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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 1960's, 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

Seyedehsan Hosseini and Abhijit Venkatesh contributed equally to this study.

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flour.^[5] 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.^[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.^[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.^[9–11] 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.^[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.^[14] Among the common external lubricants, molybdenum disulphide (MoS_2), which has a lamellar structure, has become popular and it has been shown to interact with the aromatic structure in lignin.^[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.^[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,^[19,20] and aqueous slurries of magnesium stearate (MgSt) have been used with textile fibers.^[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.^[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 cellulosic 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 MoS_2 , that has been shown to interact with

aromatics, were used. It was assumed that MgSt would have a stronger affinity towards DP fibers whereas MoS_2 would exhibit a stronger interaction with TMP due to lignin- MoS_2 interactions. Since MoS_2 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.^[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.^[19,20,24] MoS_2 has, to our knowledge, not previously been used as a lubricant in lignocellulose fiber-polymer composites.

2 | MATERIALS AND METHODS

Thermomechanical pulp (TMP) was obtained from StoraEnso, Hyltebruk, and bleached kraft dissolving pulp from eucalyptus, with an average degree of polymerization (DP_w) 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.^[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^[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 (MoS_2) and magnesium stearate (MgSt) were obtained from Sigma Aldrich. According to the supplier, MoS_2 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.^[19] The pulp (TMP or DP), the EAA dispersion and an additive (MgSt or MoS_2) 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

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

Sample designation	Pulp (wt%)	Additive (wt%)	EAA (wt%)
TMP, DP	100	0	0
EAA	0		100
EAA-MoS ₂	0	0.5	99.5
		1.5	98.5
		5	95
EAA-MgSt	0	0.5	99.5
		1.5	98.5
		5	95
TMP30, DP30	30	0	70
TMP50, DP50	50	0	50
TMP70, DP70	70	0	30
TMP30-MgSt, DP30-MgSt	30	1.5	68.5
TMP30-5MgSt		5	65
TMP50-MgSt, DP50-MgSt	50	2.5	47.5
TMP70-MgSt, DP70-MgSt	70	3.5	26.5
TMP30-MoS ₂ , DP30-MoS ₂	30	1.5	68.5
TMP30-5MoS ₂		5	65
TMP50-MoS ₂ , DP50-MoS ₂	50	2.5	47.5
TMP70-MoS ₂ , DP70-MoS ₂	70	3.5	26.5
DP30-MgSt + MoS ₂ , TMP30-MgSt + MoS ₂	30	0.75 + 0.75	68.5
TMP30-2.5 (MgSt + MoS ₂)		2.5 + 2.5	65
DP50-MgSt + MoS ₂ , TMP50-MgSt + MoS ₂	50	1.25 + 1.25	47.5

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.

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 ΔH_c is the specific heat of fusion of the composite, w_{EAA} the weight fraction of the matrix and ΔH_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 unlubricated 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

TABLE 2 Mechanical properties, thermal onset temperatures (T_{onset}) and crystallinity of the TMP-based and DP-based composites with EAA as matrix. Standard deviations in parentheses

