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Alkyl ketene dimer modification of thermomechanical pulp promotes processability with polypropylene

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Abstract

Alkyl ketene dimers (AKDs) are known to efficiently react with cellulose with a dual polarity in their structure: a polar component and a nonpolar component. AKD of three different carbon chain lengths, 4, 10, and 16 carbons have been synthesized, and thermomechanical pulp (TMP) fibers were modified by them. The modification of TMP fibers with AKD resulted in an increased water contact angle, showing the presence of the AKDs on the TMP fibers and a new carbonyl peak in the IR spectra, suggesting modification of the TMP fibers with AKD groups. Calculating the Hansen solubility parameters of AKD and AKD conjugated to TMP in polypropylene (PP) indicates improved compatibility, especially of longer chain AKD and TMP AKD. The rheological studies of the composites showed that the AKD with the longest carbon chain decreases the melt viscosity of the PP-TMP-AKD composite, which combined with the shape and the color of the extruded composite filaments indicates improved flow properties and reduced stress build up during processing. The research findings demonstrate the ability of AKD to enhance the dispersibility and compatibility of natural fibers with PP.

KEYWORDS

alkyl ketene dimer, composite, extrusion, polypropylene, rheology, thermomechanical pulp

1 | INTRODUCTION

Climate change, reduction of fossil fuel sources, and increased nondegradable waste are reasons for replacing, or partly replacing, synthetic polymers.[1,2] Natural fibers are harnessed for their attributes encompassing nontoxicity, light weight, cost-effectiveness, and wide spectrum of typologies, thus engendering diverse application possibilities.[3] Wood is a renewable, easily accessible and inexpensive resource that has been used by humankind for thousands of years. It has various properties, such as high

stiffness and strength and low weight.[4] Wood powder, sawdust and thermomechanical pulp (TMP) are some of the cheapest processed materials when timber is converted to products; they can all be competitive in price relative to existing plastics. In the production of TMP fibers, unlike chemical pulps, that use a chemical refining procedures, a steam pressurized method is utilized, enhancing the efficiency of the pulping process.[5] This unique method not only contributes to cost-effectiveness, positioning TMP as an economical choice, but also establishes a more environmentally friendly production pathway by minimizing the

utilization of chemical agents. Indeed, WPCs have been commercial products since the 1960s. They are mostly reinforced with sawdust or wood powder to a maximum of 70 wt%.[6] Composite materials composed of natural fibers from wood or other sources find utility across diverse sectors, including the automotive, medical, and packaging industries.[7]

Decision-making frameworks has been proposed to be used to rank both the matrix polymer[8] and source of natural fiber.[9] The optimal choice of polymer matrix and or fiber, varied based on application However, polypropylene (PP) has been shown to be a favorable polymer matrix, for a range of natural fibers.[8] PP is cost-effective, and is used in a range of products, for example household items, packaging and textiles.[8,10] PP is a recyclable thermoplastic material with low-processing temperature,[8] high-temperature resistance[11] and can be processed through various techniques such as injection molding, extrusion, and compression molding.[12] The ease of processing PP extends to composite manufacturing, making it feasible to produce natural fiber composites.

Addition of TMP to PP enables an increase in tensile strength of PP, with maximum reinforcement upon the addition of 40–50 wt% TMP.[13] Two explanations for the reduced strength at higher than 40–50 wt% of TMP are: poor dispersion of fibers[14] and/or high-melt viscosity.[15] One major challenge with TMP and other fibers is that they tend to agglomerate and entangle during processing, resulting in low-bulk density and nonflow behavior in the extrusion process.[6,16,17] Natural fiber content of 50 wt% in natural fiber-PP composites, can lead to an increased presence of voids and observed fiber pullout. This phenomenon is attributed to heightened brittleness of the fibers, resulting in compromised bonding between the fiber and polymer matrix.[18]

An often-suggested route to overcome the above challenges rely on increasing the compatibility between matrix and filler. Indeed, choosing a fiber with a high-tensile strength, such as jute, does not translate to the overall strength of the composite unless compatibility between matrix and filler has been achieved.[19] In general, the surface of natural-based fibers is more hydrophilic than the commonly used polyolefins, making compounding during the process and transfer of mechanical stress of the final composite material poor.[20–23] The investigation demonstrates that PP composites utilizing various types of natural fibers without any modification such as hay, lemon, and palm exhibit a reduction in tensile strength, particularly evident when the fiber loading surpasses the range of 20–30 wt%.[24] Improved compatibility between fiber and matrix can be obtained by adding a compatibilizer to the thermoplastic polymer phase or modifying the surface of the fiber. Maleic anhydride grafted polypropylene (MAPP) is a common compatibilizer used for wood-thermoplastic composites. MAPP is usually added to the matrix, but can also be added to the fibers;[25] it increases the compatibility between fiber and matrix through hydrogen bonding or esterification between the maleic anhydride and the hydroxyl groups on the fibers.[26,27] Compared to nonlignin containing fibers,[25,27–29] MAPP is less effective as a compatibilizer between TMP and PP. This is due to the presence of lignin on the TMP surface.

