

Melt strength enhancing additives for reactive extrusion of polylactide – a comparative study

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ABSTRACT

Poly(lactide) (PLA) has a low inherent melt strength which is an obstacle to its use in film and blow-molding applications. This can be addressed through the use of reactive chain extension, but commercially available additives for this process vary widely in reactivity and chemical composition. This work compares the melt strength of polylactide modified with 11 different commercial additives marketed as chain extenders or viscosity enhancers for polyesters. To compare the effectiveness of these additives in enhancing PLA melt strength, blends were produced via both batch mixing and continuous extrusion using temperatures of 170–230 °C, processing times of 3–15 min and additive concentrations of 2–10 %. The melt strength of produced blends was evaluated using Rheotens draw-down measurement on a continuously extruded melt strand and changes to melt strength from reactive extrusion were determined through comparison with unmodified PLA processed under identical conditions. The effectiveness of melt strength enhancing additives was found to be dependent on functional group type and concentration within the additive. Maleic anhydride functionalized additives were shown to be completely ineffective. Epoxy-modified acrylates were demonstrated to provide only moderate melt strength enhancement at low functional group content but achieved up to 300 % melt strength and 400 % zero-shear viscosity over unmodified PLA when using additives with a functional group content of 15–20 %. Increasing additive concentration in the blend was found to only be an effective means of further viscosity enhancement for low-reactivity additives with a functional group content below 10 %.

1. Introduction

Worldwide plastics production has been experiencing steady growth for decades and is projected to increase up to threefold over 2019 levels by the year 2060 due to global economic growth. Since plastics are made predominantly from non-renewable resources and often used in short-term packaging applications, their production and disposal generate millions of tons of carbon dioxide emissions and non-degradable waste every year, both of which are projected to increase along with growing production volume. Rising awareness of the pollution and global warming caused by this growth has led to greater interest among both academics and industry in the development of sustainable alternatives like bioplastics [1,2].

The largest share of the current market for bioplastics is held by poly(lactic acid) (PLA), a linear aliphatic polyester produced via the ring-

opening polymerization of lactide sourced from the fermentation of starch or sugars. Due to growing production capacity, expected to exceed 2 million tons by 2027, and competitive prices, this bio-based, recyclable and compostable thermoplastic is considered a promising candidate to replace non-renewable virgin plastic in many applications, particularly those with short life cycles such as packaging and textiles [3–6].

The properties and uses of PLA have already been widely studied, and its mechanical and processing characteristics have been found to require some adaptation to make it a viable drop-in replacement for currently used fossil-based plastics. Room temperature PLA has high mechanical strength and good optical properties but is quite brittle, while in its melt state, PLA has low viscosity and low melt strength. This makes it well-suited to injection molding, but constitutes a barrier to its use in production processes where good melt strength is required for

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thermoplastics to retain their shape during processing, such as foaming, thermoforming, blown extrusion and film drawing [7–12].

Additionally, like most polyesters, PLA is subject to hydrolytic chain scission when processed at high temperatures, especially in the presence of ambient moisture. This causes a reduction in average chain length over the course of repeated processing cycles, leading to a melt strength reduction in recycled or extensively processed PLA materials [13–15].

Polyester chain length can be restored or even increased above that of virgin material via reactive extrusion, using additives that link multiple PLA chains together [16,17]. Depending on the additive used, this can lead to different kinds of chain extension, as shown in Fig. 1. Radical chain extenders such as dicumyl peroxide can react with any part of the polymer chain and are thus not limited in their effectiveness by the availability of reactive end groups [18]. However, this unselective reactivity can lead to cross-linking (1) and the loss of thermoplasticity if dosage and mixing are not carefully controlled. To avoid this, chain extension is usually carried out at the hydroxyl (OH) or carboxyl (COOH) chain end groups, which limits each polymer chain to one or two crosslinking reactions. In this case, the polymer structures obtained through chain extension are determined by the functionality of the reactive additive. Bifunctional or multifunctional small-molecule chain extenders lead to linear chain extension (2) and star-shaped polymers (3) respectively [19]. Polymeric chain extenders with reactive groups spaced out along the polymer chain lead to long-chain branched structures (4).

Long-chain branching is an effective method of improving the melt strength of PLA and other polyesters since it increases average chain length, leading to more entanglements and increased viscosity while retaining thermoplasticity [20–24]. The polymeric additives are also well-suited for use in industrial-grade extrusion, since they are commonly available in similar granule sizes as the polymer matrix and can be fed into the main hopper of the extrusion line. Small-molecule additives require specialized equipment for the dosing of liquids or powders into the extrusion line. Chain extenders whose reactive groups selectively favour a reaction with only one of the PLA chain ends, such as epoxides which react more readily with the carboxyl chain end than the hydroxyl one, also prevent crosslinking of the material. Melt strength enhancement using polymeric, epoxy-functionalized chain extenders is well-documented for rPET production to enhance processability and compensate for the molecular weight loss to hydrolytic chain scission [25,26].

Due to increased interest in bioplastics in recent years, the use of these reagents in biopolyesters has been the subject of several publications. In our research for this work, we found that the most commonly studied chain extending/long-chain branching additive is the Joncryl ADR series of products by BASF, which was used in almost half (34 out of

73) publications we found on the subject of long-chain branching of PLA as well as its blends and composites [27,28]. However, in attempting to source this material ourselves, we initially found it to be unavailable and no longer listed in the BASF product portfolio.

While a variety of alternative products with similar chemical functionality and processing properties are available from other producers, most are far less thoroughly studied than the Joncryl ADR series, and we were not able to find any studies comparing their relative effectiveness as melt strength enhancers for bioplastics. Most publications we found study the effectiveness of one or two chain-extending additives compared to unmodified material. Many studies use chain extending additives as compatibilizers for blends [29–32] and composites [33–35], so changes to rheology are not explicitly studied. Others employ chain extension as a means to improve thermal and mechanical properties, crystallization and biodegradation [36–40] but do not report rheological data. Where reported, changes to melt strength are determined from different measuring methods, using mixing torque [41–43], melt viscosity [44–46] and melt flow rates [31,47]. Direct Rheotens melt strength data is only rarely reported [48–50] and unmodified material is not always included in the study as a basis for comparison [51]. Additive concentrations, processing temperatures and screw configurations also differ between studies. No direct comparison can be made on the basis of currently available studies regarding the effectiveness of different long-chain branching additives in enhancing PLA melt strength. This paper aims to establish a clear comparison of the melt rheology changes obtained in poly (lactic acid) using 11 different additives marketed as melt strength or viscosity enhancers. All studied materials are processed under identical conditions and their effectiveness is evaluated based on Rheotens melt strength measurements.