Sample	Young's modulus (GPa)	Stress at break (MPa)	Elongation at break (%)	Izod impact strength (kJ/m ²)	T_{onset} (°C)	Crystallinity (%)
TMP	—	—	—	—	290 (3)	
DP	—	—	—	—	312 (6)	
EAA	0.3 (0.1)	24 (1)	491 (20)	— — — —	450 (4)	19
EAA-TMP30	1.4 (0.1)	28 (2)	4 (1)	6 (1)	282 (4); 441 (4)	18
EAA-TMP30-MgSt	1.5 (0.1)	35 (2)	5 (1)	7 (1)	279 (3); 441 (4)	17
EAA-TMP30-MoS ₂	1.2 (0.1)	33 (1)	6 (1)	8 (1)	285 (2); 437 (4)	18
EAA-TMP30-MgSt + MoS ₂	1.2 (0.1)	33 (3)	5 (3)	10 (1)	282 (4); 437 (4)	16
EAA-TMP30-5MgSt	1.4 (0.1)	32 (3)	4 (0.1)	7 (1)	274 (2); 445 (4)	17
EAA-TMP30-5MoS ₂	1.6 (0.1)	39 (1)	5 (0.1)	11 (2)	278 (2); 446 (3)	16
EAA-TMP30-2.5 (MgSt + MoS ₂)	1.3 (0.1)	27 (3)	3 (0.4)	7 (2)	266 (2); 440 (2)	17
EAA-TMP50	2.2 (0.03)	38 (1)	3 (1)		279 (4); 436 (4)	17
EAA-TMP50-MgSt	1.7 (0.08)	30 (5)	3 (1)		275 (1); 445 (4)	17
EAA-TMP50-MoS ₂	1.8 (0.3)	29 (3)	3 (1)		281 (5); 438 (2)	18
EAA-TMP50-MgSt + MoS ₂	1.6 (0.3)	27 (4)	3 (1)		280 (2); 439 (2)	17
EAA-TMP70	2.4 (0.4)	33 (11)	3 (1)		288 (3); 363 (9)	18
EAA-TMP70-MgSt	2.9 (0.4)	32 (6)	2 (1)		283 (3); 445 (4)	17
EAA-TMP70-MoS ₂	3.1 (0.1)	31 (6)	3 (1)		287 (4); 441 (3)	18
EAA-DP30	0.6 (0.06)	22 (1)	12 (1)	10 (1)	293 (4); 443 (3)	18
EAA-DP30-MgSt	0.6 (0.03)	22 (1)	12 (1)	8 (1)	287 (2); 446 (3)	17
EAA-DP30-MoS ₂	0.5 (0.02)	18 (1)	23 (2)	9 (2)	287 (1); 445 (3)	18
EAA-DP30-MgSt + MoS ₂	0.8 (0.1)	28 (5)	13 (3)	11 (1)	274 (4); 441 (3)	19
EAA-DP50	1.2 (0.06)	39 (3)	10 (1)		293 (1); 445 (3)	19
EAA-DP50-MgSt	1.3 (0.2)	36 (3)	7 (1)		292 (3); 444 (2)	19
EAA-DP50-MoS ₂	1.0 (0.07)	32 (1)	11 (1)		290 (3); 443 (3)	18
EAA-DP50-MgSt + MoS ₂	1.3 (0.2)	41 (4)	7 (1)		288 (2); 445 (2)	18
EAA-DP70	1.9 (0.1)	48 (4)	5 (1)		300 (3); 445 (2)	18
EAA-DP70-MgSt	2.3 (0.2)	35 (1)	5 (1)		293 (2); 444 (2)	17
EAA-DP70-MoS ₂	2.0 (0.1)	43 (4)	6 (1)		292 (3); 444 (2)	18

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 cellulosic reinforcements.^[19,33]

The addition of the cellulosic 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

TMP-based samples with MoS₂, and by a factor of 8 for the DP-based samples with MgSt. These results can be compared to those reported by Venkatesh et al.^[19] where the tensile modulus of a composite reinforced with approximately 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 lignin content (1.9 wt%) and they may have been fibrillated during the beating process.

Without additive, see Table 2, the TMP-reinforced samples 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 elongation 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 composites 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 displayed 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 prominent 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

