

Process Intensification of Thermoplastic Lignocellulose Production through High-solids Reactive Extrusion Enabled by Novel Recycle Loop

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ABSTRACT: To reduce the reactant concentration necessary for producing a newly synthesized thermoplastic lignocellulose from forestry waste, this study explores the concept of a recycle stream as a chemical unit operation in a reactive extrusion process. Modified lignocellulose from the first pass was returned to the start of the extrusion process to act as a lubricant for the lignocellulose feedstock. By this action, a high lignocellulose content could be extruded without requiring costly lubrication alternatives such as plasticizing additives, solvents, or excessive quantities of liquid reactants. With 25% recycled material, a significantly improved processing state was found, allowing for a reduction in total reactant usage by 50% without change to the degree of modification and ultimately leaving less unreacted species in the final product. The thermoplastic nature of the modified lignocellulose was characterized by thermal and rheological analysis and found to demonstrate greater flowability with any recycle stream fraction.

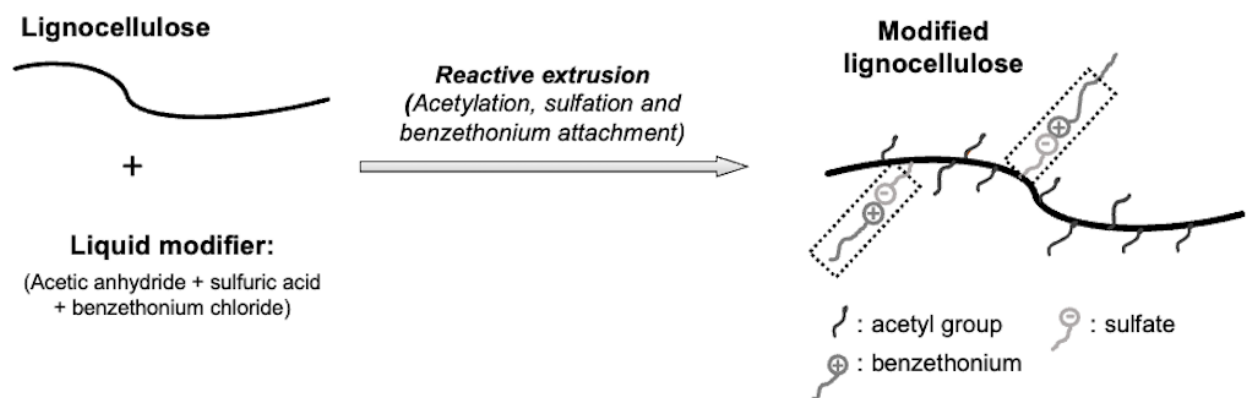
1. INTRODUCTION

The abundance and renewability of forestry biomass have attracted intense research interest in its use for producing various bio-polymeric products, *e.g.*, textile and packaging films.^{1,2} However, the conversion of forestry biomass into polymeric products requires more complicated processes than those from fossil fuels, which decreases their competitiveness in commercial applications. Scalable technologies to process forestry biomass are necessary from the point of sustainable development, in order to increase commercial viability. Extrusion technology can be considered as promising in this regard owing to its easy scale-up, cost-effectiveness and capacity for simultaneously defibrillating and modifying wood fibers.³⁻⁵

Direct screw extrusion of forestry biomass is challenging since the lignocellulosic fibers exhibit low deformability and no melting point below their decomposition temperature, thus lacking the necessary flowability for most polymer processes. The most common solution currently is melt compounding wood fibers into a thermoplastic matrix to generate wood-plastic products.⁶⁻⁸ With typically high fiber loadings (60% or higher is not uncommon), the thermoplastic matrix serves as a binder and lubricant in the process.^{9,10} Besides thermoplastic lubricants, using excessive liquid is another way to aid the extrusion of lignocellulosic fibers for preparing bio-based products, *e.g.*, preparation of cellulose nanofibers by twin-screw extrusion usually uses a high water content to assist the convey of fibers inside the extruder.¹¹⁻¹³ In some cases, soluble sugars or polymers are added along with the liquid to act as a lubricant for the fibers, thereby allowing extrusion at higher solids contents.¹⁴⁻¹⁷ In cases of reactive extrusion, since many added lubricants can produce undesirable side reactions, an excess of reactants, if liquid, or added solvents are ideal for conveying lignocellulose inside the twin-screw extruder. However, this significant excess of reactants requires complex separations afterwards from the product, leading

to increased production capital and energy costs. As an alternative, this paper considers the concept of a recycle stream as a chemical unit operation in a unique reactive extrusion process for producing thermoplastic lignocellulose, whereby the modified material acts as a lubricant for the wood pulp feedstock to promote conveying and mixing. Surprisingly, the concept of a recycle stream has not been studied until now for reactive extrusion processes.

Our previous work¹⁸ introduced a reactive extrusion approach (Scheme 1) to modify lignocellulose into thermoplastics, where excess liquid reactant was used to aid the extrusion of lignocellulose by twin-screw extruder. For this study, the focus will be on the lubricating benefits of the recycle stream as a means to replace the excess reactant currently necessary for processing, though the final goal of the work is ultimately to identify an operating state where the exiting polymer requires no post-modification cleaning before use. To examine this lubrication effect, experimental trials were carried out with different percentages of modified material being recycled while varying the amount of reactant added to the reactive extrusion process. The effectiveness of the process with a recycle stream was assessed by measuring the degree of modification and thermoplasticity of resulting modified samples.



Scheme 1: Mechanism of the reaction used in the present study for modifying lignocellulose into thermoplastic by reactive extrusion.

2. EXPERIMENTAL

2.1. Materials. Lignocellulose, received as a high-yield Aspen mechanical pulp, was supplied by Tembec (Montreal, Canada), which contains 8.2 wt% Klason lignin as determined by the TAPPI-T method 222 om-02. The received lignocellulosic fibers were mechanically pre-treated before reactive extrusion by using a 27 mm 40 L/D twin-screw extruder (Leistritz, USA) according to a previously established method.¹⁹ As a result of the treatment, the received fluffy lignocellulosic fibers had become compacted into fine granules, making it convenient for feeding into the extrusion process but also improving its chemical accessibility by partial micro-fibrillation. Benzethonium chloride (hyamine, HPLC grade), sodium bicarbonate and phenolphthalein (ACS grade) were purchased from Sigma Aldrich (Oakville, Canada). Acetic anhydride (reagent grade), sulfuric acid (trace metal grade), anhydrous ethanol (reagent grade), and 1.0 M sodium hydroxide and hydrochloric acid solutions were obtained from Caledon Laboratory Ltd. (Georgetown, Canada).

