
<td>—</td>
</tr>
<tr>
<td>EAA</td>
<td>0.3 (0.1)</td>
<td>24 (1)</td>
<td>491 (20)</td>
<td>—</td>
<td>450 (4)</td>
<td>19</td>
</tr>
<tr>
<td>EAA-TMP30</td>
<td>1.4 (0.1)</td>
<td>28 (2)</td>
<td>4 (1)</td>
<td>6 (1)</td>
<td>282 (4); 441 (4)</td>
<td>18</td>
</tr>
<tr>
<td>EAA-TMP30-MgSt</td>
<td>1.5 (0.1)</td>
<td>35 (2)</td>
<td>5 (1)</td>
<td>7 (1)</td>
<td>279 (3); 441 (4)</td>
<td>17</td>
</tr>
<tr>
<td>EAA-TMP30-MoS2</td>
<td>1.2 (0.1)</td>
<td>33 (1)</td>
<td>6 (1)</td>
<td>8 (1)</td>
<td>285 (2); 437 (4)</td>
<td>18</td>
</tr>
<tr>
<td>EAA-TMP30-MgSt+MoS2</td>
<td>1.2 (0.1)</td>
<td>33 (3)</td>
<td>5 (3)</td>
<td>10 (1)</td>
<td>282 (4); 437 (4)</td>
<td>16</td>
</tr>
<tr>
<td>EAA-TMP30-5MgSt</td>
<td>1.4 (0.1)</td>
<td>32 (3)</td>
<td>4 (0.1)</td>
<td>7 (1)</td>
<td>274 (2); 445 (4)</td>
<td>17</td>
</tr>
<tr>
<td>EAA-TMP30-5MoS2</td>
<td>1.6 (0.1)</td>
<td>39 (1)</td>
<td>5 (0.1)</td>
<td>11 (2)</td>
<td>278 (2); 446 (3)</td>
<td>16</td>
</tr>
<tr>
<td>EAA-TMP30-2.5 (MgSt + MoS2)</td>
<td>1.3 (0.1)</td>
<td>27 (3)</td>
<td>3 (0.4)</td>
<td>7 (2)</td>
<td>266 (2); 440 (2)</td>
<td>17</td>
</tr>
<tr>
<td>EAA-TMP50</td>
<td>2.2 (0.03)</td>
<td>38 (1)</td>
<td>3 (1)</td>
<td>—</td>
<td>279 (4); 436 (4)</td>
<td>17</td>
</tr>
<tr>
<td>EAA-TMP50-MgSt</td>
<td>1.7 (0.08)</td>
<td>30 (5)</td>
<td>3 (1)</td>
<td>—</td>
<td>275 (1); 445 (4)</td>
<td>17</td>
</tr>
<tr>
<td>EAA-TMP50-MoS2</td>
<td>1.8 (0.3)</td>
<td>29 (3)</td>
<td>3 (1)</td>
<td>—</td>
<td>281 (5); 438 (2)</td>
<td>18</td>
</tr>
<tr>
<td>EAA-TMP50-MgSt+MoS2</td>
<td>1.6 (0.3)</td>
<td>27 (4)</td>
<td>3 (1)</td>
<td>—</td>
<td>280 (2); 439 (2)</td>
<td>17</td>
</tr>
<tr>
<td>EAA-TMP70</td>
<td>2.4 (0.4)</td>
<td>33 (11)</td>
<td>3 (1)</td>
<td>—</td>
<td>288 (3); 363 (9)</td>
<td>18</td>
</tr>
<tr>
<td>EAA-TMP70-MgSt</td>
<td>2.9 (0.4)</td>
<td>32 (6)</td>
<td>2 (1)</td>
<td>—</td>
<td>283 (3); 445 (4)</td>
<td>17</td>
</tr>
<tr>
<td>EAA-TMP70-MoS2</td>
<td>3.1 (0.1)</td>
<td>31 (6)</td>
<td>3 (1)</td>
<td>—</td>
<td>287 (4); 441 (3)</td>
<td>18</td>
</tr>
<tr>
<td>EAA-DP30</td>
<td>0.6 (0.06)</td>
<td>22 (1)</td>
<td>12 (1)</td>
<td>10 (1)</td>
<td>293 (4); 443 (3)</td>
<td>18</td>
</tr>
<tr>
<td>EAA-DP30-MgSt</td>
<td>0.6 (0.03)</td>
<td>22 (1)</td>
<td>12 (1)</td>
<td>8 (1)</td>
<td>287 (2); 446 (3)</td>
<td>17</td>
</tr>
<tr>
<td>EAA-DP30-MoS2</td>
<td>0.5 (0.02)</td>
<td>18 (1)</td>
<td>23 (2)</td>
<td>9 (2)</td>
<td>287 (1); 445 (3)</td>
<td>18</td>
</tr>
<tr>
<td>EAA-DP30-MgSt+MoS2</td>
<td>0.8 (0.1)</td>
<td>28 (5)</td>
<td>13 (3)</td>
<td>11 (1)</td>
<td>274 (4); 441 (3)</td>
<td>19</td>
</tr>
<tr>
<td>EAA-DP50</td>
<td>1.2 (0.06)</td>
<td>39 (3)</td>
<td>10 (1)</td>
<td>—</td>
<td>293 (1); 445 (3)</td>
<td>19</td>
</tr>
<tr>
<td>EAA-DP50-MgSt</td>
<td>1.3 (0.2)</td>
<td>36 (3)</td>
<td>7 (1)</td>
<td>—</td>
<td>292 (3); 444 (2)</td>
<td>19</td>
</tr>
<tr>
<td>EAA-DP50-MoS2</td>
<td>1.0 (0.07)</td>
<td>32 (1)</td>
<td>11 (1)</td>
<td>—</td>
<td>290 (3); 443 (3)</td>
<td>18</td>
</tr>
<tr>
<td>EAA-DP50-MgSt+MoS2</td>
<td>1.3 (0.2)</td>
<td>41 (4)</td>
<td>7 (1)</td>
<td>—</td>
<td>288 (2); 445 (2)</td>
<td>18</td>
</tr>
<tr>
<td>EAA-DP70</td>
<td>1.9 (0.1)</td>
<td>48 (4)</td>
<td>5 (1)</td>
<td>—</td>
<td>300 (3); 445 (2)</td>
<td>18</td>
</tr>
<tr>
<td>EAA-DP70-MgSt</td>
<td>2.3 (0.2)</td>
<td>35 (1)</td>
<td>5 (1)</td>
<td>—</td>
<td>293 (2); 444 (2)</td>
<td>17</td>
</tr>
<tr>
<td>EAA-DP70-MoS2</td>
<td>2.0 (0.1)</td>
<td>43 (4)</td>
<td>6 (1)</td>
<td>—</td>
<td>292 (3); 444 (2)</td>
<td>18</td>
</tr>
</tbody>
</table>
TMP-based samples with MoS₂, and by a factor of 8 for the
DP-based samples with MgSt. These results can be com-
pared to those reported by Venkatesh et al.[19] where the
tensile modulus of a composite reinforced with approxi-
mately 80 wt% highly beaten never-dried bleached softwood
in the same EAA matrix, was increased by a factor of 16.3.
The pulp fibers used in their study had however a lower li-
gnin content (1.9 wt%) and they may have been fibrillated
during the beating process.