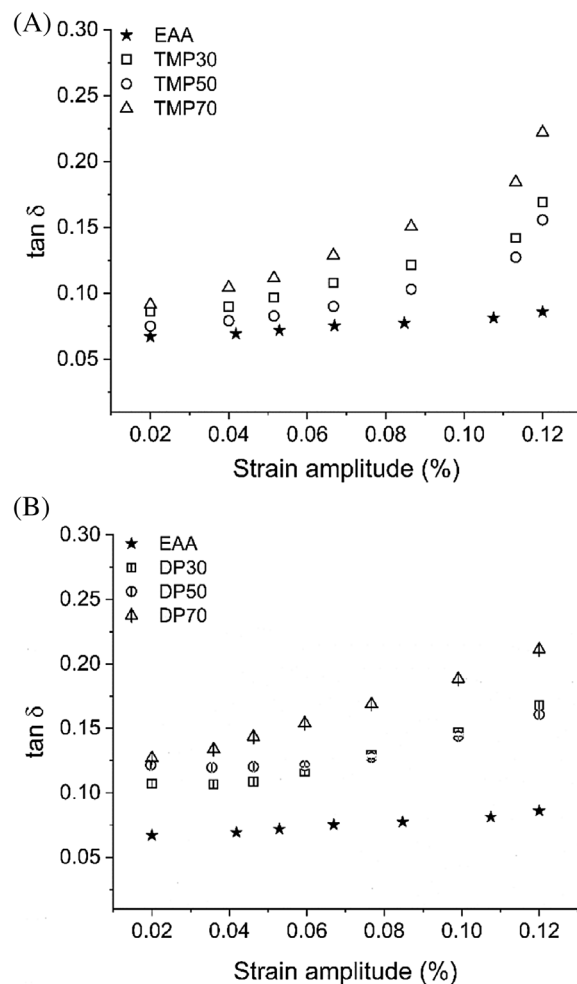


FIGURE 1 Mechanical loss factor as a function of applied strain amplitude for composites containing 30 wt%, 50 wt%, and 70 wt% (A) TMP and (B) DP

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 samples was poor, especially in the case of MoS₂, unless they

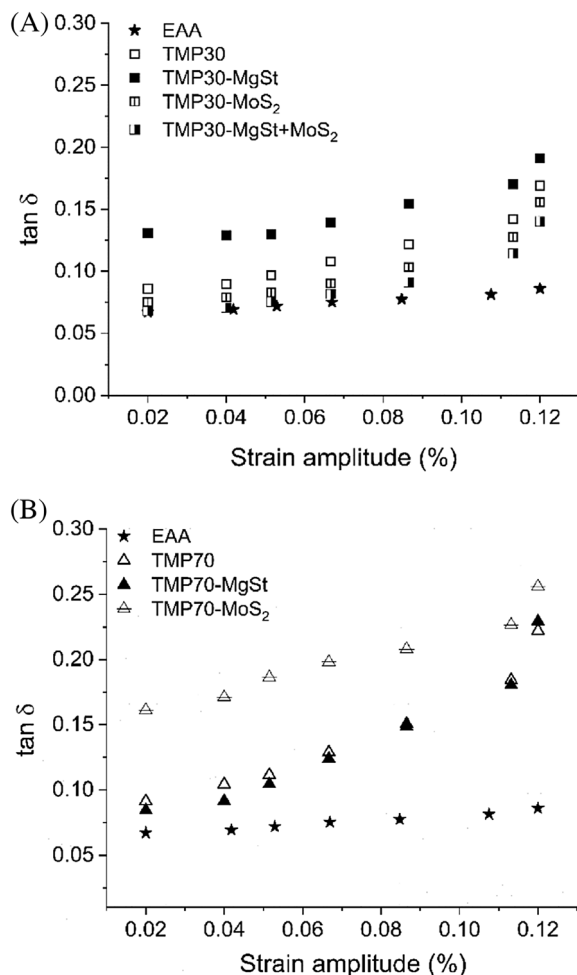


FIGURE 2 Mechanical loss factor as a function of applied strain amplitudes for (A) 30 wt% and (B) 70 wt% TMP samples containing MgSt and/or MoS₂

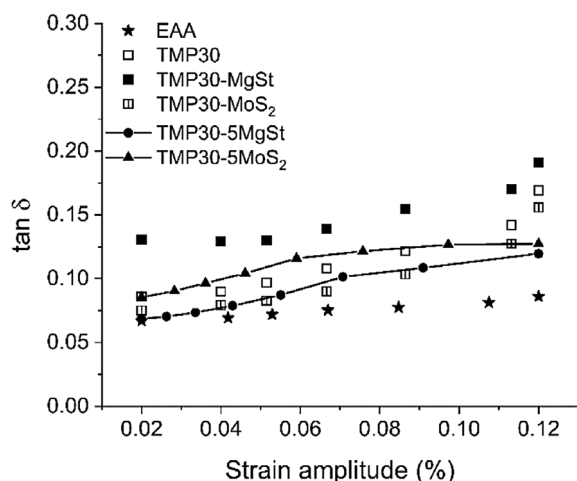


FIGURE 3 The mechanical loss factor as a function of applied strain amplitude for 30 wt% TMP samples containing different amounts of MgSt and MoS₂