2.2. Extrusion Setup. All reactive extrusion processing was conducted in an 18 mm (40 L/D) twin-screw extruder (Leistritz, USA) configured for solids to enter at the feed port and liquids to be metered at the second barrel zone (Figure 1), according to a previously established method.¹⁸ Air-dried pre-treated lignocellulose was fed by a gravimetric feeder (Coperion, Germany) at a rate of 500 g/h. A liquid modifier comprised of acetic anhydride, benzethonium chloride and sulfuric acid with a molar ratio of 13:1:0.95 was injected using an Optos series metering pump (Eldex, USA) for differing liquid/solids ratios. The feeding zone was water-cooled to 25 °C while other zones were all heated to 120 °C; the screw speed was set to 100 rpm.

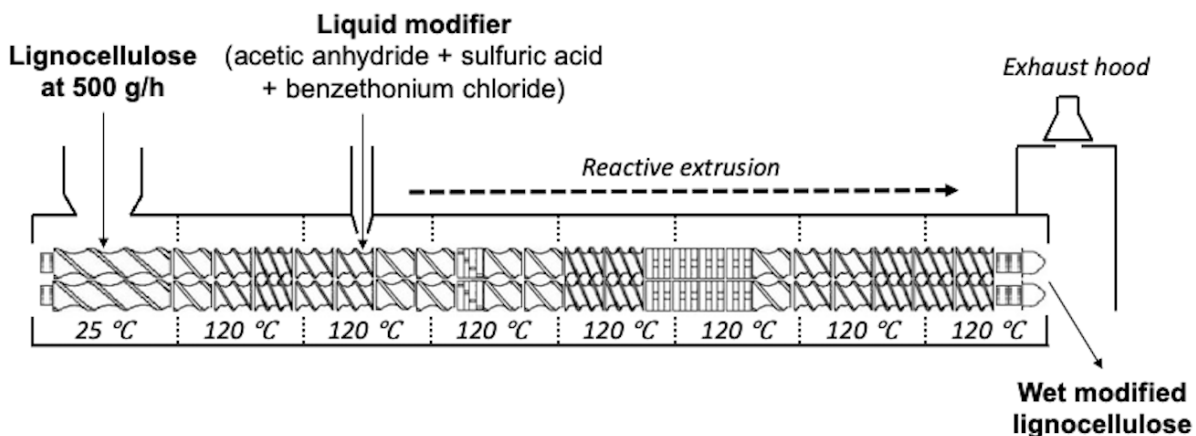


Figure 1. Configuration of an 18 mm, 40 L/D, Leistritz twin-screw extruder for the reactive extrusion of lignocellulose.

2.3. Preparation of the Innate Lubricant (Recycle Stream Material). The liquid modifier was injected at a rate of 32 mL/min corresponding to a 19 wt% solids content (Table 1). The extruded mass was collected and air-dried to constant weight in a fume hood for 1 week. Admittedly, the drying and subsequent loss of residual anhydride reactant were undesirable from an optimization viewpoint since even greater reductions in the concentration of liquid modifier for the overall process may have been realized in the recycle trials if the wet extruded mass had been used as the lubricant instead. However, the purpose of the present study was primarily to understand how a polymer melt acted as a lubricant and how effective the recycle stream could be at reducing excess liquid modifiers. As a result, the drying was considered necessary, and this material is referred to as the innate lubricant. The persistence of unreacted hyamine and sulfuric acid (and their intermediates, ex. benzethonium bisulfate²⁰) in the dried lubricant needed to be corrected for the reactive extrusion process with a recycle stream, as described in the next section. The air-dried innate lubricant was ground into fine particles by a countertop blender for 10 mins at a speed of 750 rpm, and the generated fine particles were able to pass through a 20-mesh sieve.

2.4. Reactive Extrusion Process with a Recycle Stream. A reactive extrusion process with recycle stream is shown conceptually in Figure 2; due to the desired intent to understand process changes caused by the recycling of well-characterized material, we recognize that the system does not include a recycle stream in the truest sense of a chemical unit operation since there is no continuous flow back to the feed opening, but it was considered sufficient to recognize the benefits. The innate lubricant was dry blended with unmodified (neat) lignocellulose at either 25 wt% (R-25 series) or 50 wt% (R-50 series) of the total mass.

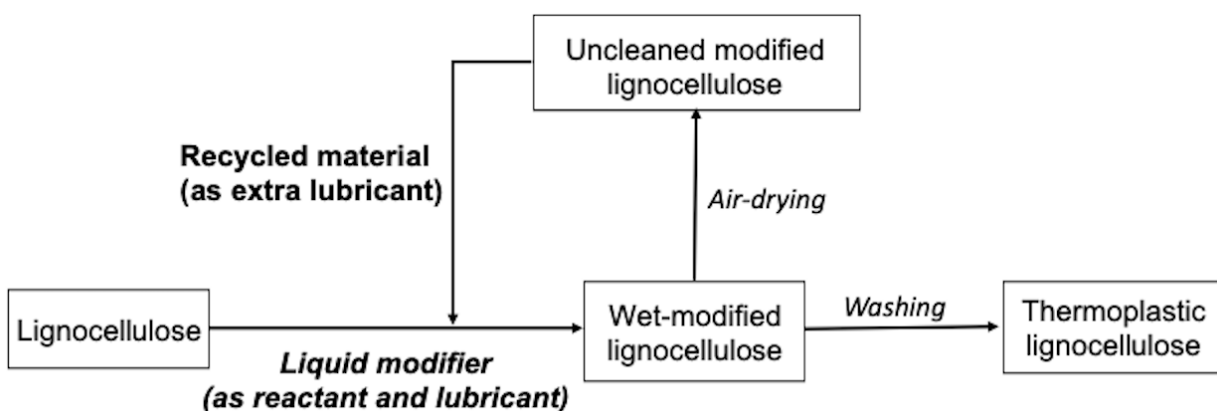


Figure 2. Flow diagram of the reactive extrusion process with a recycle stream.