Different modifications could be made to further improve the usage of fibers. One example is modifying cellulose microfibers with a coating based on polydopamine and octadecylamine,[30] resulting in improved dispersibility in PP. Another example of improving the dispersibility of fibers in PP involves modifying bleached TMP, after co-precipitation of layered double hydroxide particles with sodium dodecyl sulphate.[31] Urea- and phenol-formaldehyde increases the tensile strength of TMP hand-sheets and PP films,[32] similar to maleic anhydrate and benzoyl peroxide, and is taken as an indication of improved compatibility between TMP and PP.[33] TMP modified with benzoyl or lauroyl shows good melt and process properties when used as a composite.[34]

Alkyl ketene dimer (AKD) is one of the most commonly used sizing agents in papermaking,[35,36] used to control hydrophobicity/hydrophilicity of fibers in the pulp and paper industry. The addition of AKD to fiber–PP composites has been studied in kraft pulp-PP sheet[37] and red algae fiber-PP composites.[38] AKD treatment resulted in weaker fiber interactions in the sheets, due to covering of the hydrophilic cellulose surface. This is explained by compatibilized surface energies between the components; cellulose and PP.[37] Adding AKD to red algae fibers was also proposed as a mean of increasing its compatibility with PP matrix, as indicated by the increased storage modulus of the composite upon the addition of AKD.[38] The results from the studies performed by Quillin and co-workers, suggest that AKD exhibits the potential to enhance dispersibility and compatibility of wood-based fibers in PP matrix. However, studies were done with processing units not relevant for composite materials. In addition, no study has, as far as the authors are aware, investigated the effect of AKD carbon chain length on compatibility and processability of TMP, AKD and PP composites.

We have used AKD of three different carbon chain lengths, with the Hansen solubility parameters (HSP) calculated for these samples. The rheological properties of the PP-TMP AKD melts were characterized, and the mechanical properties of the extruded and hot-melt compressed PP-TMP AKD materials were determined.

2 | MATERIALS AND METHODS

2.1 | Materials

The TMP used was made from *Picea abies* (Norway spruce), kindly provided by Stora Enso Hyltebruk, Sweden. Fiber analysis of the TMP, performed using a Kajaani FS300, gave a respective mean fiber length, width and fines distribution of 3.2 mm, 35 μm, and 3%.[39] According to the literature, TMP has 50 wt% of polysaccharides and ca. 30%–35 wt% lignin.[40] The PP used in the study had a melt flow rate of 100 g/min, density of 0.902 g/ml, melting point of 160°C, M_w of 137.2 kD, M_n of 26.4 kD, and polydispersity of 5.2.

Hexanoyl chloride, lauryl chloride, stearoyl chloride, triethylamine, butyl acetate, diethyl ether, formamide, ethylene glycol, and polyethylene glycol were purchased from Sigma Aldrich, Sweden. All chemicals were used as received.

2.2 | Synthesizing AKD molecules from fatty acid chlorides

Triethylamine was dissolved in butyl acetate in a round-bottomed flask. A stoichiometric amount of fatty acid chloride (stearoyl chloride, lauryl chloride, or hexanoyl chloride) relative to triethylamine was dissolved in butyl acetate in a beaker, and then added dropwise to the round-bottomed flask while stirring. After the whole amount of fatty acid chloride had been added, the reaction temperature was set at 45°C for 2 h. At the end of the reaction, the reaction mixture was filtered to remove formed trimethylammonium chloride salt. After washing with diethyl ether, the residual solution was evaporated in a rotary evaporator. The AKDs derived from hexanoyl chloride, lauryl chloride, and stearoyl chloride will hereinafter be referred to as AKD Hex, AKD Lau, and AKD St.

2.3 | Chemical modification of TMP fibers

The different AKD molecules (1 g AKD Hex, 1.25 g AKD Lau, and 1.5 g AKD St) were dissolved in 50 ml ethanol and then sprayed onto 10 g of TMP fibers. The systems were subsequently placed in an oven for 2 h at 90°C, after which the fibers were washed in ethanol at 40°C in a round-bottomed flask. Finally, the fibers were filtered and washed twice with DW and ethanol at ambient temperature. The fibers were placed in a fume hood for 1 day prior to use.