2. Experimental

2.1. Materials

Poly (lactic acid) (PLA) grade Luminy LX 175 was obtained from TotalEnergies Corbion. It is a high viscosity amorphous PLA grade containing 96 % L-lactide units.

Melt strength enhancing additives used are listed in Table 1. All are polymeric materials containing different amounts and types of reactive

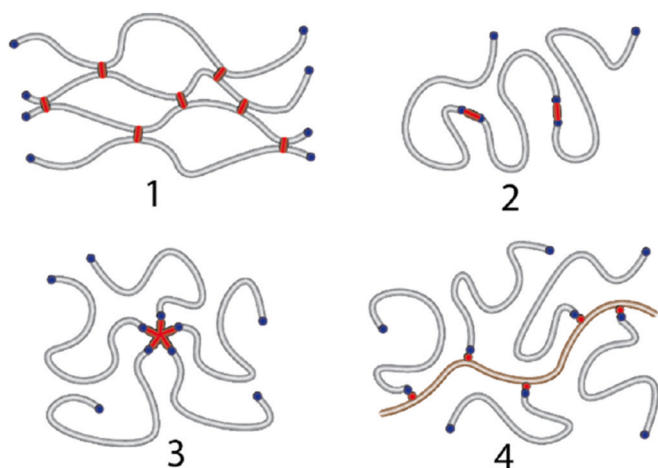


Fig. 1. Polymer structures obtainable via reactive extrusion.

Table 1

List of reactive extrusion additives used in this work.

	Reactive group	Incorporation	M (g/mol)	Name	Supplier
1	14 % MA	Copolymerization	10,000	Xibond 250	Aurorium
2	15 % GMA	Copolymerization	85,000	Xibond 950	Aurorium
3	20 % GMA	Copolymerization	50,000	Xibond 920	Aurorium
4	2 % GMA	Grafting	no data	Scona TPPL 1214	BYK
5	3 % GMA	Grafting	no data	Scona TPKD 8304 PCC	BYK
6	1.3 % MA	Grafting	no data	Scona TSKD 9103	BYK
7	8 % GMA	Copolymerization	no data	Lotader AX 8900	SK Functional Polymer
8	3 % GMA	Copolymerization	no data	Lotader AX 8930	SK Functional Polymer
9	3 % NCO	Grafting	no data	Graftabond EB-NCO 00330	Graft Polymer
10	5 % GMA	Grafting	no data	Graftabond EB-GMA 01050	Graft Polymer
11	29 % GMA	Copolymerization	7100	Joncryl ADR 4400	BASF

groups which can react with PLA chain ends. Structures of the base polymer and reactive units of all additives used in this work are provided in Fig. 2. The additive base structure may be a homopolymer (additive 4), random copolymers consisting of styrene, ethylene and different acrylates (additives 1,2,3,7,8,9,10,11) or block copolymers (additives 5,6). Functional groups for the reaction with PLA may be glycidyl methacrylate (GMA), maleic anhydride (MA) or an acrylate-isocyanate group (NCO) for which only an approximate chemical structure can be provided due to lack of specification by the supplier. Functional groups may be incorporated into the base polymer through copolymerization with a functional group monomer or radical-initiated grafting-to. Molecular weight of additives according to supplier data is listed in Table 1 if available.

Additives were selected to cover a range of polymer backbones, functional groups and functionalization levels within the bounds of commercially available materials. MA- and GMA-functionalized additives are available in a variety of compositions, however MA-based additives have poor reactivity with PLA according to both literature and preliminary findings in this study. Therefore, only one each of MA-based additives with a high and low functionalization rate were selected. GMA-based additives were selected to provide variety in functional group content, molecular weight, grafting-to or copolymerization of functional groups as well as miscibility of the base polymer with PLA in order to determine the effect of these factors on melt strength enhancement effectiveness. As the frequently studied Joncryl ADR series additives proved difficult both to obtain and to process with consistent quality, only one material from this product series was included. Also, only one additive with NCO functionalities could be obtained, as the use of this functional group is uncommon in industrially produced chain extension additives.

Reaction mechanisms between the functional groups of the additives and the PLA chain ends are shown in Fig. 3. While epoxides can react with both the carboxyl and hydroxyl end groups of PLA chains, carboxyl groups are reported to have a higher reactivity [52,53]. The carboxyl reaction shown in Fig. 3 is therefore expected to be the dominant chain reaction mechanism for glycidyl-functionalized additives due to the short reaction times and relatively mild temperature of the reactive extrusion of PLA.

These reactive groups are incorporated into the polymeric additive in one of two ways: via grafting onto the polymer chain or via copolymerization of the reactive group containing monomer with the backbone monomer(s). Both lead to a random distribution of the functional groups along the polymer chain. Since grafting-to is usually carried out using free radical reactions, only low levels of modification are possible without risking cross-linking of the polymer and the loss of thermo-plasticity, therefore additives produced via grafting contain low amounts of reactive groups (up to 5 %), while additives produced via copolymerization may contain a larger percentage of reactive groups.

The polymer backbone (for grafted additives) or non-functionalized repeating units (for copolymerized additives) do not participate in chain extension reactions, but determine miscibility of the additive with PLA, which can affect reaction rates. Incorporating poly (methyl methacrylate) (PMMA) improves miscibility with PLA, which is immiscible with polyethylene (PE) and polystyrene (PS). However, the exact PMMA percentage in the products is not always provided by suppliers.

2.2. Processing

Batch processing was carried out on 50 g batches for 15 min each in a Brabender Plasti-Corder (Duisburg, Germany) with a 50 cm³ measuring mixer. PLA and additives were added simultaneously, and the mixing chamber was filled and closed over the course of the first minute of measurement. The reaction's progress was monitored using torque measurements. The processing temperature and additive concentration were varied to optimize processing parameters for extrusion.

Continuous extrusion was carried out in a Berstorff ZE 25 A (Hannover, Germany) co-rotating twin-screw extruder. The screw configuration was composed of one 210 °C mixing zone followed by a compression zone for initial melting and homogenization, then a 230 °C reaction zone which included four additional short mixing zones. Die temperature was set to 190 °C and residence times were determined using coloured PLA masterbatch. To achieve a residence time of 3 min, feed and screw speed were set to 5 kg/h and 50 rpm respectively. After extrusion, the extrudates were quenched in a water bath, granulated and dried.