As shown in Table 1, for the 25% recycle series, liquid injection rates were either 18, 15, 12, 9 or 6 mL/min, corresponding to a solids content of 30, 34, 39, 46 or 56 wt%, respectively. For the 50% recycle series, the liquid injection rate was either 12, 10, 8, 6 or 4 mL/min, with a corresponding solids content of 39, 43, 49, 56 or 65 wt%, respectively. The liquid/lignocellulose ratios were considered identical between the two states of recycling when neat lignocellulose was considered reactive. The extrudate of each series was collected, cooled in distilled water, and neutralized with 1 M sodium bicarbonate solution before being washed with distilled water until the filtrate conductivity (determined by a Mettler Toledo S230 conductivity meter) was similar to distilled water. The modified samples were then vacuum oven dried at 75 °C for 24 hours prior to

storage and characterization. A set of baseline conditions were attempting using the same solids content from the two series for 100% neat lignocellulose; not all these conditions were successful as the liquid content became too low to prevent the extruder motor from seizing. Each baseline condition had a matching amount of unbound benzethonium salt (hyamine and sulfuric acid) to the corresponding recycle series, recognizing the residual salt was different in the two recycling trials.

Table 1. Feeding Compositions of Reactive Extrusion of Lignocellulose for Preparing Lubricant and Thermoplastics.

Series	Lubricant in solids (wt%)	Neat lignocellulose in solids (wt%)	Liquid injection rate (mL/min)	Liquid/neat lignocellulose (mL/g)	Solids content (wt%)	Total lignocellulose content (wt%)
Lubricant	0	100	32	3.8	19	19
R-25	25	75	6, 9, 12, 15, 18	1.0-2.9	30-56	27-51
B-25	0	100	*9, 12, 15, 18	1.1-2.2	30-46	30-46
R-50	50	50	4, 6, 8, 10, 12	1.0-2.9	39-65	32-55
B-50	0	100	*8, 10, 12	1.0-1.4	39-49	39-49

*Lower liquid injection rates did not work for B-25 and B-50 series, extruder motor load exceeded the maximum.

2.5. Gravimetric Analysis. After air-drying the innate lubricant, the residual liquid left in the modified lignocellulose material was estimated by vacuum drying. Five air-dried samples were further dried under a 30 Hg vacuum until reaching constant weight. The weight change was determined as the residual anhydride in the innate lubricant (for which the liquid injection rate was adjusted in the two recycle series to obtain the desired solids ratio). After vacuum drying, the

modified lignocellulose was cleaned by repeated soaking in distilled water until the filtrate conductivity matched the water. The weight change after washing was attributed to unreacted hyamine/sulfuric acid (and their intermediates, ex. benzethonium bisulfate²⁰) remained in the lubricant; the baseline samples were corrected for the unreacted benzethonium functionalizing agent.

2.6. Degree of Chemical Modification and Reaction Effectiveness. Acetyl and benzethonium sulfate contents of the modified pulp were determined by colorimetric titration and elemental analysis, following a previously established approach by the same authors¹⁸. Briefly, 0.05 g dried modified lignocellulose was soaked in 5 ml of 0.25 M NaOH and 5 mL of anhydrous ethanol for 24 h to completely hydrolyze acetyl species and partially hydrolyze sulfate ester in the modified lignocellulose. The total amount of the two hydrolyzed esters was estimated by adding 10 mL of 0.25 M HCl and then back titrating the mixture with 0.25 M NaOH and a phenolphthalein indicator.

The amount of benzethonium sulfate species in the modified lignocellulose before and after NaOH treatment was determined by elemental analysis. Elemental nitrogen (N) and sulfur (S) contents were determined with a UNICUBE elemental analyzer (Elementar, German). Approximately 2 mg powder sample was sealed in Tinfoil for the elemental testing.

Based on the measured acetyl and benzethonium sulfate content in the modified lignocellulose, the reaction effectiveness (mmol/g) were the amounts of the two grafted species, corrected for the amount of lignocellulose in the feedstock to the extruder. The baseline conditions contained 100% neat lignocellulose, while for the recycle series, contained a mixture of neat lignocellulose and modified lignocellulose in the innate lubricant.

2.7. Thermal and Rheological Properties. Glass transition temperature (T_g) was determined by a Q200 differential scanning calorimeter (TA Instruments, USA) operating in modulated mode.

Modified lignocellulose, 9 mg, was loaded and sealed into a Tzero aluminum pan. A hole was punched into the lid to allow moisture evaporation during the test. Samples were equilibrated at -20 °C, then scanned till 220 °C at a ramp rate of 5 °C/min and an oscillation of 1.00 °C every 60 seconds. The reversible heat flow component was separated from the total heat flow by the Universal Analysis software (TA Instruments, USA) and used to determine T_g of the modified samples.

The flowability of the innate lubricant and the modified samples were measured with a Discovery HR-2 hybrid rheometer (TA Instruments, USA) by conducting. Approximate 0.5 g powder was evenly loaded onto the plate of the rheometer and compressed with a 10 N axial force. A temperature sweep was conducted with a heating-cooling mode over a temperature range of 50-210 °C at a rate of 5 °C/min and under a constant shear rate of 0.1 s⁻¹. The viscosity of the cooling recycle was reported. A flow sweep at 120 °C was conducted for the lubricant over a shear rate range of 0.1-100 s⁻¹.

Tensile testing was conducted by following standard ASTM D638 and measured with dog-bone shaped specimens prepared by compression molding. The tensile testing was performed at a 5 mm/min crosshead speed, with forces recorded using a 500 N load cell. Tensile properties were reported as an average of three repeats. Compression molding of the modified samples was done with a benchtop hydraulic press (Carver 4389) with heated platens. Molding was done at 180 °C; a 2.5 MPa pressure was applied for 3 mins and then 6 MPa for another 12 mins.

3. RESULTS AND DISCUSSION

3.1. Influence of the Recycle Stream on Processing of Lignocellulose by Twin-screw Extrusion. Insights into the processability of lignocellulose using a recycle stream were based on the twin-screw extruder's torque. Figure 3 shows the torque (as a percentage of maximum torque

capacity) for the 18 mm twin-screw extruder with different lubrication schemes. For the same solids content, the torque for extruding lignocellulose with the internal lubricant as representative of a varying recycle stream (R-25 and R-50) was notably lower than the baseline conditions extruding neat lignocellulose (B-25 and B-50) for most conditions. Only at the two lowest solids content, while at 30% or 34% for the 25% group (R-25 and B-25), did the liquid modifier show similar lubricity as the innate lubricant on the process (approx. 16% torque). At higher solids ratios, the torque rose exponentially for the B-25 series, and the extruder could not handle the torque demand associated with solids ratios above 46% (50% torque). Comparatively, the torque rose gradually to only 18% at solids ratio of 46% for the R-25 series and reached only 20% at the highest tested condition of 56%.