2.4 | Paper sheets for contact angle analysis

The 6 g TMP, corresponding to three sheets, (unmodified and modified TMP) was measured and diluted in 1.2 L of deionized water before being mixed at room temperature in an L&W pulp disintegrator (Lorentzen & Wettre, ABB) for 60,000 revolutions at 2900 rpm. Thereafter, the sheets were made according to the TAPPI/ANSI T 205 sp-18 standard[41]

2.5 | Compounding of modified and unmodified TMP fibers with PP

2.5.1 | Extrusion

Unmodified TMP and PP, as well as blends of PP and AKD-modified TMP, were used to produce PP-fiber composites (a total of 12 g of composite for each sample). The materials were compounded for 10 min at 190°C (lower than the decomposition temperature of TMP fibers, from TGA results in the supplementary information, Table S1) and then extruded using a Haake Minilab 3 Micro Compounder, a conical twin-screw compounder with an integrated backflow channel.

2.5.2 | Compression molding

The extruded filaments obtained from the Haake Minilab were placed in a pre-heated (190°C) mold of 100 × 150 × 10 mm. The filaments were aligned one to one another, placed and compression molded for 1 min at a temperature of 190°C, and a pressure of 150 kN. When 190°C was reached, the pressure was increased at a rate of 50 kN/min. The samples were cooled to 30°C at a rate of 10°C/min, while maintaining the pressure at 150 kN, after which the pressure was released. The extruded and compression molded samples are shown in Table 1, with their composition in wt%.

2.6 | Attenuated total reflectance Fourier transform infrared spectroscopy

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed using a Perkin Elmer Frontier FT-IR Spectrometer (Waltham, MA, USA) equipped with a diamond GladiATR ATR attachment from Pike Technologies. The samples, which were measured in triplicates, were placed directly on the ATR crystal without further preparation. The spectra were

TABLE 1 Composition of extruded and compression molded samples

Sample	TMP (wt%)	AKD (wt%)	PP (wt%)
PP	0	0	100
PP-TMP	50	0	50
PP-TMP AKD Hex	50	10	40
PP-TMP AKD Lau	50	12.5	37.5
PP-TMP AKD St	50	15	35
PP-AKD Lau	0	12.5	87.5
PP-AKD St	0	15	85

recorded between 4000 and 400 cm^{-1}, and 32 scans with a resolution of 2 cm^{-1} at intervals of 0.5 cm^{-1} were collected.

2.7 | Nuclear magnetic resonance spectroscopy

Solution phase nuclear magnetic resonance spectroscopy (NMR) was used to verify synthesized AKD molecules. The spectra were recorded at room temperature on a Varian MR-400 (Varian, Palo Alto, CA, USA), operating at 399.95 MHz for proton detection. Chloroform-d was used as the solvent for all samples.

2.8 | Tensile testing

Tensile test bars with width, thickness and length of 4, 1, and 40 mm (known as "dog-bones") were cut from the compression molded plates. The tensile properties (Young's modulus, stress at break, and elongation at break) were measured at room temperature with a strain rate of 6 mm/min using an Instron 5565A tensile tester with a grip-to-grip separation of 40 mm and a load cell of 5 kN. The reported values are the average of five separate measurements.

2.9 | Rheology

Oscillatory shear rheology measurements were made with a DHR-3 (TA Instruments) using a parallel plate geometry (diameter = 25 mm, gap = 4000 μm) at 180°C on the compression molded extrudates. The temperature was controlled using an environmental test chamber provided by TA Instruments. Measurements were performed at a strain of 0.25% between frequencies of 0.1 and 100 Hz.

2.10 | Hansen solubility parameters

HSP are solubility parameters that together represent the total energy of vaporization of a liquid.[42] This means that the energy of vaporization, which is identical to the total cohesive energy, is represented by the three HSP: dispersion forces (δ_D), the polar cohesive energy (δ_P), and hydrogen bonding (δ_H). The total HSP squared δ_{tot}^2 is total cohesive energy (E) divided by the molar volume (V) and is calculated from the sum of the squares of each solubility parameter according to the following equation:

$$\delta_{tot}^2 = \delta_D^2 + \delta_P^2 + \delta_H^2. \tag{1}$$

The HSP were calculated according to the group contribution method of Hoftyzer and van Krevelen,[43] Equations 2–4.

$$\delta_D = \frac{\sum n_i F_{di}}{\sum n_i V_{Fi}}, \tag{2}$$

$$\delta_P = \frac{\sqrt{\sum n_i F^2_{pi}}}{\sum n_i V_{Fi}}, \tag{3}$$

$$\delta_H = \sqrt{\frac{\sum n_i E_{hi}}{\sum n_i V_{Fi}}}, \tag{4}$$

where F_{di}, F_{pi}, and E_{hi} are dispersion forces, polar forces and hydrogen bond energies for each type of chemical group, taken from table values of Hoftyzer and van Krevelen.[43] n_i is the number of chemical groups of each type, and V_{Fi} is the Fedor's molar volume of each group.