Without additive, see Table 2, the TMP-reinforced sam-
ples showed an increase in the stress-at-break from 24 MPa
to 28 MPa at 30 wt% and to 38 MPa at 50 wt% TMP, but a
further increase in TMP content to 70 wt% resulted in a
decrease in strength to 33 MPa. On the other hand, the DP-
based samples showed an increase in strength at a content
higher than 50 wt%. The stress at break increased from
24 MPa to 39 MPa at 50 wt% and 48 MPa at 70 wt% DP
content. The elongation at break was drastically reduced
when either TMP or DP was added, from 491% to 4% and
12% at 30 wt% TMP and DP, respectively. In case of the
30 wt% TMP-containing composites the addition of MgSt
increased the tensile modulus, the stress-at-break, the elon-
gation at break and the impact strength from 1.4 GPa,
28 MPa, 4.1% and 6 kJ/m² to 1.5 GPa, 35 MPa, 5% and
7 kJ/m², respectively, and the addition of MoS₂ at the same
fiber content of 30 wt% led to an increase in stress at break,
toughness, and elongation at break to 33 MPa, 8 kJ/m² and
6%, respectively. As expected, the addition of the lubricant
increased the ductility of the composites, and at 30 wt% the
MgSt-containing and MoS₂-containing samples behaved in
a fairly similar manner.