Torque for the higher recycle condition, R-50 series, showed a similar trend to the R-25 series, and yet R-50 always experienced lower torque than B-50. Torque for the baseline series B-50 showed a similar exponential rise as seen with the B-25 series, as the solids ratio increased above 43%. The machine could not be operated above solids ratio of 49% for B-50. In contrast, the presence of innate lubricant enabled the R-50 series to be operated at the highest solids ratio of 65% at only 23% torque.

The torque for the B-50 series was slightly lower than for B-25 because the liquid modifier of the former contained more hyamine/sulfuric acid to correct for the higher amount of unbounded benzethonium functionalizing agent in the R-50 series from the innate lubricant. Overall, the results show that recycling a portion of the modified lignocellulose back to the feed stream was much more effective at lowering motor demand than using the liquid modifier. Reactive extrusion at very high solids content was found to be feasible with a recycle stream.

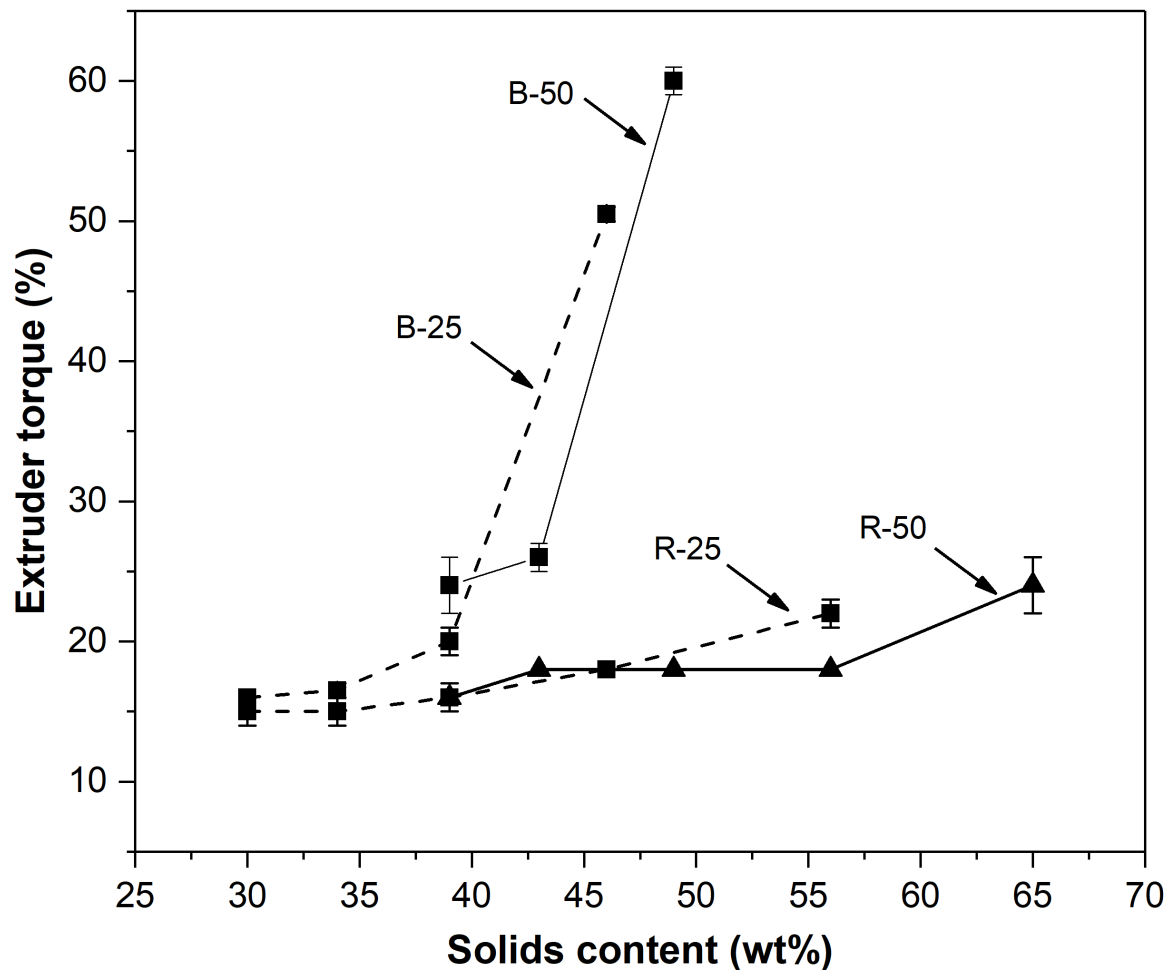


Figure 3. Extruder torque during reactive extrusion of lignocellulose with (R-25 and R-50) and without a recycle stream (B-25 and B-50) based on different solids content.

Understanding how the innate lubricant promoted neat lignocellulose's conveyance in the twin-screw extruder was considerably clearer by the rheological analysis of the lubricant. Figure 4 presents the viscosity curves versus temperature and shear rate for the innate lubricant. Plot (a) shows that system temperatures above 105 °C were necessary for this thermoplastic lignocellulose to transition from a solid-like response to an increasingly viscous response. For a temperature of 120 °C, as used in the extruder, its viscosity was around 1.5×10^5 Pa-s, even at the low shear rate of 0.1 s^{-1} used for the temperature sweep.

Plot (b) shows shear dependency at 120 °C, with the innate lubricant showing significant shear thinning over the three decades of shear rate and no evidence of a Newtonian plateau. At a shear rate of 10 s⁻¹, the viscosity had dropped to around 1000 Pa-s which is comparable to commercial resins used for profile applications. The average shear rate ($\dot{\gamma}$) for the innate lubricant in the extruder corresponding to the gap clearance in the kneading sections could be estimated by the following equation according to Vergnes's method²¹:

$$\dot{\gamma} = -\frac{1}{2} \frac{V \cos \theta}{h} + \frac{3Q_{ch}}{Wh^2} \quad (1)$$

Where h and W were the depth and width of the screw channel assumed to be rectangular, which can be estimated from the screw's actual demensions according to Booy's method.²² For a 90 ° kneading disk of the 18 mm Leistritz twin-screw extruder, the $h = 2.9$ mm and $W = 6.1$ mm. V , Q_{ch} and θ were defined as:

$$V = \frac{2\pi NR}{60} \quad (2)$$

$$Q_{ch} = \frac{Q}{\rho(2n - 1)} \quad (3)$$

$$\tan \theta = \frac{B}{2\pi R} \quad (4)$$

Where N was the screw rotation speed (100 rpm), R was the screw radius (8.8 mm), Q was the mass flow rate (0.5 kg/h), ρ was the melt density (1.3 g/mL), n was the number of flights (4), and B was the screw pitch (10.7 mm). At the chosen screw speed of 100 rpm, the estimated average shear rate was 62 s⁻¹, corresponding to a viscosity of 108 Pa-s for the lubricant. Its flowability and hence lubrication behavior were comparable to rosin or a polyethene wax.