Out of all additives used in this work, only Joncryl ADR 4400 was

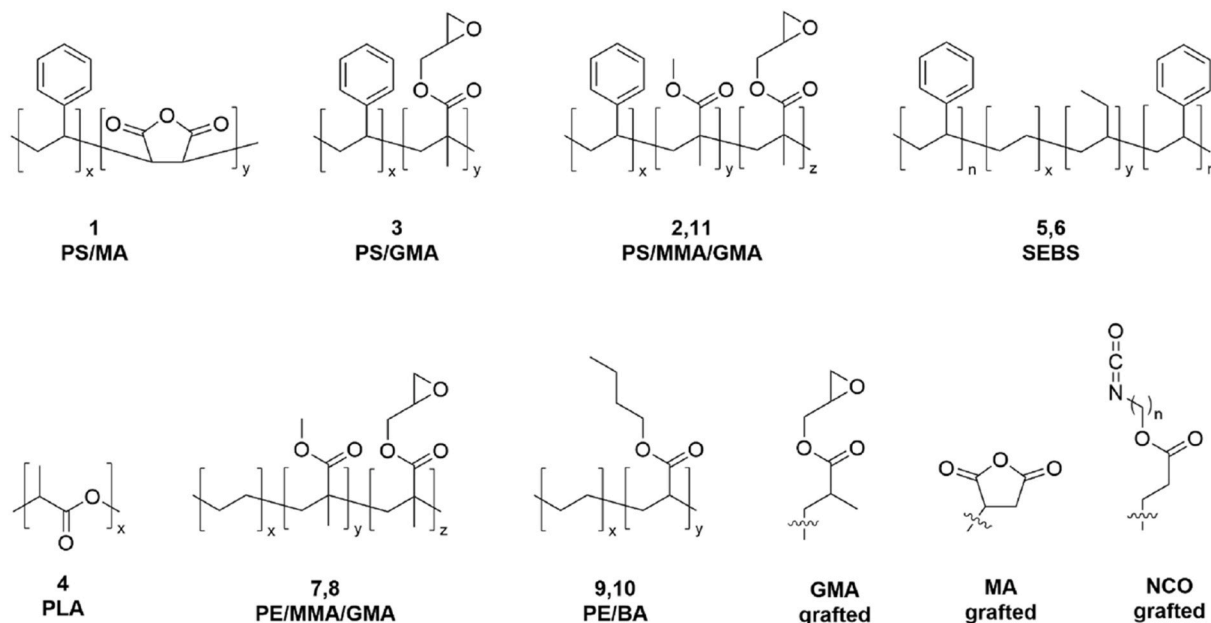


Fig. 2. Chemical structures of additives used in this work. Exact structure information is proprietary, and supplier structure claims may cover variations with additional alkylic groups of varying chain length under the same product name. For clarity, only the base monomer repeating units as named in product data sheets are included in this graphic.

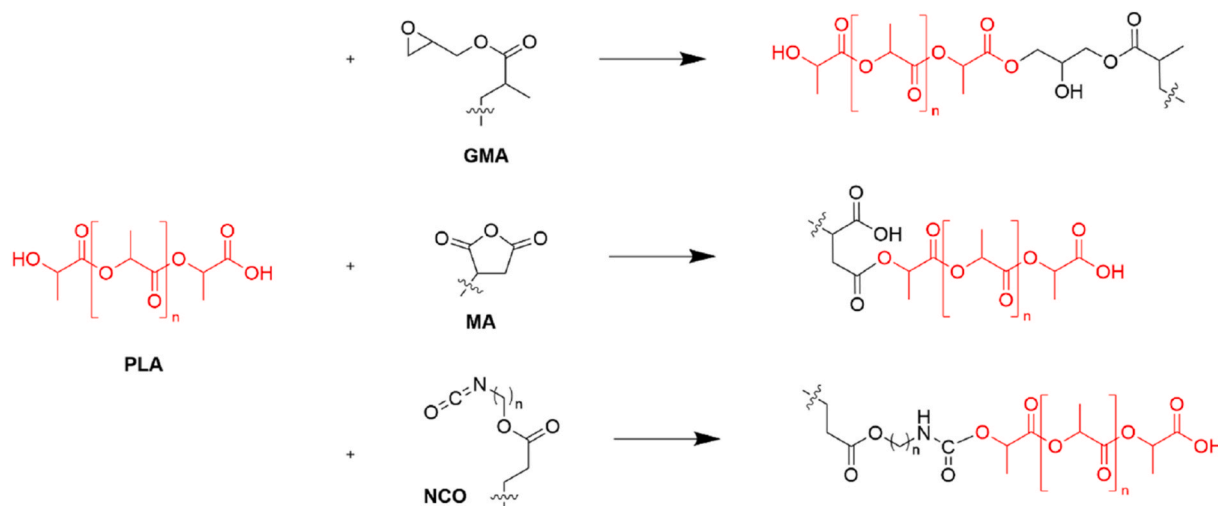


Fig. 3. Reactions of additive functional group with PLA chain ends.

found to be difficult to process, as it showed a tendency to separate from PLA granulate and stick to the sides of the feed hopper, likely due to partial melting when in contact with warm surfaces. This led to visible inhomogeneity of the extrudate that could not be corrected even by controlling the additive's particle size. While homogeneity improved with the second extrusion process in film production and Rheotens measurements, some Joncryl material inevitably remained in the hopper during extrusion, causing actual additive concentrations in those batches to be marginally lower than the feed compositions listed in this work. For all other additives, both visual appearance and torque remained consistent throughout extrusion and no loss of material occurred.

For tensile testing, the modified PLA was processed into films of 0.1 mm thickness using a Labtech LCR-300 (Bangkok, Thailand) sheet line. All mechanical and rheological tests were carried out on materials obtained via continuous extrusion.

Modified PLA materials produced for this work will be referred to by numbers such as 7-10-200 for batch processing or ex_3-5 for continuous processing. The first number refers to the additive used, as listed in Table 1, the second number is the weight percentage of the additive in the feed, and the third number (for batch processing) indicates the processing temperature in °C. To account for viscosity loss from hydrolytic chain scission during processing, unmodified PLA samples were processed at identical conditions to provide baseline melt strength values. A full list of produced blends can be found in the supplementary materials.

2.3. Characterization

Melt viscosity during processing as an indicator of reaction rates was tracked via continuous torque measurements in batch processed materials.

Melt flow rates and melt densities were measured on an Instron Ceast Modular Melt Flow type 7026 (Norwood, USA) at 210 °C under a 2.16 kg weight.