However, when both these lubricants were added
together to the DP30 and TMP30 composites, the impact
resistance increased further suggesting an influence on
the competition between fiber breakage and interfacial failure,
which is a factor that determines the impact behavior of a
composite material.[34] The impact strength of the TMP30
composites increased from 6 kJ/m² to 7, 8, and 10 kJ/m²
when MgSt, MoS₂ and MgSt + MoS₂, respectively, were
added. However, the impact strength of the DP30 comos-
des decreased from 10 kJ/m² to 8 and 9 kJ/m² with the
addition of MgSt and MoS₂, respectively. However, when
both the lubricants were added the impact strength dis-
played a minor increase by 1 kJ/m².

At higher loadings of TMP or DP, the addition of MgSt
and MoS₂ reduced the stress-at-break. This was most promi-
nent with 50 wt% TMP where the strength decreased from
38 MPa to approximately 30 MPa. In this case, the tensile
modulus decreased from 2.2 GPa to 1.7 GPa in the presence
of a lubricant. At 70 wt% TMP content, despite the increase
in tensile modulus from 2.4 GPa to 2.9 GPa and to 3.1 GPa
with MgSt and MoS₂, respectively, there were no significant
changes in the strength-at-break and elongation-at-break of
the composites. When both Mg-stearate and MoS₂ were
added to the 30 and 50 wt% TMP samples, no increase in
either in the strength-at-break and elongation-at-break of
the composites was observed.

The addition of MgSt and MoS₂ for the DP-containing
composites resulted in a reduced stress-at-break at all filler
contents except when both the lubricants were added,
where it increased to 28 MPa and 41 MPa, respectively, at
30 and 50 wt% DP. On the other hand, the tensile modulus
increased with the addition of MgSt at all loading contents,
whereas the elongation-at-break was unchanged (except for
the 50 wt% DP sample where it was reduced from 10% to
7%) whereas the addition of MoS₂ led to an increase in the
elongation-at-break from 12% to 23% at 30 wt% DP and by
1% for the 50 and 70 wt% DP, see Table 2.

The addition of a lubricant was beneficial for the
mechanical properties of the TMP-based samples at lower
loadings, 30 wt%, but their effect on the DP-based sam-
A FIGURE 1 Mechanical loss factor as a function of applied
strain amplitude for composites containing 30 wt%, 50 wt%, and
70 wt% (A) TMP and (B) DP
ples was poor, especially in the case of MoS₂, unless they
were added in combination. For the DP-based samples containing MoS$_2$, at 30 and 50 wt%, the elongation-at-break was significantly greater than that of the corresponding samples with MgSt as additive or of those without any additive. This may be because the MoS$_2$ particles interact only weakly with cellulose, but act as spacers reducing the direct contact/interaction between fiber and matrix and improving the sliding between fiber-fiber and fiber-matrix, as reported by Tong et al.\textsuperscript{[23]}

The TMP30 samples with the lubricants added separately showed the greatest overall improvement in the mechanical properties. When MgSt was added to these samples the tensile modulus and strength respectively decreased from 1.5 GPa and 35 MPa at a lubricant content of 1.5 wt% to 1.4 GPa and 32 MPa at a lubricant content of 5 wt%, but, when MoS$_2$ was used as the lubricant, the tensile modulus and strength respectively increased from 1.2 GPa and 32 MPa at a lubricant content of 1.5 wt % to 1.6 GPa and 39 MPa, at a lubricant content of 5 wt%. When both the lubricants were added together (2.5 wt%
MgSt and 2.5% wt% MoS2) the values however were lower than that of the TMP30 without additive. The samples with 5 wt% lubricant showed a small decrease in the elongation-at-break for all the samples, whereas the impact strength increased to 11 kJ/m2 with MoS2 and decreased to 7 kJ/m2 with MgSt and with both lubricants. TMP30 samples with MoS2 exhibited increased mechanical properties, supporting the hypothesis that the dispersion and interphase between the TMP and the matrix are improved due to an interaction between the lignin and MoS2.