A way to compare two materials' HSP is to use Equation 5, which shows the distance (Ra) between two materials regarding their partial solubility parameter components. A small Ra between two materials indicates large similarities between the materials, and vice-versa for a large Ra:

$$(Ra)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2, \tag{5}$$

where 4 is an experimentally determined constant, the numbers 1 and 2 represent two different materials.

2.11 | Contact angle

The contact angles of the liquids and substrates were determined using a theta optical tensiometer (Attension, Finland). In this work, the same method was used as in the TAPPI/ANSI T 205 sp-18 standard[41] employed by

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Moutinho et al.[44] The initial resting drop image (<3 s after application of the liquid) was acquired by a charge-coupled device camera. Five liquids were used as probes: deionized water (DW), DW/ethylene glycol (50/50), formamide, ethylene glycol, and propylene glycol.

2.12 | Calculation of die ratio

Die ratio, B_{swell}, of the extruded filaments was calculated through:

$$B_{swell} = \frac{d_e}{d_d}, \qquad (6)$$

where d_e is the extrudate diameter and d_d is the die diameter. The d_d in our case was 1.98 mm.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and modification of TMP with AKD

Three different AKD molecules were synthesized, AKD Hex, AKD Lau and AKD St. As an example, the 1H NMR signals obtained for the synthesized AKD Hex were as follows: 1H NMR (399.95 MHz, CDCl3) δ: 4.71 (t, 1H), 3.97 (t, 1H), 2.17 (m, 2H), 1.78 (m, 4H), 1.2–1.75 (m, mixture of alkyl chains), 0.92 (m, 3H). Unreacted reagents such as the acyl chlorides at δ: 2.88 (m, 2H) and butyl acetate at δ: 4.06 (m, 2H) were detected and found to appear at respective intervals of 0–3% and 20–30 wt%. The H NMR spectra can be found in the supplementary information, Figure S1.

Figure 1 shows the IR spectra of TMP and TMP-modified with AKD Hex, AKD Lau, and AKD St. The intensity of the carbon chain peak at 2800–3000 cm^{-1} increased for both AKD Lau and AKD St, whereas a lower increase was observed for AKD Hex. This may indicate less efficient modification with AKD Hex compared to AKD Lau and AKD St. A new carbonyl peak emerged between 1700 and 1750 cm^{-1}, suggesting modification of the TMP fibers with AKD groups.

3.2 | Surface properties of AKD-modified TMP

The effect of AKD modification on the surface properties of TMP was determined through contact angle measurements, and calculation of HSP.
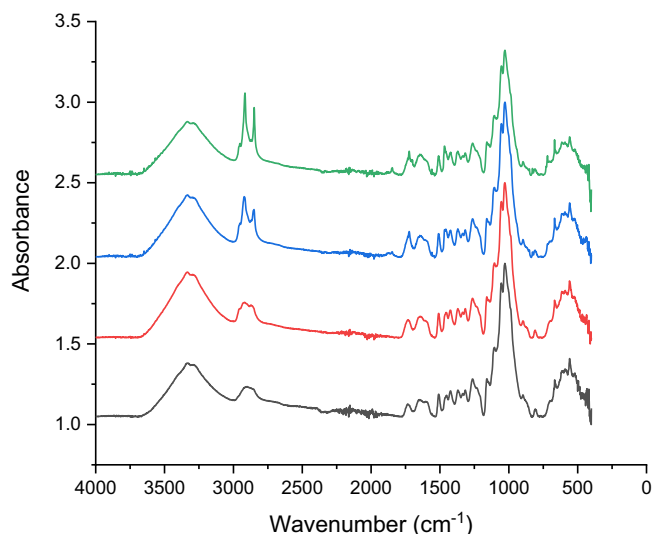

FIGURE 1 IR spectra of TMP (black), TMP AKD Hex (red), TMP AKD Lau (blue) and TMP AKD St (green).

3.2.1 | AKD modification of TMP increases the contact angle

The contact angle of deionized water increased with AKD modification of TMP paper sheets (Table 2, supporting information Figure S4). The highest contact angle of 126° was obtained when modifying the TMP surface with the longest AKD carbon chain (AKD St), compared to unmodified TMP with a contact angle of 83°. An increase in contact angle with modification and increasing AKD carbon chain length was also observed for formamide, ethylene glycol, and propylene glycol solutions. The 50:50 mixture of water and ethylene glycol showed a less pronounced increase in the contact angle with increasing AKD carbon chain length compared to the other solvents. The results show that AKD modification can increase the hydrophobicity of TMP, as already known for cellulose paper sheets[45]

3.2.2 | Theoretical compatibility of TMP-AKD in PP through HSPs

HSPs are widely used when identifying solubility, where materials with similar HSP have similar types of interactions and thus also a high affinity for each other. Gårdebjer et al.[46] extended the use of HSP to also predict the dispersibility of modified cellulose nanocrystals in different solvents, and in the matrix polymer (LDPE). This strategy was also applied here to predict the compatibility between AKD and PP, as well as TMP-AKD and PP. In the cellulose-AKD in PP