Tensile testing was carried out on an Instron Universal Testing System 5567A (Norwood, USA) according to DIN EN ISO 527 testing standards. Testing specimens were cut from 100 μm thin films extruded on a Labtech LCR-300 (Bangkok, Thailand) cast film line. Each measurement was carried out five times.

Melt strength measurements were carried out on a Göttfert Rheotens 71.97 (Buchen, Germany) tensile test system after extrusion in a Brabender (Duisburg, Germany) measuring extruder, maintaining constant extrusion pressure. This method measures the drawing force required to stretch a melt extrudate strand as a function of the draw-down speed.

The experiments starts at drawing force zero, with the Rheotens wheels' turning speed adjusted to the extruded strand velocity, then gradually increases draw-down speed until filament breakage occurs [54,55]. Rheotens measurements for each material were repeated ten times. The distance between extrusion nozzle and Rheotens wheels was a constant 100 mm, ensuring that cooling of the extruded strand before measurement was minimal and strand elongation occurred under quasi-isothermal conditions.

Since the samples showed a wide range of viscosities and successful Rheotens measurement strongly depends on the viscosity and adhesion of the polymer melt to the Rheotens wheels, not all samples could be measured at the same temperature. Rheotens measurements for low-viscosity materials ex_1 and ex_6 had to be carried out at 180 °C while all other measurements were carried out at 210 °C. Unmodified PLA was measured at both temperatures as a baseline value to compare results.

3. Results and discussion

3.1. Investigation of additive reactivity

For a preliminary estimate of the selected additives' reactivity, batch mixing with PLA was carried out for 15 min to track viscosity changes. This provides a much longer reaction time than typical residence times in continuous extrusion. The processing temperature was set to 200 °C and additive concentration was 10 %. These conditions were chosen to ensure high reactivity while screening additives for their effectiveness.

Regardless of reactivity, adding a polymeric additive to PLA results in the creation of a polymer blend. The thermal and mechanical properties of polymer blends are highly dependent on phase morphology, which is affected by the polymers' relative viscosities, miscibility and shear forces during mixing [56–58]. While a detailed study of the mixing process was not carried out as a part of this work, blend composition does affect the observed melt viscosities. Since no more than a 10 % additive weight percentage was used at any point in this work, additives are presumed to always be the dispersed phase in the blend. Blend properties are thus expected to be dominated by the rheological properties of the continuous phase (PLA), though the use of a low-viscosity blend partner may still reduce the overall melt viscosity of the blend. Additive molecular weight and melt viscosity are not always provided by suppliers, but where available are below that of PLA. In that case, blending of PLA with the additive may cause an initial reduction in overall melt viscosity which must be offset by the viscosity increase from chain extension for the additive to be considered effective.

Additive effectiveness is also affected by miscibility, as shown in Fig. 4. If an additive is fully miscible with the PLA matrix (A), a reaction

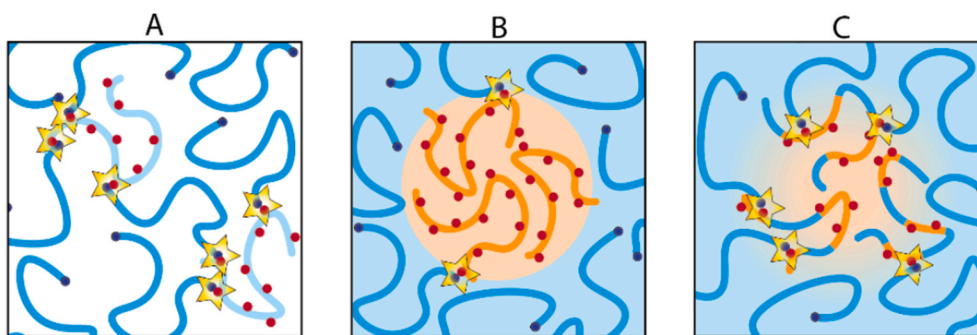


Fig. 4. Effect of miscibility on reaction rate in blends that are (A) fully miscible (B) immiscible (C) partially miscible.

between the PLA chain ends and the additive's reactive group may occur anywhere within the melt. If the additive is immiscible with PLA (B), it is dispersed within the PLA matrix in the form of droplets, and a reaction between the two may only occur at the phase interface. This drastically reduces reaction rates compared to a fully miscible blend. Miscibility can be improved by using copolymeric additives containing segments that are miscible with PLA. (C) This causes polymer chain interpenetration at the phase interface, effectively widening the available reaction zone in which chain extension may occur. The branched additive-PLA copolymers created via this reaction also act as compatibilizers, further improving miscibility.

Fig. 5 shows torque changes over the reaction time for each additive. For unmodified PLA 0–200, torque decreases steadily over time as hydrolytic chain scission occurs. The effect of melt strength enhancing additives can be observed if torque remains steady or increases, indicating that chain length losses are made up for by increased average molecular weight caused by long-chain branching.

Out of all additives tested in this work, only five showed a significant torque increase over unmodified PLA in batch processing, all of which are additives functionalized with GMA. Other additives exhibited only the steady torque decrease associated with PLA thermal degradation. PLA functionalized with additives 2 and 3 exhibited the strongest torque increase, followed by a decrease after several minutes due to shear scission of the highly viscous long-chain branched structures, after which torque remained steady and no further decrease could be observed. PLA functionalized with additive 5 exhibited stable torque for a time before it began to decrease, indicating that a long-chain branching reaction between the additive and PLA occurred but only countered the effects of thermal degradation for a limited time. Additives 7, 8 and 11 show a significantly slower loss of viscosity to thermal degradation than unmodified PLA, indicating that a chain extension reaction occurred to offset loss of chain length, but the reaction rate was

too low to increase viscosity over time. Additive 4 increased torque when added to unmodified PLA, but showed no increase or plateau in torque over time. This additive is a functionalized PLA and thus exhibits full miscibility with the PLA matrix. When heated, grafted-on GMA functional groups may initially react with carboxyl chain ends within the additive itself, reducing the available functional groups for reaction with the surrounding PLA matrix. This produces highly long-chain branched PLA-g-GMA, which has reduced reactivity but can still increase the overall viscosity when added to virgin PLA.

The amount of maleic anhydride (MA) functional groups cannot be observed to have any effect on reactivity, as additives 1 and 6 lead to no notable torque increase. This matches the observations of Jazkiewicz et al. who found MA functional groups to exhibit no reactivity at typical PLA processing temperatures [59]. The NCO-functionalized additive only minimally reduced the rate of viscosity loss to thermal degradation and did not increase torque.