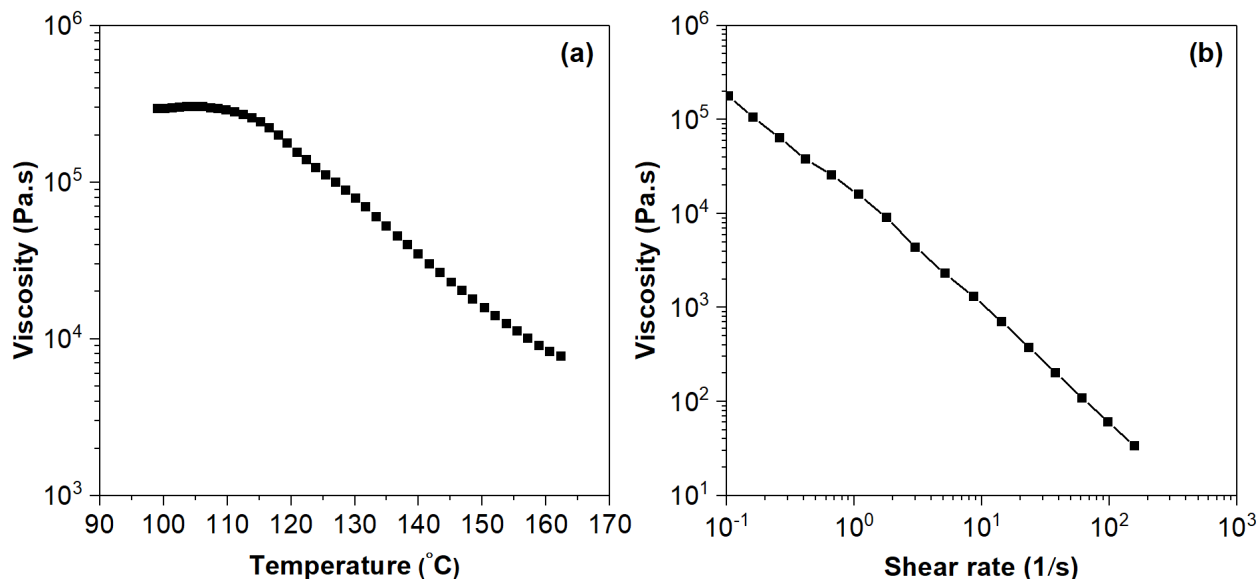


Figure 4. Viscosity of the innate lubricant verse (a) temperature at 0.1 s⁻¹ and (b) shear rate at 120 °C.

3.2. Modification effectiveness of the reactive extrusion with a recycle stream. A previous study has demonstrated that the modified lignocellulose exhibits grafted acetyl group and, to a lesser degree, grafted benzethonium sulfate groups, with both being important to the flowable nature of the biopolymer.²⁰ Figure 5 shows the reaction effectiveness based on the amounts of acetyl and benzethonium sulfate groups grafted during the reactive extrusion (with functionalities present in the lubricant from the first pass of extrusion, being removed from the results). It should be recognized that reaction effectiveness assumes the modified lignocellulose in the innate lubricant will undergo further significant modification since it is calculated based on the amount of total lignocellulose fed into the extruder.

For the baseline series B-25 without innate lubricant, its reaction effectiveness declined with higher lignocellulose content (LC); grafting attachments decreased for acetyl and benzethonium sulfate in this case. However, the R-25 series found a significant increase in reaction effectiveness with increasing LC, reaching a maximum at 36 wt% LC and subsequently declined at very high

LC to ultimately match the other series. The reaction effectiveness at 36 wt% LC was based on 9.3 mmol/g of newly acetyl grafted content, and 1.6 mmol/g of newly benzethonium sulfate grafted content, which was even higher than the values found in the innate lubricant. As a matter of reference, the cleaned modified lignocellulose in the innate lubricant had 7.7 mmol/g acetyl content and 1.6 mmol/g benzethonium sulfate content despite being prepared with an excess of reactant (LC of 19 wt%). These results show that there can be some synergies found in terms of the extent of reaction by relying on the innate lubricant rather than an excess of liquid modifier to aid flowability (and mixing) inside the extruder. However, the results below show that too many recycled materials will have a negative effect on the extent of reaction.

The reaction effectiveness in the R-50 series for both acetylation and benzethonium sulfate attachment was significantly lower than the R-25 series. There was a significant increase in acetyl content but a significant decline in benzethonium sulfate content for the R-50 series compared to the B-50 series over the range of tested LC; acetyl content reached a maximum of 4.6 mmol/g at 41 wt% LC. Several possible factors could have contributed to the low reaction effectiveness of the R-50 series: (i) the innate lubricant mixed well the neat lignocellulose and consequently decreased accessibility of the neat lignocellulose to the liquid modifier; and (ii) the innate lubricant at this high concentration interfered with defibrillation as a necessary action inside the extruder for chemical access to the lignocellulose.

Between the two-baseline series, B-25 and B-50, the extent of acetylation was the same, but the benzethonium sulfate attachment was slightly greater for B-50, possibly because of the higher hyamine/sulfuric acid functionalizing agent which was being compensated for in the R-50 series.