TABLE 2 Contact angle (°) for DW, DW/ethylene glycol blend, formamide, ethylene glycol, and propylene glycol on sheets prepared from TMP or AKD-modified TMP

Solvent sample	Contact angle (°)				
	DW	DW/ethylene glycol 50/50	Formamide	Ethylene glycol	Propylene glycol
TMP	83 (5)	71 (9)	54 (10)	56 (14)	53 (20)
TMP AKD Hex	105(13)	107 (10)	71 (11)	96 (13)	65 (13)
TMP AKD Lau	116 (11)	111 (8)	108 (10)	108 (11)	75 (11)
TMP AKD St	126 (9)	112 (12)	112 (4)	111 (10)	97 (11)

Note: The contact angles were determined as the angle the drops had when they first came in contact with the surface of the sheets. The contact angles are given as the average of at least eight measurements. Values of standard deviations are given within the parentheses.

TABLE 3 HSP parameters, the total HSP and Ra for AKD Hex, AKD Lau, AKD St, cellulose-AKD Hex, cellulose-AKD Lau and cellulose-AKD St in PP and water

Sample	δ_D ($[J/cm^3]^{1/2}$)	δ_P ($[J/cm^3]^{1/2}$)	δ_H ($[J/cm^3]^{1/2}$)	δ_{tot} ($[J/cm^3]^{1/2}$)	Ra in PP	Ra in water
AKD Hex	17.5	2.8	6.3	18.8	7.0	38.5
AKD Lau	17.1	1.3	4.4	17.7	4.9	40.8
AKD St	17.0	0.9	3.5	17.4	4.2	41.7
Cellulose-AKD Hex	19.1	4.2	14.9	24.6	15.7	30.6
Cellulose-AKD Lau	18.1	2.3	11.2	21.4	11.4	34.4
Cellulose-AKD St	17.7	1.6	9.3	20.1	9.5	36.2
PP (Hansen)	18	3	3	18.5	41.7	41.7
Water (single molecule)[47]	15.5	16	42.3	47.8	39.2	0

calculations, it was assumed that one AKD molecule was attached per repeating cellulose unit. Table 3 shows the calculated HSP parameters and Ra. All the HSP decreased with increasing carbon chain length increases in the AKDs. The squared total Hansen parameter, δ_{tot}^2, corresponds to the cohesive energy per volume, meaning the energy density of the molecule, and Table 3 shows that it decreases as the carbon chain in AKD lengthens.

The Ra shows the difference between the two materials regarding their respective partial HSP components; when Ra decreases, the theoretical solubility of the two materials increases.[43] As shown in Table 3, Ra values for the AKDs in PP decrease with the length of the side chains for both free AKD in PP and cellulose-AKD in PP. Therefore, the theoretical dispersibility of the stated materials in PP is in this order: AKD Hex < AKD Lau < AKD St and cellulose-AKD Hex < cellulose-AKD Lau < cellulose-AKD St. In contrast, the Ra between water and the AKDs increased with increasing carbon chain length, indicating that an increase in carbon chain length of AKD increases their hydrophobicity.

3.3 | Compounding and extrusion of TMP, AKD-modified TMP and PP blends/composites

TMP and AKD-modified TMP was compounded for 10 min and extruded through a mini-compounder at a pressure of 150 kN and temperature of 190°C. Figure 2 shows a reduction in the roughness of the filaments upon AKD addition, especially for the AKDs with the longer carbon chain length (AKD Lau and AKD St). Smooth filaments are an indication of reduced shear pressure build-up in the extruder for polyethylene wood composites.[48] This means the rougher the surface, the higher the shear stress during the process, and the filaments needed a greater force to get out of the extruder.

The observation is consistent with values of B_{swell}, which is reduced upon modification of TMP with AKD (Table 4). Ariffin et al.[49] investigated the effect of shear stress on B_{swell}, showing that B_{swell} increases with increasing shear stress. The increased smoothness of the filaments and reduced B_{swell} values indicate that less pressure is required to extrude composites comprising

FIGURE 2 A visual impression of filaments composed of (A) PP-TMP, (B) PP-TMP AKD Hex, (C) PP-TMP AKD Lau, and (D) PP-TMP AKD St, as compounded for 10 min and extruded at 150 kN and 190°C.

TABLE 4 Diameter of extrudate filaments and die swell numbers are based on the average of 10 measurements

Sample	Diameter (mm)	B_{swell}
PP-TMP	2.14 (0.07)	1.08 (0.04)
PP-TMP AKD Hex	2.02 (0.03)	1.02 (0.02)
PP-TMP AKD Lau	2.00 (0.03)	1.01 (0.02)
PP-TMP AKD St	1.99 (0.03)	1 (0.02)

TMP AKD and PP compared to unmodified TMP and PP composites.