3.2 Dynamic mechanical analysis (DMA)

Figure 1 shows the mechanical loss factor (tan δ) as a function of the strain amplitude of the sinusoidal deformation applied to the composite. The addition of either TMP or DP leads to a steeper slope of the tan δ with increasing strain amplitude indicating a weaker interphase due to a poor adhesion between the phases that promotes friction losses during the imposed sinusoidal deformation. The TMP-based composites exhibited a better interphase region up to 50 wt% loading comparable to some extent with the tensile properties given in Table 2. At higher TMP contents, the smaller proportion of EAA resulted in a poorer interphase region and greater increase in the slope of tan δ with increased strain amplitude. In Figure 3(B), the slope of the tan δ for the 70 wt% DP sample increased with increasing strain amplitude whereas tan δ for the 30 and 50 wt% DP sample appears to exhibit a plateau up to a certain strain amplitude after which an increase in the slope of the tan δ was observed.

The properties of the composites containing TMP and lubricants are illustrated in Figure 2. Except for the samples containing MgSt, the 30 wt% TMP composites containing lubricants and their combinations exhibited a tan δ...
dependence on the strain amplitude similar to that of the sample without lubricant, suggesting a rather stable interphase region. The MgSt-containing sample showed an initial plateau up to a certain strain amplitude after which a marked increase in the slope of the $\tan \delta$ was observed suggesting that the interphase region was more stable than that of the other composites at low strain amplitudes. In Figure 2(B) (70 wt% TMP), the slopes remained similar to each other with increasing strain amplitude, suggesting a rather poor interphase region, as expected due to the small proportion of EAA with loadings of 70 wt%.

In Figure 3, the effect of lubricant concentration on the mechanical loss factor of the TMP30 composite is shown. When the MgSt concentration was increased from 1.5 wt% to 5 wt% in the TMP30 composite, the $\tan \delta$ slope and the initial plateau observed at lower strain amplitudes at a lubricant concentration of 1.5 wt% was not visible. These results agree with the mechanical properties in Table 2 which showed a reduction in the overall mechanical performance with increasing lubricant concentration in the composite. When the MoS$_2$ concentration was increased, a plateau was observed at higher strain amplitudes which was not present with 1.5 wt% MoS$_2$. The relatively more stable interphase agreed with the increase in the mechanical properties observed.

Figure 4 shows the results when DP was added to the EAA matrix. The combination of lubricants in the 30 wt% sample clearly had a positive impact where the variation in the slope of the $\tan \delta$ was similar to that of the matrix up to a certain strain after which the slope increased. The interphase region in this case was better than that of the DP30, DP30MgSt, and DP30MoS$_2$ samples, contributing to the increase in mechanical properties given in Table 2. A similar behavior was observed for the 50 wt% DP samples, with
both the lubricants, where the loss factor had a plateau at low strain amplitudes followed by a tan $\delta$ slope comparable to that of the other samples; both of which displayed better mechanical properties than the other 50 wt% DP samples.

### 3.3 Melt rheology

Figure 5 shows the steady-state shear viscosity at 170°C of the 30 wt% TMP and DP samples with and without lubricants across a shear rate range of 0.01–10 s$^{-1}$. A shear thinning behavior was first observed and the addition of TMP or DP led to an expected increase in the melt viscosity compared to that of the unfilled matrix. For the TMP30-containing composites, the sample with MoS$_2$ and that with a combination of MoS$_2$ and MgSt showed the highest melt viscosity, but the magnitude of the increase was slightly less with MgSt than with MoS$_2$. The higher melt viscosity of the samples containing lubricants suggests an improved interaction between the fibers and the matrix, which has also been observed in composites where the lubricants tend to behave as compatibilizers at low contents.$^{[13,35]}$

The higher viscosity of the TMP-based samples containing MoS$_2$ may be due to the ability of MoS$_2$ to interact with the aromatic structure of the lignin present in the TMP.$^{[15]}$ In case of the DP-based samples, which have a negligible lignin content, the addition of MoS$_2$ showed no variation in the melt viscosity and it behaved more like a lubricant. In case of the DP30 samples, however, the MgSt behaved more like a compatibilizer and led to an increase in the viscosity although the magnitude of the increase was smaller than that of the TMP30-based samples with MoS$_2$. In both the TMP30 and DP30...
samples, the viscosity of the composites was highest with both the lubricants indicating a synergetic effect.