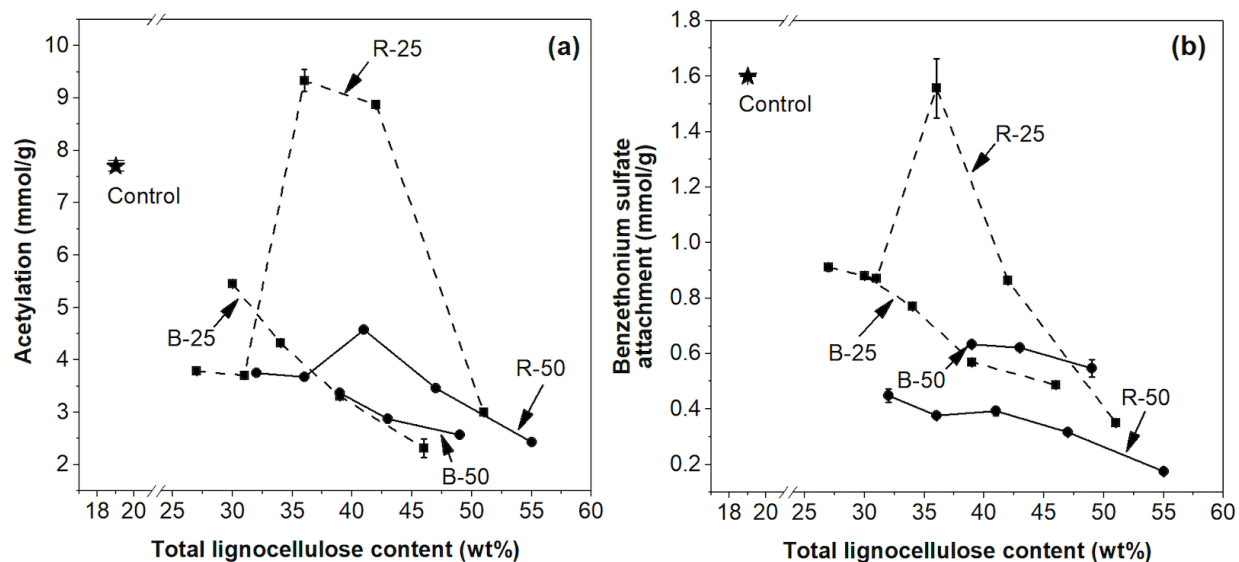


Figure 5. Reaction effectiveness of acetylation (a) and benzethonium sulfate attachment (b) of the reactive extrusion processes with and without a recycle stream. The control was the cleaned sample of the lubricant.

3.3. Thermoplasticity of the modified lignocellulose based on recycle series. According to our previous study,¹⁸ the reactive extrusion would modify lignocellulose into a thermoplastic. Figure 6 shows the modified lignocellulose's T_g for varying LC and different lubrication schemes. As a baseline for this discussion, a cleaned sample of the innate lubricant had a T_g of 105 °C (based on its preparation with an LC of 19 wt%, far lower than used in the recycle series). Only one of the recycle series samples at 36 wt% LC in the R-25 series showed a lower T_g (103 °C), and hence by the definition being used in this paper, it displayed improved thermoplasticity over the innate lubricant. Since this recycle condition used almost less than half of the amount of liquid modifier in the process compared to the condition used for the innate lubricant, it was considered a massive improvement for this process (albeit at too narrow of an operating point at present if the T_g must be as low as 105 °C).

Among the baseline conditions, B-25 and B-50 series, their T_g ranged from 120-135 °C, much higher than their corresponding recycle series samples, though decreasing in value with lower LC to suggest an almost linear trend till reaching the T_g of the innate lubricant. Conversely, for very high LC, the modified samples eventually showed no detectable T_g (which in the case of the B-25 series occurred at an LC of 46 wt%). The R-25 series showed T_g varying between 104-124 °C while the R-50 series showed T_g varying between 114-126 °C; both series exhibited much lower T_g than their corresponding baseline samples. Although the R-50 series had a similar reaction efficiency to its corresponding B-50 series, it contained a high content of innate lubricant with low T_g (105 °C) to aid both processability but also the thermoplasticity of the final material.

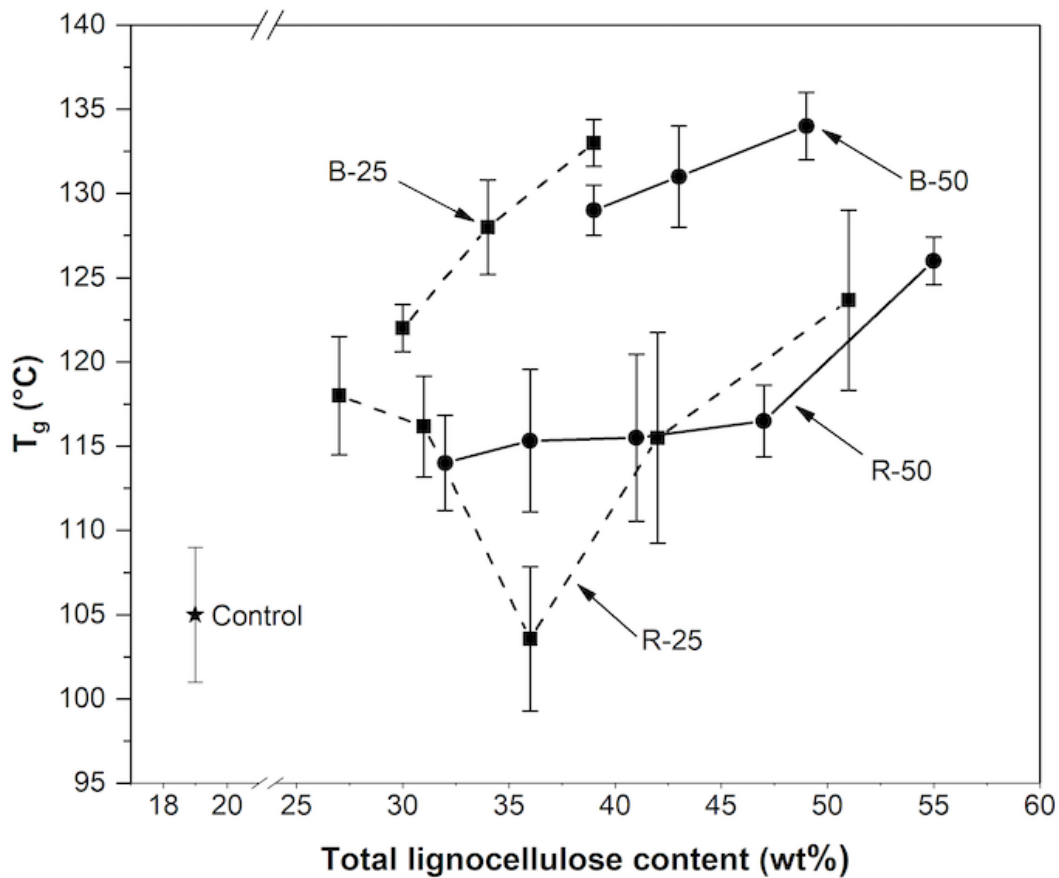


Figure 6. T_g temperatures of the modified lignocellulose prepared by reactive extrusion with and without a recycle stream. The control was the cleaned sample of the lubricant.