Figure 3 shows the appearance of the different dog-bones made from PP-TMP, PP-TMP modified composites, and PP. As seen in Figure 3, although the TMP AKD Lau and AKD St samples have a lower PP content, they have a brighter color compared to the unmodified TMP sample. Local thermal degradation due to high-shear stress is often used as an explanation for the dark color of wood-based composites.[50–52] The brighter colors of extruded AKD Lau and AKD St-modified TMP/PP indicate easier processing.

3.4 | Rheological and mechanical evaluation of PP-TMP and PP-TMP AKD composites

Due to the results from previous sections, the filament shapes and colors of dog-bones, it was decided not to
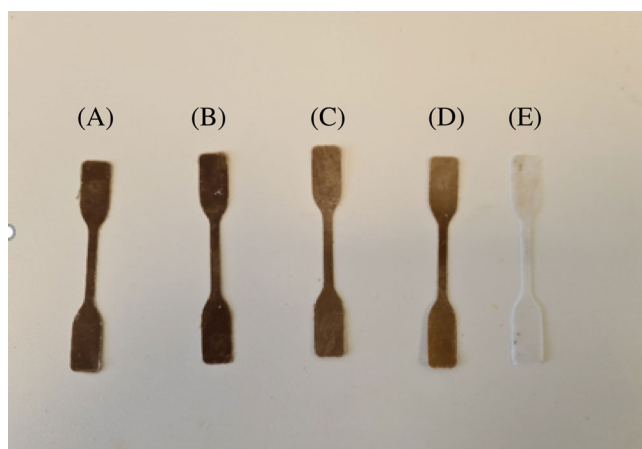

FIGURE 3 Hot-melt-compressed dog-bones of (A) PP-TMP, (B) PP-TMP AKD Hex, (C) PP-TMP AKD Lau, (D) PP-TMP AKD St, and (E) PP filaments.
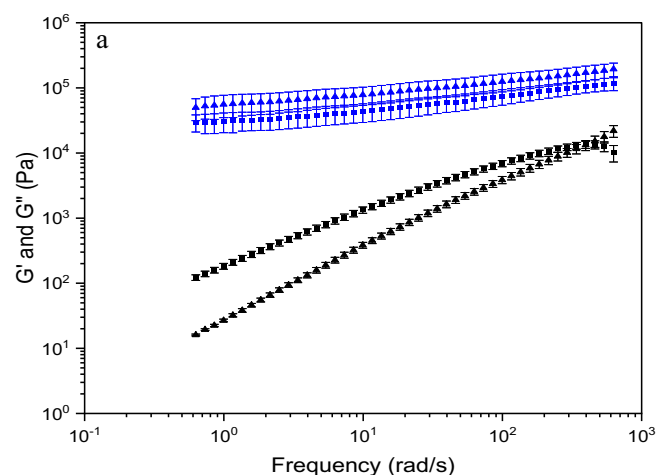

FIGURE 4 G' (triangles) and G" (squares) for PP (black) and PP-TMP (blue) as a function of frequency at strain = 0.25% and T = 180°C.