The increase in viscosity suggests that the concentration of the lubricant was too low for the lubricating effect to be observed. The effect of a higher concentration of lubricant was therefore explored to assess whether such an increase had a lubricating effect. An initial study of the pure EAA matrix with different amounts of additives revealed that the viscosity of the EAA melt decreased at concentrations of lubricants as low as 0.5% as shown in Figure 6(A) (MgSt values not shown as they overlap with those of the MoS2). In the presence of the TMP fibers, however, the lubricants behaved like a compatibilizer at low concentrations and had a lubricating effect at higher concentrations.\[13,35\] When the MgSt content was increased to 5 wt% in the TMP30-containing composite, the viscosity profile was same as that of the samples containing 1.5 wt% MgSt. With 5 wt% MoS2, a slight reduction in the viscosity was observed, as shown in Figure 6(B). At higher shear rates, all the curves coincided with the curve for the EAA. In case of the MoS2-containing TMP30-based samples, the reduction in viscosity was low, but the MoS2 behaved as both a lubricant and a compatibilizer at a concentration of 5 wt%, reinforcing the hypothesis that MoS2 interacted strongly with the lignin in TMP and that an excess of MoS2, which does not interact with the lignin, provides a lubricating effect.

3.4 Field emission scanning electron microscopy (FESEM) and energy dispersive X-ray analysis (EDX)

In order to study the effect of additives on the pulp fibers, scanning electron micrographs of the fibers and additives without the matrix were captured. Samples with 95 wt% of pulp (DP or TMP) and 5 wt% of an additive (MgSt or MoS2) were prepared and micrographs in Figures 7 and 8, show a smoother fiber surface in the presence of the lubricants with the TMP-based samples but not with the DP-based samples where the fibers appear to be the same in all cases. The EDX analysis of the samples confirmed that the additives were adsorbed onto the fibers. In the case of the TMP fibers containing MgSt, Figure 7(A), Mg was detected at the position which exhibited a higher intensity of carbon, suggesting that both Mg and carbon-rich molecules such as alkanes are present and that MgSt was adsorbed onto the TMP samples (more details can be found in the supporting information). For the DP samples, the adsorption of MgSt was less clear. The mappings of Mo and S coincide in both Figures 7(B) and 8(B) confirming the presence of MoS2. The Mo and S peaks had a higher intensity in the TMP sample indicating a greater adsorption of MoS2 to TMP than to DP, which is in agreement with an earlier report that MoS2 adsorbs onto aromatic systems like graphene and lignin.\[15\] The samples based on TMP were much easier to analyze and the micrographs of the EAA-TMP30 composites in Figure 9 show the effect of the additives in the composites where the samples with lubricants (at a concentration of 1.5 wt%) have a more compact structure.

4 Conclusion

The wet adsorption of MgSt and MoS2 to pulp fibers is an efficient method to coat the fibers with a lubricant additive. Both MgSt and MoS2 had a positive impact on the mechanical properties of the composites. The greatest increase in the tensile modulus of the composites was
noted for the TMP70-MoS2 and DP70-MgSt samples. The lubricant-containing samples also exhibited an increase in viscosity, at a concentration of 1.5 wt%, in the 30 wt% TMP-based and DP-based samples, presumably due to the improved interactions and fiber dispersion. At the higher lubricant concentration of 5 wt%, in the TMP30 samples, only the MoS2 behaved as both a lubricant and a compatibilizer, showing an increase in tensile properties with a relatively lower melt viscosity. The composition of the fibers determined the effectiveness of the lubricant in the composites, the MoS2 being more efficient with the TMP-based samples while MgSt behaved similarly with both the TMP-based and DP-based samples. The adsorption of MgSt and MoS2 was confirmed through EDX analysis, and the scanning electron micrographs showed that the lubricants formed a layer on the surface of the pulp fibers, more evident on the TMP, through the strategic innovation program BioInnovation, a joint venture by Vinnova, Formas and the Swedish Energy Agency. Thanks are due to Professor Mikael Hammar, A. Peterson, C. Müller, A. Boldizar, C. Müller, J. Thunberg, A. Ström, R. Rojas, M. Andersson, L. A. Berglund, J. M. Rodriguez, J. M. Gess, J. Kogovsek, M. Remškar, Wear 2012, 280–281, 36. https://doi.org/10.1016/j.wear.2012.01.011

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