As most additives acquired for this study were GMA-based, the effect of the additive's reactive group content on reactivity were studied for epoxy-functionalized additives only. Fig. 6 compares the additives' GMA content as supplied by the manufacturer to the torque observed in batch processing as an approximation for the viscosity change caused by reactive chain extension. While highly functionalized additives 2 and 3 showed the greatest torque increase, no correlation between degree of functionalization and viscosity changes could be found for additives below 10 % functionalization rate. We surmise that this is because at slow reaction rates due to low functionalization, the effect of chain extension on viscosity is weaker and thus more easily overshadowed by mixing effects based on the intrinsic viscosities of the additives and miscibility of the additives with PLA. Since only limited information on the chemical makeup and molecular weight of the additives are provided by suppliers, these effects were not precisely quantified in this study. However, the effects of miscibility can be observed in the performance of additive 4, which is PLA-based and therefore has the best

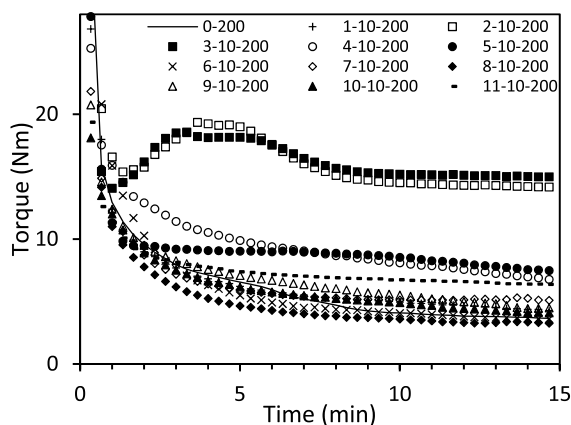


Fig. 5. Measured torque curves of PLA samples in batch processing with 10 % additive content at 200 °C compared to unmodified PLA (continuous line).

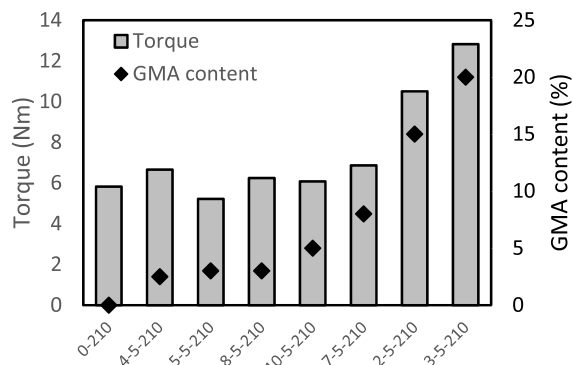


Fig. 6. Torque values after 4 min of mixing of PLA samples modified with 5 % GMA-based additives in batch processing compared to the additives' reactive group content.

miscibility with PLA out of all studied additives. It causes a strong torque increase despite its low epoxy content of 2.5 %, showing a performance comparable to that of additive 7 with 8 % epoxy content. The effect of molecular weight can be observed in additive 11, which has a similar chemical composition as additive 2 and a higher functionalization rate, but only 1/12th the molecular weight. It shows very little effect on viscosity compared to additive 2 when 10 % additive are used. In this case, chain extension effects are likely outweighed by mixing effects from the additive's very low melt viscosity.

3.2. Effect of reaction conditions

To determine optimum reaction conditions for continuous extrusion, the effect of temperature and additive concentration on obtained viscosity increases was studied in batch mixing. Additive 3 was used for this study because it showed good reactivity in previous tests. Temperature was varied between 170 °C and 230 °C and additive concentrations between 2 % and 10 % were used.

Fig. 7 shows torque changes over time for a representative series of samples. Maximum torque values (excluding initial torque during melting) which indicate the occurrence of chain extension reactions are reached significantly earlier at higher reaction temperatures. At 170 °C, peak torque is not achieved until after 7 min of reaction time, compared to only 3 min at 230 °C. Since residence times in continuous extrusion are typically under 3 min, heating to 230 °C is required to achieve sufficient chain extension reaction speed to produce a noticeable viscosity increase in such short reaction times. While higher temperatures also lead to increased hydrolytic chain scission of PLA, the resulting loss of chain length is not significant compared to the chain length increase due to reactive long-chain branching.

Table 2 shows the reaction time until the torque maximum is reached, and Table 3 lists the torque difference at this maximum between each sample and an unmodified PLA sample processed at the same temperature for the same amount of time. High processing temperatures were found to significantly decrease reaction times and increase PLA viscosity as tracked via torque measurements, indicating that the reactivity of GMA-based chain extension is highly temperature-dependent. Increasing the amount of additive in the blend significantly improves reaction speed and viscosity increase at low concentrations (2 %–6 %) but provides little additional benefit at higher concentrations. Increasing additive concentration can even cause a slight torque decrease due to the blending of PLA with an increased amount of the lower chain length, less viscous additive polymer.

Since only a limited amount of reactive PLA end groups are initially present in the material, the limiting factor of the chain extension reaction is the generation of new chain ends via thermal and hydrolytic chain scission during processing. This can be seen in several of the

Table 2

Time (min) to reach the torque maximum when varying additive content and reaction temperature.

	170 °C	185 °C	200 °C	215 °C	230 °C
2 %	10.4		5.7		4.1
4 %		6.4		4.3	
6 %	7.3		4.5		3.1
8 %		6.0		3.8	
10 %	7.5		4.2		3.2

Table 3

Δ Torque (Nm) over unmodified PLA at torque maximum when varying additive content and reaction temperature.

	170 °C	185 °C	200 °C	215 °C	230 °C
2 %	6.1		3.5		9.8
4 %		6.5		11.6	
6 %	6.6		10.6		13.8
8 %		9.3		12.4	
10 %	7.8		11.0		13.2

torque curves, particularly of samples processed at high temperatures and with a high amount of additive, where the viscosity of the mixture reaches a plateau or resumes a gradual increase after around 10 min of reaction time, indicating a continued chain extension reaction. This can be attributed to additional PLA chain ends becoming available for reaction with the chain extender due to PLA chain scission over time.

Based on these results, additive concentrations of 2.5 % and 5 % were chosen for continuous extrusion as well as a reaction time of 3 min and a screw temperature profile reaching 230 °C in the reaction zone.