continue with AKD Hex. Figure 4 shows the frequency dependence of storage (G') and loss (G") moduli of PP and PP-TMP composites. The frequency sweep is recorded at 180°C. Adding TMP to PP changes the frequency behavior drastically compared to pure PP. The PP matrix can be defined as fluid-like (increasing moduli as a function of frequency, in combination with G" > G') under the measured conditions. The PP-TMP composites have larger absolute values of moduli and G' > G" across the frequency sweep, showing the change from fluid-like behavior in the case of PP to a network in the case of PP-TMP. These results are comparable with other studies in the literature[48,53–56] that have investigated the effect of natural fibers on the rheology of fiber-matrix composites.
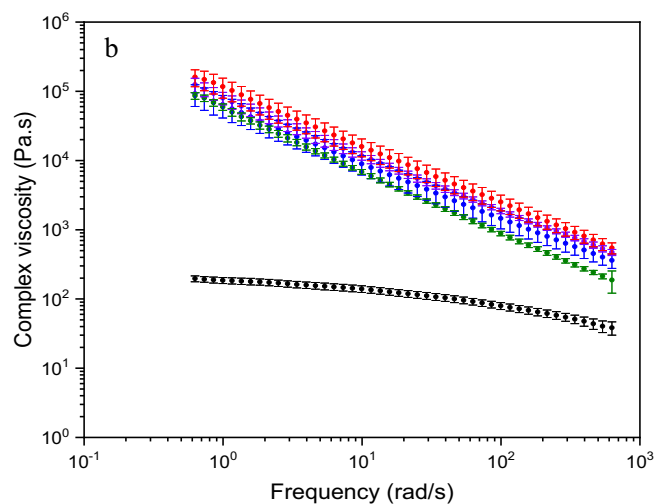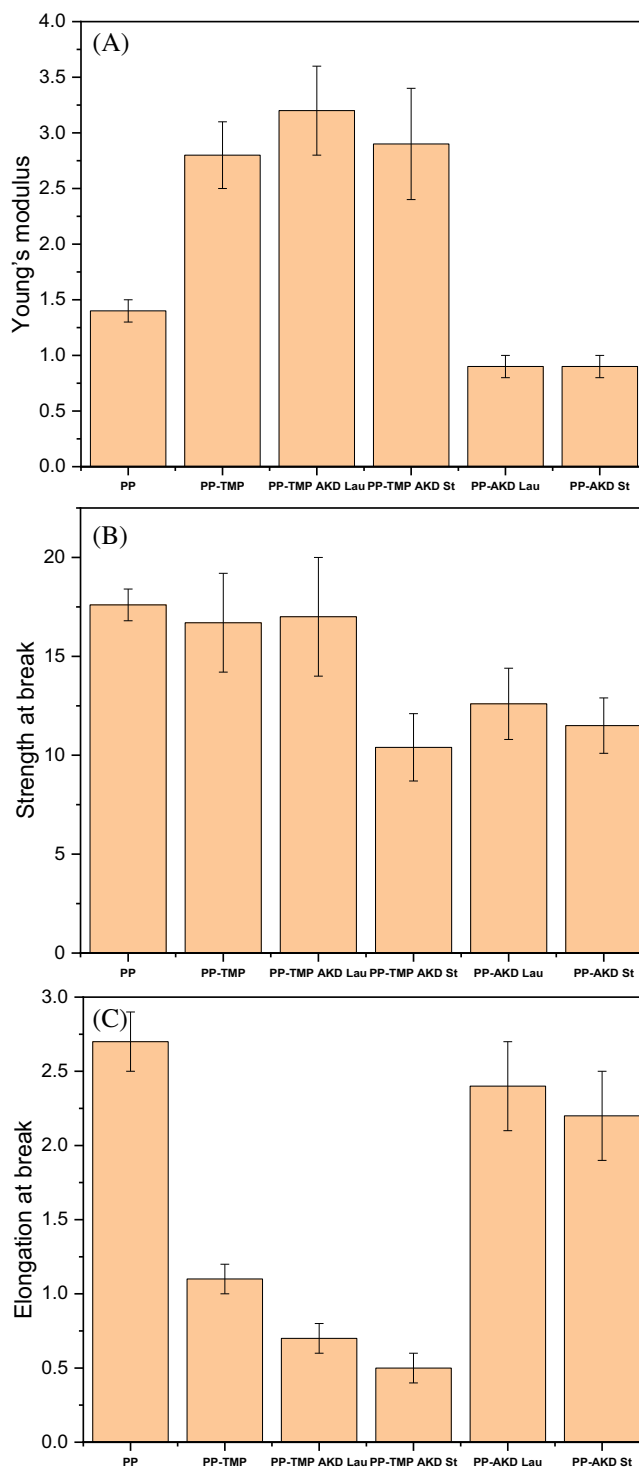
FIGURE 5 Complex viscosity (η*) of PP (black), PP-TMP (blue), PP-TMP AKD Lau (red) and PP-TMP AKD St (green) as a function of frequency at strain = 0.25% and T = 180°C.
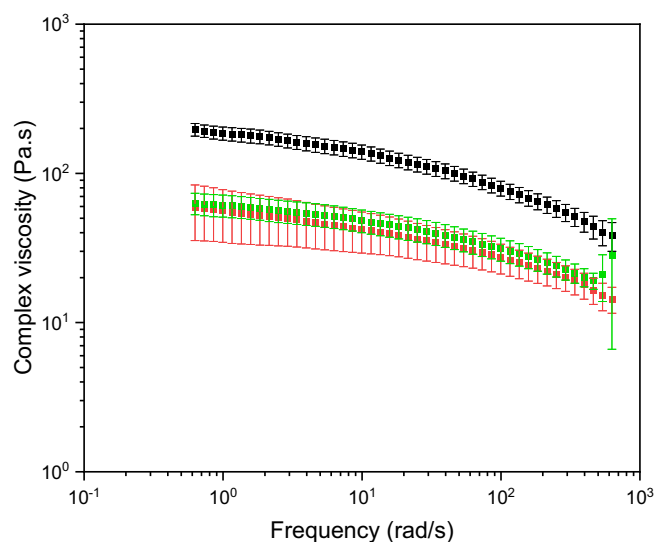
FIGURE 6 Complex viscosity (η*) of PP (black), PP-TMP (blue), PP-TMP AKD Lau (red) and PP-TMP AKD St (green) as a function of frequency at strain = 0.25% and T = 180°C.