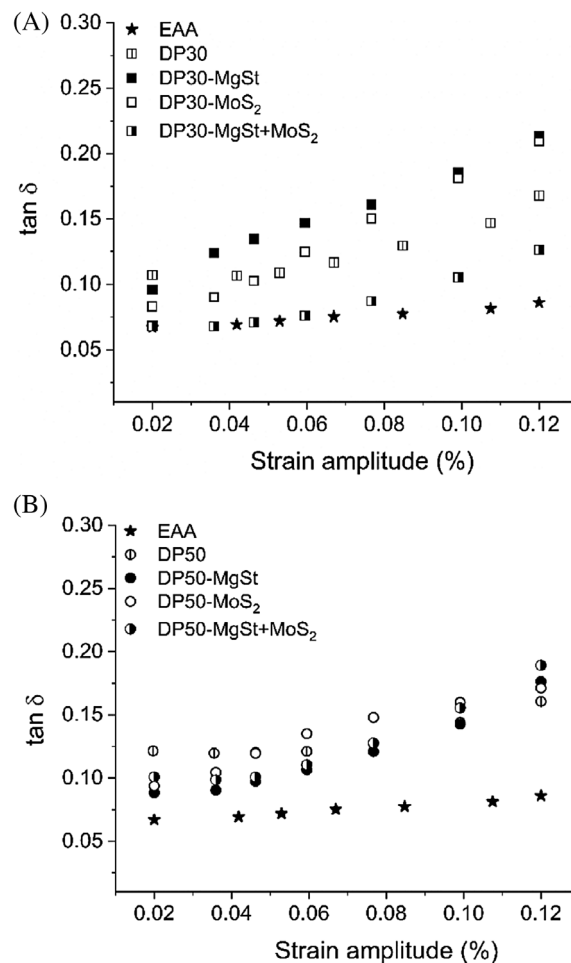


FIGURE 4 The mechanical loss factor as a function of applied strain amplitude for (A) 30 wt% and (B) 50 wt% DP samples containing MgSt and/or MoS₂

were added in combination. For the DP-based samples containing MoS₂, 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 MoS₂-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.^[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 MoS₂ 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%

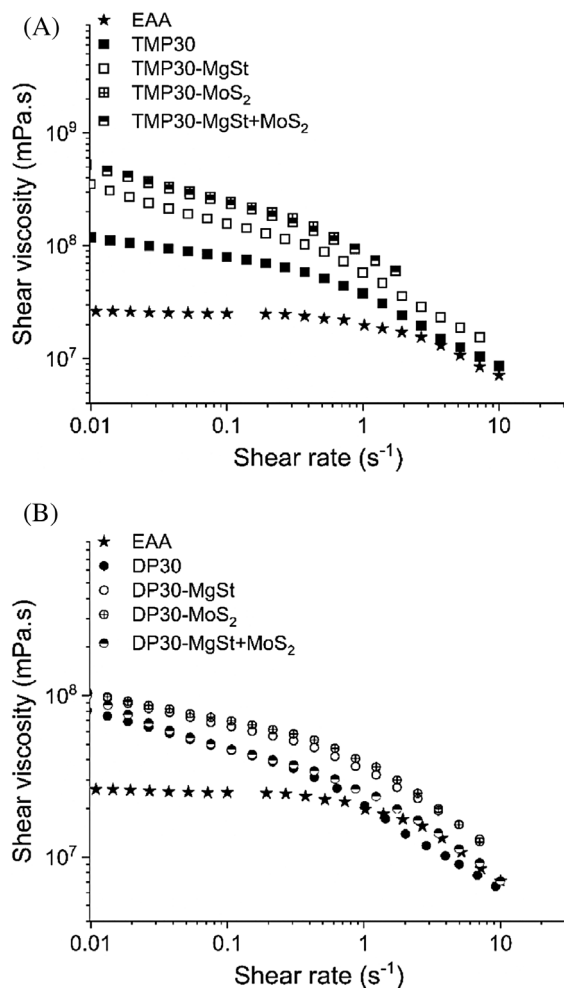


FIGURE 5 The shear viscosity as a function of shear rate for (A) 30 wt% TMP-containing and (B) 30 wt% DP-containing composites with and without lubricants

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 ($\tan \delta$) as a function of the strain amplitude of the sinusoidal deformation applied to the composite. The addition of either TMP or DP