3.3. Additive performance after continuous extrusion

After reactive extrusion, melt flow rate and density of the granulated and dried additives were determined in preparation for Rheotens measurements. The results are listed in Table 4. Only minor changes in density were observed compared to unmodified PLA, which are attributed to the admixture of up to 5 % of a lower-density additive. This effect is most clearly observed in the ethylene-containing additives 5–10, since polyethylene has a significantly lower density than PLA.

The melt flow rates show significant differences which align with the viscosity changes observed in batch processing. PLA modified with high epoxy content additives 2 and 3 showed a significant increase in viscosity during extrusion and very low melt flow rates. PLA modified with maleic anhydride based additives 1 and 6 showed decreased viscosity, increased melt flow rate as well as an opaque appearance after processing, whereas other modified PLAs retained some degree of

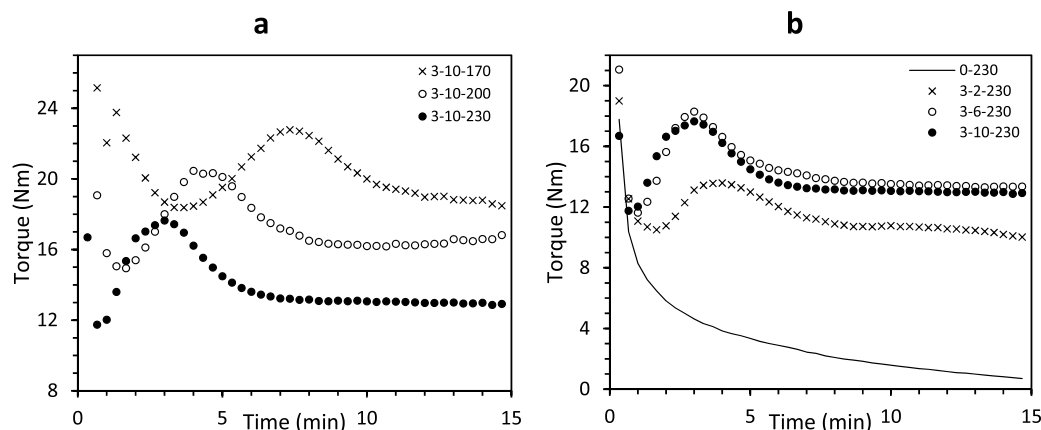


Fig. 7. Torque curves of PLA reaction with Additive 3 when varying (a) temperature and (b) additive content.

Table 4
Tensile and rheological properties of all continuously extruded materials.

Additive	% in blend	MFR (g/10min)	ρ (g/cm ³)	ϵ_B %	σ_B (MPa)
None	–	7.60	1.099	2.96	75.8
1	5	8.71	1.094	2.72	71.1
	2.5	8.53	1.101	2.76	69.5
2	5	0.91	1.093	3.01	81.0
	2.5	1.61	1.095	3.12	81.7
3	5	0.70	1.091	2.82	73.2
	2.5	0.94	1.095	2.89	77.9
4	5	5.89	1.098	2.88	74.6
	2.5	6.50	1.098	2.93	74.1
5	5	6.19	1.084	2.85	71.2
	2.5	6.74	1.093	2.88	73.9
6	5	8.46	1.083	2.94	71.3
	2.5	8.28	1.094	2.90	73.4
7	5	6.75	1.085	2.93	69.7
	2.5	6.89	1.089	2.82	72.5
8	5	7.27	1.083	2.80	68.2
	2.5	6.88	1.087	2.82	70.8
9	5	7.36	1.075	2.73	64.7
	2.5	7.09	1.092	2.82	68.3
10	5	8.14	1.082	2.77	66.2
	2.5	7.29	1.085	2.73	66.5
11	5	4.66	1.103	3.00	74.7
	2.5	3.49	1.105	3.06	75.0

transparency.

Tensile strength of all modified samples remained comparable to that of unmodified PLA. Only samples modified with additives 2 and 11 showed a slight increase in elongation and strain at break, while most had similar (additives 3, 4, 5, 6) or slightly reduced (additives 1, 7, 8, 9, 10) tensile strength compared to unmodified PLA.

The decrease in melt flow rates (in %) achieved through reactive extrusion with all additives is shown in Fig. 8. As in batch processing, epoxy-based additives with high functional group content (2, 3, 11) performed best, though a clear correlation between epoxy group content and melt flow reduction could not be established. Additive viscosity, miscibility, and in the case of additive 11, the aforementioned strong inhomogeneity of extruded material all affect the melt flow rate of the modified PLA materials. We also found that increasing the dosage of the reactive additive does not consistently lead to an increase in its viscosity-enhancing effects, as the materials with 5 % additive frequently exhibit a lower or comparable viscosity to those with only 2.5 % of the same additive. In additives with high functional group content, the lack of a further viscosity increase can be attributed to a saturation effect where no additional benefit can be gained from increasing the excess of

functional groups. For additives where the 5 % mixture shows lower viscosity than the 2.5 % mixture, we attribute this to the low viscosity of the additive itself, which decreases the overall viscosity of the mixture. When added in increasing amounts, this effect can cancel out the viscosity increase gained through chain extension, as seen for additives 8, 9, 10 and 11.

Results of tensile tests of all materials produced via continuous extrusion are displayed in Fig. 9. Only materials ex_2 and ex_11, which showed high levels of long-chain branching in melt flow rate testing, exhibit a slight increase in both force and extension at break, while for others, a slight decrease in both can be observed, which is attributed to the admixture of the polymeric additives. Extension at break of all samples remains within the range of 2.7–3.2 % and tensile strength between 60 and 80 MPa, both within the normal range of values for PLA as a strong but brittle plastic. This indicates that melt strength enhancement via reactive additives does not result in a significant change to mechanical material properties in the solid state.

3.4. Rheotens results

The melt strength of an extruded polymer strand is defined as the drawing force required for strand breakage. In Rheotens experiments, data obtained is the draw-down force (F) as a function of drawing speed (v), as well as draw ratio (V) and stress (σ). Drawing speed is steadily

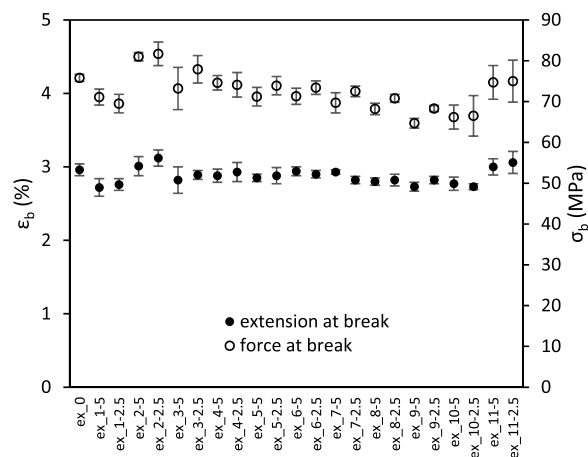


Fig. 9. Extension at break (black circles) and force at break (white circles) of all continuously processed materials.