Thermoplasticity can also be conveyed by rheological characterization. Figure 7 shows the viscosity curves of the modified lignocellulose. Significant transition behavior, shown by a steep decline in viscosity with increasing temperature, was observed for the modified lignocellulose samples. Generally, samples with lower T_g presented a more significant transition, which was particularly noteworthy for the one sample from the R-25% series with the lowest T_g of 103 °C (Figure 7b). Comparatively, the two samples (highlighted with dash arrows) with the highest T_g of 133 °C (Figure 7a) and 134 °C (Figure 7c) from the baseline series showed no apparent transition behavior in their viscosity curves (highlighted by arrows). In our previous study,¹⁸ one of the other favoured methods for demonstrating thermoplasticity of the modified lignocellulose was to visually consider moldability, although in that case, the LC used was relatively low (14-19 wt%) versus 32-55 wt% in the present recycle stream series. Samples of any T_g in the R-25 or R-50 series showed good thermoplasticity by compression molding, with smooth surfaces to denote that the polymer flowed as a liquid under heat and pressure. However, not all samples of the B-25 or B-50 series showed the same good thermoplasticity, with the two samples of high T_g , either 133 °C or 134 °C showing poor filling of the mold due to incomplete melting.

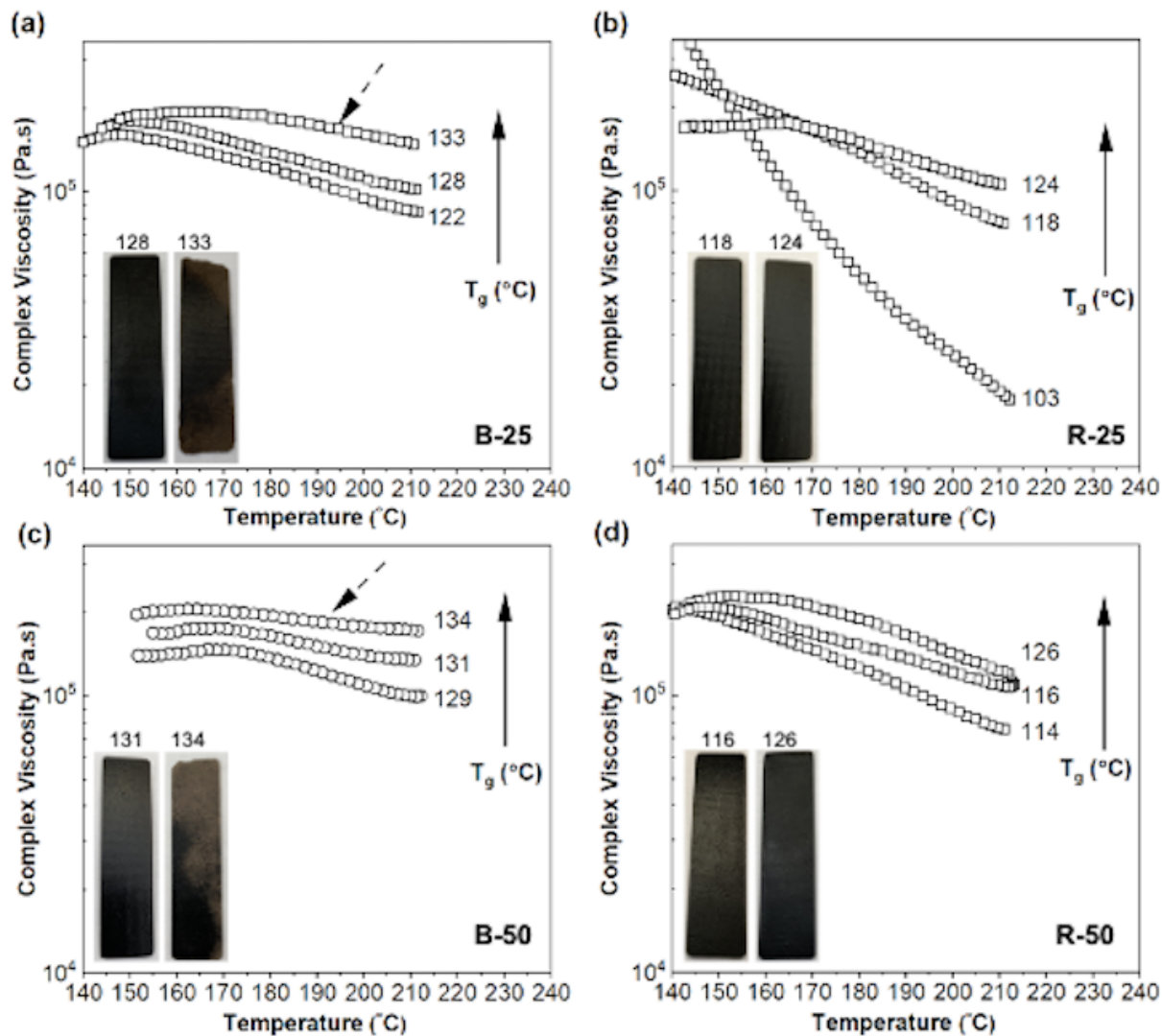


Figure 2. Viscosity curves of samples with different T_g from (a) B-25, (b) R-25, (c) B-50 and (d) R-50 series. The inserts were images of the compression-molded samples with different T_g .

3.4 Tensile property of the modified lignocellulose. Besides processability, mechanical property was one of the critical parameters determining the applicability of the modified materials as suitable thermoplastics. Figure 8 shows the tensile properties of the modified lignocellulose by reactive extrusion, including the cleaned sample of the innate lubricant. For the baseline series (B-25 and B-50), tensile measurement was limited to samples with T_g below 133°C since the other samples from these series exhibiting higher T_g had poor compression moldability and could not be

prepared as specimens. The thermoplastic lignocellulose prepared by reactive extrusion in the present study had tensile strength of 18-31 MPa, modulus of 816-1570 MPa and elongation-at-break of 2.6%-6.1%, respectively. The new thermoplastic lignocellulose showed similar mechanical properties to commercial resins, e.g., polylactide acid, suggesting its suitability for practical industrial applications.