FIGURE 7 Mechanical properties of the composites, Young's modulus (A), strength at break (B) and elongation at break (C). The standard deviations are represented as black vertical lines for each bar, and the SD is calculated based on five repetitions.

The complex viscosity of the TMP and TMP AKD-modified composites is considerably higher than that of the PP. In addition, the complex viscosity reduces faster with frequency compared to pure PP. The sample containing AKD St shows the largest reduction in complex viscosity with frequency. The complex viscosity of the AKD St-containing sample resembles the other samples (PP-TMP and PP-TMP AKD Lau) at low frequency; approx. The 80 kPa.s at a frequency of 1 rad/s. However, the complex viscosity approaches 0.3 kPa.s at higher frequencies (300 rad/s) for the AKD St-containing sample, whereas the other samples show complex viscosities of 1 kPa.s (Figure 5). No significant statistical difference between the complex viscosity of PP-TMP AKD Lau and PP-TMP was observed (Figure 5).

The observed reduction in complex viscosity could be related to the plasticizing effect of AKD St migrating into the PP matrix. Indeed, SEM images (supplementary information Figure S3) showed needle-shaped crystals, indicating unbound AKD St. To investigate the plasticizing effect of AKD on PP, we prepared PP AKD Lau and PP AKD St blends for melt viscosity and mechanical testing. Figure 6 shows that both AKD Lau and St have a plasticizing effect on PP, as the absolute value of the complex viscosity is reduced by 30 Pa.s at a frequency 300 rad/s. However, PP-TMP AKD St is reduced by 700 Pa.s compared to PP-TMP or PP-TMP AKD Lau, indicating that the modification of TMP with AKD St is beneficial in reducing complex viscosity.

Adding TMP to PP at 50 wt% gives composite materials of similar strength at break but reduced elongation (Figure 7). It is established that elongation at break will be reduced when TMP fibers are added.[39,57–60] Modification of TMP with AKD Lau generates materials with similar stress and elongation at break as unmodified PP-TMP composites. However, modifying the TMP with AKD St generates a reduction in stress (Figure 7A). The reduction in tensile strength at break can indicate reduced crystallinity of the composite, poor dispersion of the fiber in the matrix, or poor adhesion between fiber and matrix. Thus, the crystallinity of the pure PP and composite materials was tested, showing a similar degree of crystallinity for all materials (supplementary information, Table S2 and Figure S2). The reduction in strength of the PP-TMP AKD St cannot, therefore, be explained by reduced crystallinity.

Quillin et al.[37] showed that modifying bleached kraft cellulose pulp with long-chain AKDs improved dispersion of the cellulose in surface-modified PP with a poly(viny1 alcohol) matrix. Still, they observed a reduced strength of the composites, which they hypothesized was related to a reduction in hydrogen bonds between the AKD-modified cellulose fibers and surface-modified PP with poly (viny1 alcohol) PP. We also note that the addition of AKD (AKD St and AKD Lau), itself to PP generates materials with reduced stress upon breaking compared to PP on its own, but there is little effect on the elongation upon breaking. This may be related to the amount of AKD added to the PP, 20:80. Thus, the strength of the pure PP sample is compared to a sample with 80% PP and 20% AKD.

As mentioned above, the HSPs indicated improved miscibility between AKD-modified cellulose and PP. This is possibly the reason for the eased processing, as indicated by a smoother filament surface, reduced B_{swell}, and discoloration of the AKD-modified PP-TMP composites.

4 | CONCLUSION

We hypothesized that modifying the TMP surface with AKD of increasing carbon chain length would increase its hydrophobicity, and thereby improve the processability and mechanical strength of the composites. A new carbonyl peak in the IR spectra, suggesting modification of the TMP fibers with AKD groups. Experimental values of contact angles of various solvents indicated increased hydrophobization of the TMP after AKD modifications. This also increased with increased carbon chain length of the AKD. Visual impressions of extruded PP-TMP AKD material and calculated B_{swell} data supported the idea that TMP increases processability with PP. The surface of the die filaments was smoother for the PP-TMP AKD St sample compared to the PP-TMP sample, and the discoloration was reduced for the hot-melt-pressed dog-bone containing AKD-modified TMP. The melt viscosity of the PP-TMP AKD St was lower compared to PP-TMP or PP-TMP AKD Lau at the higher frequency range. The reduced mechanical properties for the AKD-modified TMPs in PP are consistent with the data report by Quillin[37] using cellulose and PP sheets. The findings of the study regarding the modification of TMP fibers with AKD suggest only a slight improvement in processability, but do not provide conclusive evidence of an increase in the strength of the interaction between PP and TMP. Further research is necessary to establish the full impact of these modifications.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.