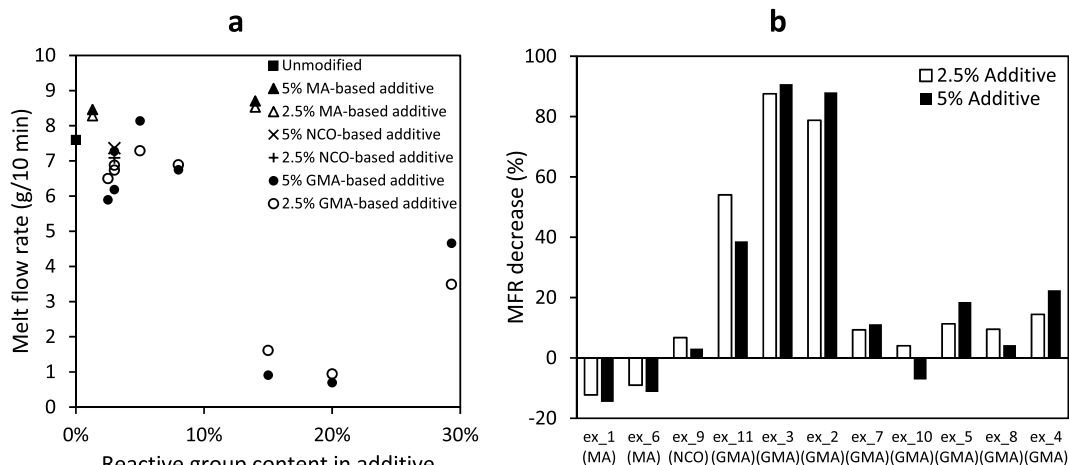


Fig. 8. a) Melt flow rates of all additives and b) changes in melt flow rate compared to unmodified PLA. Additives are listed in order of functional group type and content.

increased until rupture occurs. However, measured draw-down forces become imprecise at high draw ratios due to the hydrodynamic draw-resonance effect, which causes increasing fluctuation in the mass distribution of the drawn melt strand as draw speed increases. The resulting oscillation of the drawing force was observed to affect strand rupture, therefore precise measurement of rupture points could not be carried out for most materials.

Examples of the Rheotens curves of long-chain branched and unmodified PLA are shown in Fig. 10a. Material ex_2–2.5, which exhibited a significant viscosity increase in MFR measurement, required a much higher draw-down force over unmodified PLA in Rheotens experiments, and strand rupture occurred at a draw-down force of around 0.2 N and draw speeds between 700 and 1000 mm/s, preceded by only minimal oscillation due to the draw-resonance effect. Conversely, unmodified PLA ex_0 exhibited a strong draw-resonance effect at high draw speeds, which caused significant fluctuation in the drawn strand thickness, making a precise rupture point impossible to measure. However, draw-down force remained steady and/or oscillated around a melt strength value of 0.1 N in the range where strand rupture occurred. The draw-down force behaviour of all samples not shown here ranges somewhere between those two examples, with strand rupture often only occurring after significant draw-resonance oscillation. Rheotens raw data for all samples can be found in the supplementary materials.

Fig. 10b shows Rheotens mastercurves obtained by plotting against draw ratio and introducing a correction factor to bring starting values in line with a selected reference curve. Elongational viscosity curves in Fig. 10c were calculated from measured draw ratios and stress values for each material. Since the draw-down force at rupture could not be measured due to inconsistent rupture behaviour, melt strength was instead compared at mastercurve V/b value of 10, equivalent to a draw-down speed of ca. 700 mm/s, which lies before the onset of strong draw-

down force oscillation and/or rupture for most samples. Values were averaged across all repeat measurements of each sample and are shown in Fig. 10d. Samples were measured at 210 °C where possible and at 180 °C if no stable die pressure could be reached at 210 °C.

To obtain approximate zero-shear viscosity values for each sample, the viscosity at the lowest measured draw rates was averaged across all repeat measurements of the sample. Viscosity and melt strength changes in samples with additives were calculated by comparing their zero-shear viscosity and 700 mm/s melt strength to that of unmodified PLA measured at the same temperature. The obtained melt strength and viscosity increases compared to unmodified PLA are shown in Fig. 11.

As was already the case in melt flow rate measurements, samples modified with maleic anhydride based additives exhibited a decrease in melt strength and viscosity compared to unmodified PLA. The highest melt strength and viscosity increase is seen in samples modified with epoxy-based, high functional group content additives 2, 3 and 11 which already performed well in batch processing. Samples also show a clear correlation between additives' reactive group content and the effectiveness of increasing additive concentration in the blend. For additives with a GMA content of more than 10 %, raising additive concentration from 2.5 % to 5 % decreased viscosity significantly, indicating that even at the shorter reaction times in continuous extrusion, full saturation of reactive PLA chain ends can be achieved, rendering the further addition of excess epoxy groups ineffective. For all additives with less than 10 % GMA, increasing additive concentration in the blend further increased melt viscosity, indicating that unreacted PLA chain ends remained available for reaction with additional GMA functional groups. The decrease in viscosity by using more additive was also found to be more pronounced for low chain length additive 11 compared to additives 2 and 3. The latter have a similar chemical composition but greater molecular weight, which gives the additive itself higher viscosity and thus