Compared to the sample of the lubricant prepared at the highest LC in the study, all samples of the recycle and baseline series displayed higher tensile strength and modulus, which was consistent with that most of the samples in the recycle and baseline series had higher T_g than the control sample. Only the sample in the R-25 series prepared with a 36 wt% LC had a lower T_g value than the control (103 °C versus 105 °C). However, it still displayed a better tensile property than the control, indicating that using a recycle stream was beneficial for not only using less liquid modifier to in the extrusion process but also to obtain stiffer final product. Because of the acidic nature of the liquid modifier, in the case of the control sample, too high liquid modifier content in the extruder appeared to cause more significant degradation of the lignocellulose molecules²⁴, which explained the lower mechanical strength.

The tensile properties of evaluated modified samples were noted to be higher with higher T_g values. But the influence of T_g on tensile property became invalid when very high extrusion LC was used. Namely, LC > 42 wt% for R-25 series or LC > 47 wt% for R-50 series, although the T_g of the corresponding samples increased, their tensile property showed a significant decline, as the samples became poorly moldable. A similar decreasing tendency in tensile strength was observed for the two-baseline series with high T_g . However, the tensile modulus increased, which was probably because of the reinforcement by some unmelt fibrils.”

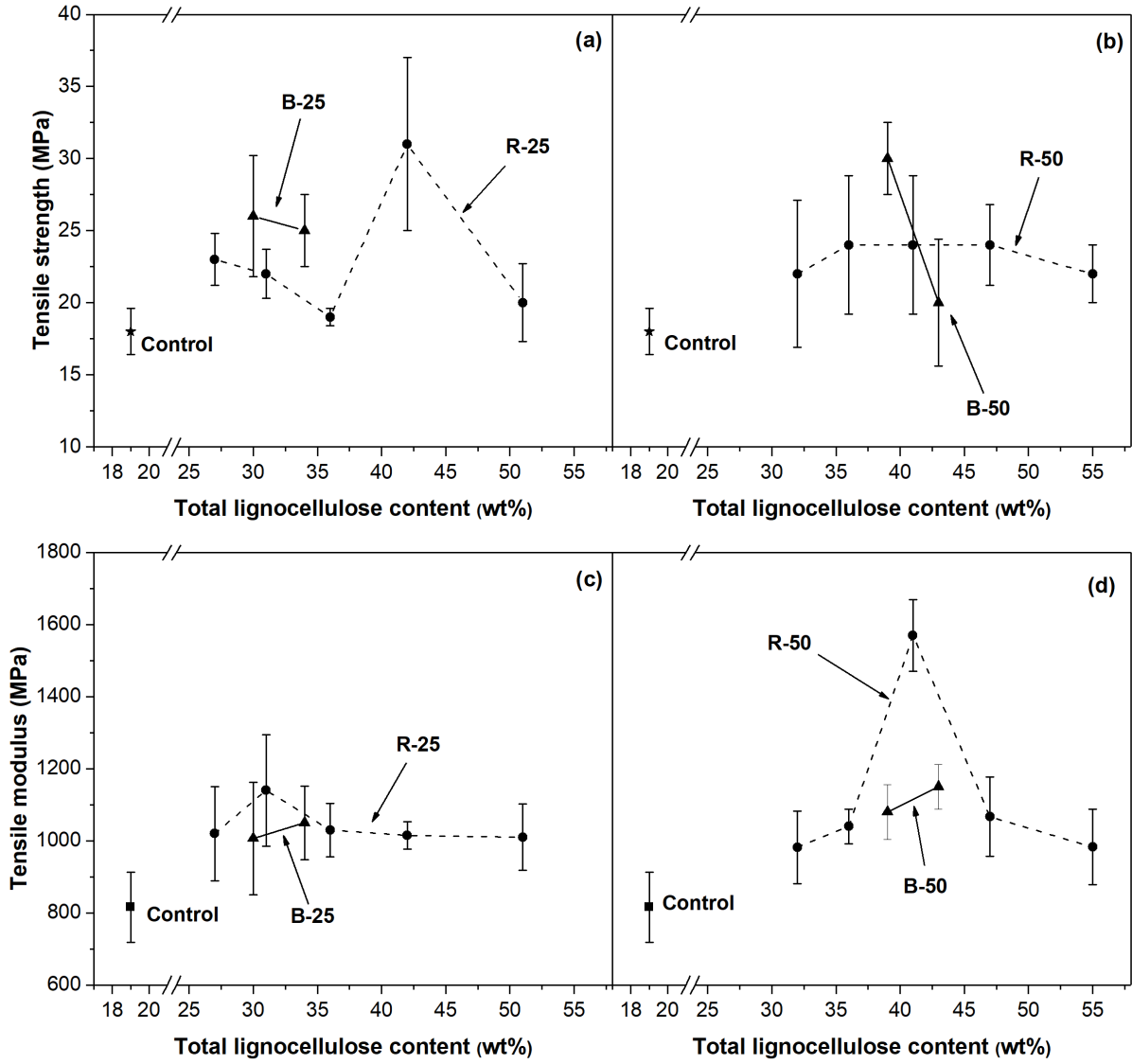


Figure 8: Tensile strength and modulus of the modified lignocellulose prepared by reactive extrusion with and without a recycle stream. The control was the cleaned sample of the lubricant.

4. CONCLUSIONS

The bulk acetylation reaction for lignocellulose requires lubrication in order to be carried out with a twin-screw extruder. Low viscosity solvents or an excess of the anhydride reactant is the common lubricant in this case, but such use require expensive recovery operations at the end of the reaction to produce a ready-to-use sustainable thermoplastic. The concept of a recycle stream was considered for the first time in a reactive extrusion process to use the modified lignocellulose as its own innate lubricant instead of excess reactants. Reducing the reactant concentration relative to the neat lignocellulose produced less functionalization of the biopolymer but the materials created with the recycled content showed higher flowability relative to comparable conditions where only the reactants lubricated the system. The majority of these samples showed good thermoplasticity to be melt molded. Only for one specific condition, using 25% recycled content at a total lignocellulose content of 36 wt% produced a synergistic improvement in reaction system to higher grafted content (and lower T_g) compared to modified materials created with a large excess of reactant (19 wt% of the lignocellulose). With 25% recycle stream, the process showed a higher reaction effectiveness, better than the extrusion process operated without recycle content. With a 50% recycle stream, the process showed some negative effects on the reaction, suggesting the innate lubricant was shielding the reactive sites in lignocellulose from the reactants. The tensile testing demonstrated that a recycle stream also benefited to the final product to have better mechanical property. Overall, the study has shown a viable approach to the bulk modification of lignocellulose from a commercial viewpoint where any subsequent cleaning step would lower the competitiveness of the biopolymer in a synthetic resin market.

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Notes

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