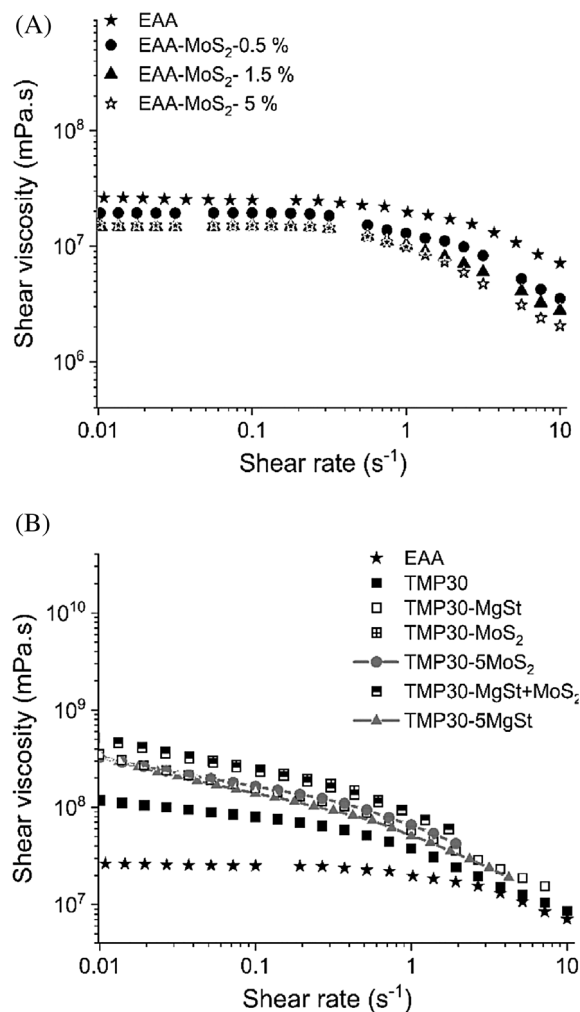
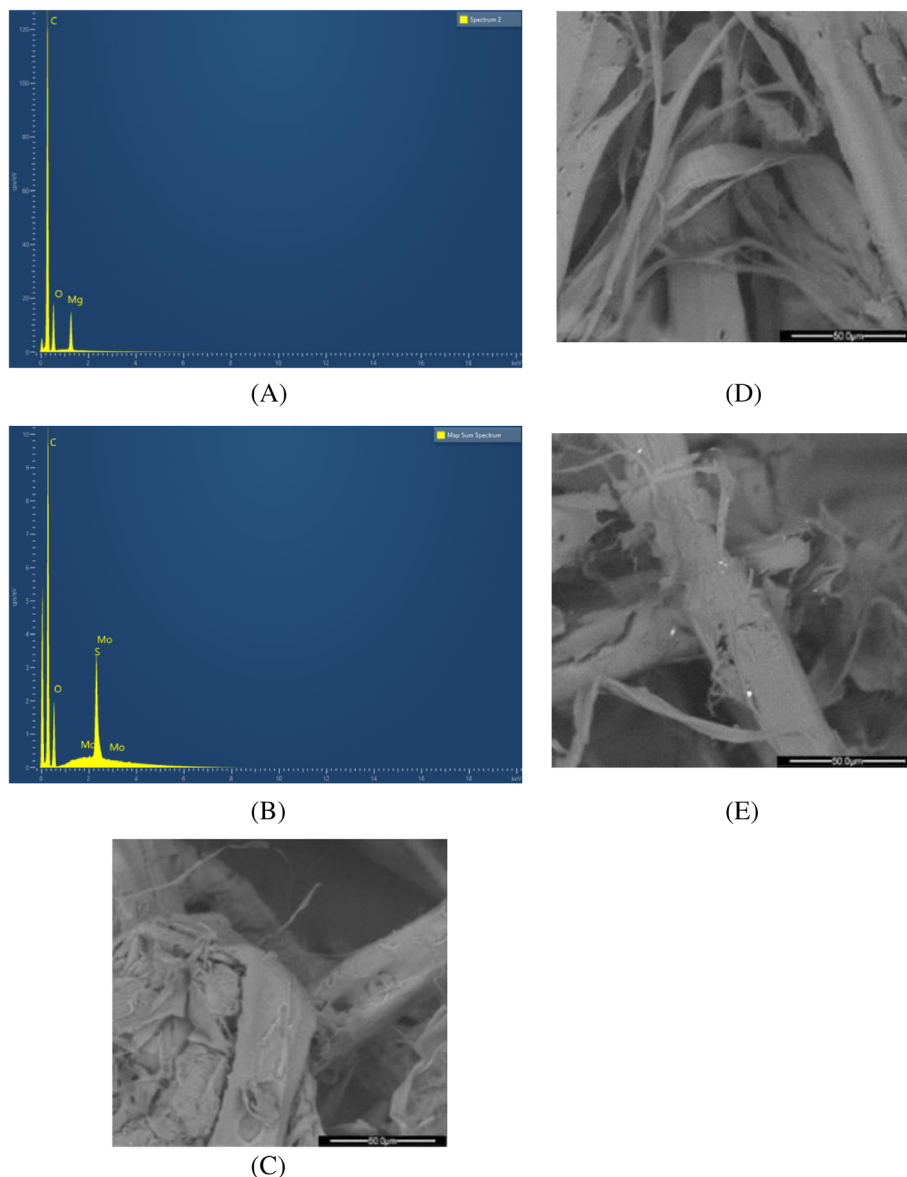