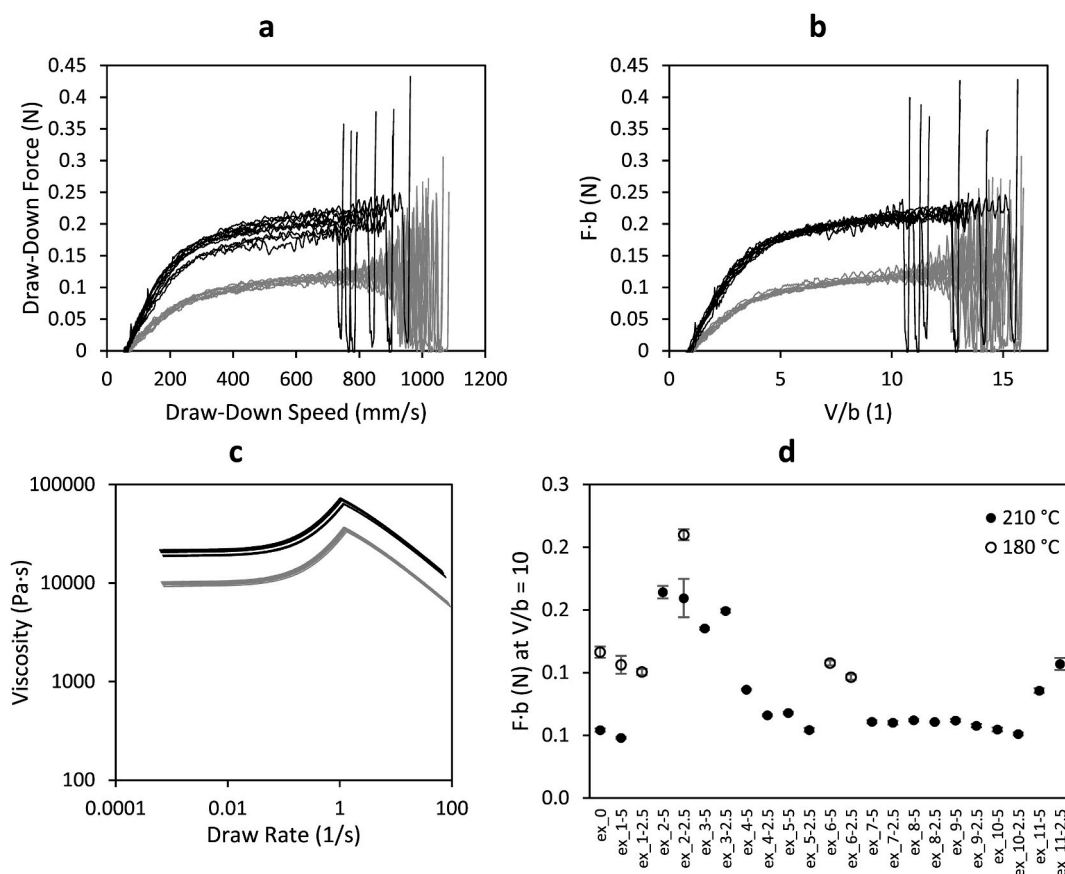


Fig. 10. Rheotens (a) raw data, (b) mastercurves and (c) elongational viscosity curves of unmodified PLA ex_0 (grey) and chain-extended PLA ex_2–2.5 (black) as well as (d) mastercurve melt strength values of all continuously processed materials at a draw speed of $V/b = 10$.

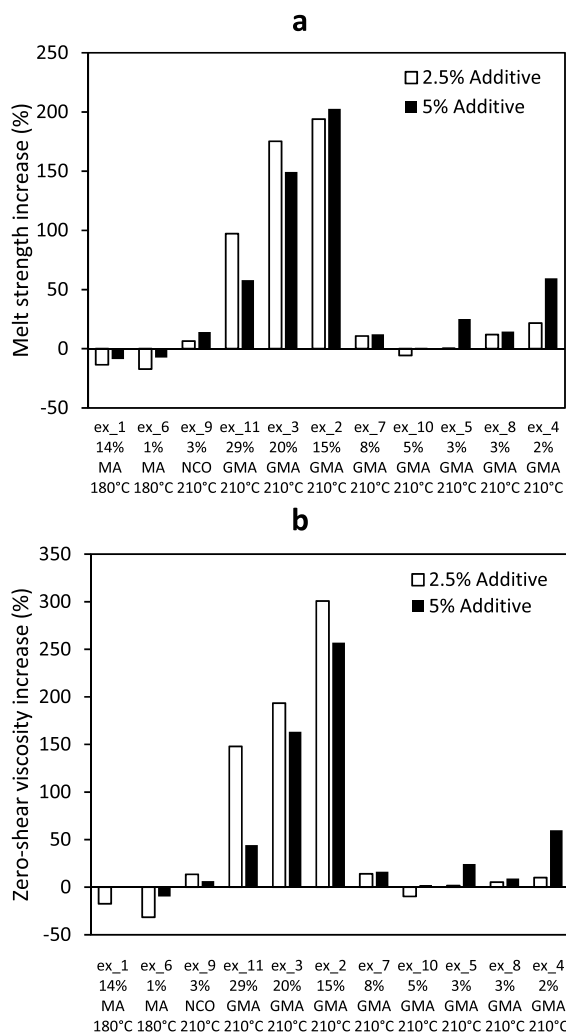


Fig. 11. Changes compared to unmodified PLA to (a) melt strength at $V/b = 10$ and (b) zero-shear viscosity of all continuously extruded materials. Additives are listed in order of functional group type and content and Rheotens measurement temperature is provided.

reduces the inherent viscosity decrease from polymer blending.

4. Conclusions

In this work, the melt strength enhancing properties of multiple additives in PLA reactive extrusion were confirmed. Additives with maleic anhydride functional groups were found to be ineffective at PLA processing temperatures up to 230 °C, while those with epoxy and isocyanate groups proved to be functional melt strength enhancers of varying effectiveness.

Reaction speed was found to increase with temperature, and a reaction temperature of 230 °C is required to achieve complete long-chain branching within continuous extrusion residence times. The maximum achievable melt strength increase was found to be dependent on additive concentration, and a trade-off between melt viscosity increase due to reactive long-chain branching and melt viscosity decrease due to low intrinsic viscosity of the polymeric additive was observed when varying additive concentration. Using these results, it is possible to tailor PLA melt strength to specific requirements within the range of a 10–300 % viscosity increase by selecting a suitable additive and blend percentage.

The highest melt strength increase achieved in this work used 2.5 % copolymerized acrylate additives with 15–30 % GMA content, yielding a 2x increase in draw-down force in Rheotens measurements and a 3x

increase in zero-shear viscosity over unmodified PLA. In a comparison between additives with similar GMA content, those with greater chain length and better miscibility with PLA show stronger melt strength enhancement. Tensile strength of PLA drawn films was shown to not be notably impacted by modification with melt strength enhancing additives.

This work provides a framework and a reproducible basis for comparison to aid in the selection and use of chain extension additives in both research and industrial applications. As additive effectiveness can vary within a wide range, the structure-property relationships explored in this study can inform the selection of additives and processing parameters. It provides a data basis for targeted PLA melt strength enhancement to adapt it to the requirements for many industrial processes, which will aid in the adoption of PLA as a viable and sustainable alternative to conventional fossil-based plastics.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2026.109104>.

Data availability

Data will be made available on request.

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