FIGURE 6 The viscosity as a function of shear rate for (A) EAA samples containing 0.5, 1.5, and 5 wt% of MoS₂, and (B) 30 wt% TMP samples with and without lubricants

leads to a steeper slope of the $\tan \delta$ 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.^[29,30] 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 $\tan \delta$ with increased strain amplitude. In Figure 3(B), the slope of the $\tan \delta$ for the 70 wt% DP sample increased with increasing strain amplitude whereas $\tan \delta$ 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 $\tan \delta$ 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 $\tan \delta$

FIGURE 7 EDX analysis of (A) 95 wt% TMP + 5 wt% MgSt and (B) 95 wt% TMP + 5 wt% MoS₂, showing the map sum spectrum and scanning electron micrographs of (C) TMP fibers; (D) 95 wt% TMP + 5 wt% MgSt; (E) 95 wt% TMP + 5 wt% MoS₂, at a magnification of 800×



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 MoS₂ concentration was increased, a plateau was observed at higher strain amplitudes which was not present with 1.5 wt% MoS₂. 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 DP30MoS₂ samples, contributing to the increase in mechanical properties given in Table 2. A similar behavior was observed for the 50 wt% DP samples, with

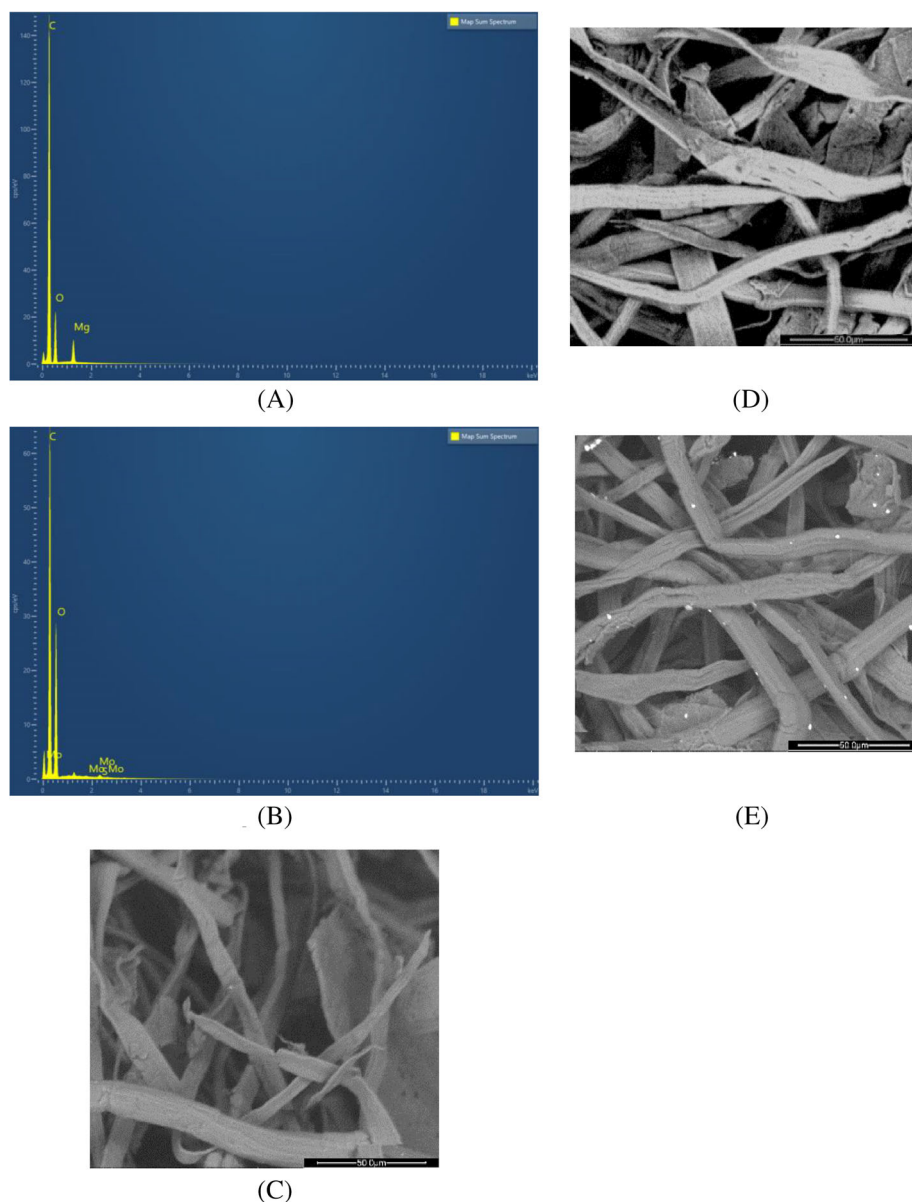


FIGURE 8 EDX analysis of (A) 95 wt% DP + 5 wt% MgSt and (B) 95 wt% DP + 5 wt% MoS₂, showing the map sum spectrum and scanning electron micrographs of (C) DP fibers; (D) 95 wt% DP + 5 wt% MgSt; (E) 95 wt% DP + 5 wt% MoS₂, at a magnification of 800×

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 MoS₂ and that with a combination of MoS₂ and MgSt showed the highest melt viscosity, but the magnitude of the increase

was slightly less with MgSt than with MoS₂. 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 MoS₂ may be due to the ability of MoS₂ 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 MoS₂ 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 MoS₂. In both the TMP30 and DP30

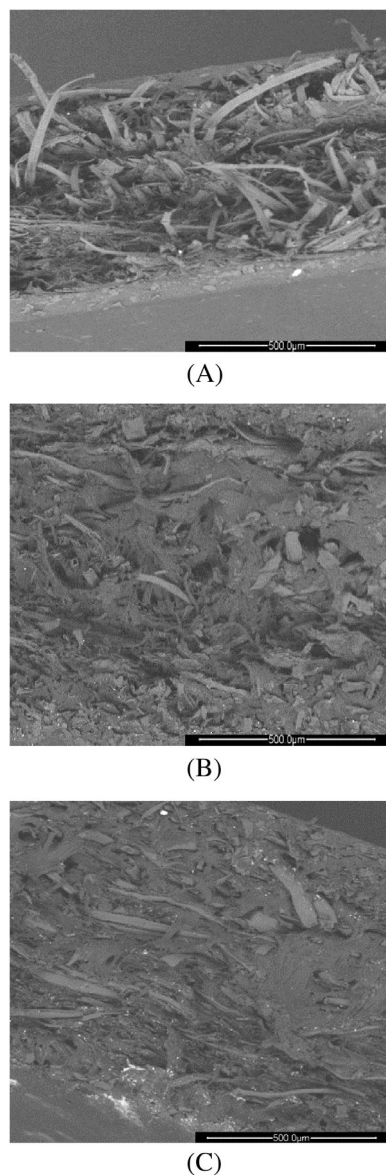


FIGURE 9 Scanning electron micrographs of (A) TMP30; (B) TMP30-MgSt; (C) TMP30-MoS₂, at a magnification of 115×

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 however 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, which made the surface smoother and the composite structure more compact. The observation that MoS₂ had quite a strong effect on the interphase region in TMP-containing composites, presumably due to the presence of aromatic structures, may be important when tailoring the flow properties of the corresponding melts for large-scale melt processing methods such as extrusion. The lubricant concentration, type of lubricant and fiber composition determine whether the lubricant behaves as a compatibilizer, as a lubricant or as a combination of both.

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