**REVIEW ARTICLE** 



# A review on rheological approaches as a perfect tool to monitor thermal degradation of biodegradable polymers

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#### Abstract

This review provides an in-depth analysis of the thermal degradation of biodegradable polymers through rheological methods. Focusing on key techniques such as time sweep tests, frequency sweep tests, and nonlinear rheological analyses gained at higher shear tests, the review highlights how these approaches offer critical insights into polymer stability and degradation kinetics. It entails an understanding of how molecular weight reduction, a common degradation mechanism, significantly impacts the performance of biodegradable polymers, and how the use of appropriate fillers can enhance thermal stability by mitigating chain scission. The review also discusses the application of the Arrhenius equation in modelling thermal degradation, helping predict degradation rates and optimize processing conditions. Time sweep tests are particularly emphasized for their ability to monitor polymer stability under various environmental conditions, while frequency sweep tests provide insights into the effects of processing/thermal history on material degradation. Tests at higher shear rates, which simulate real-world processing conditions such as extrusion and injection moulding, are explored for their role in understanding how processing-induced shear forces accelerate polymer degradation. Various biodegradable polymers are considered in this review, with polylactic acid (PLA) being the dominant polymer studied across most research, providing a clear picture of its degradation behaviour and strategies for enhancing its thermal stability. Therefore, it is expected that this review will be a comprehensive guide for researchers and engineers looking to optimize the thermal stability and performance of biodegrad-able polymers.

#### **Graphical abstract**



Extended author information available on the last page of the article

Keywords Biodegradable polymers · Thermal degradation · Chain scission · Molecular weight · Rheology

# 1 Introduction

The increasing environmental concerns associated with traditional, non-biodegradable polymers have accelerated a significant shift towards the development and utilization of biodegradable polymers. These materials, derived from renewable resources, offer a promising alternative to conventional plastics due to their ability to decompose naturally, thereby reducing pollution and reliance on fossil fuels [1–3]. However, the practical application of biodegradable polymers is often hampered by their susceptibility to thermal degradation during processing [4-6]. This degradation can adversely affect their mechanical properties, limiting their performance and durability. Consequently, understanding and characterizing the thermal degradation behaviour of biodegradable polymers are essential for optimizing their processing and expanding their industrial applications. Biodegradable polymers can be broadly classified into several categories based on their origin and chemical structure. Bio-based polymers are chemically synthesized from renewable resources. Poly(lactic acid) (PLA), poly(glycolic acid) (PGA), and polyhydroxyalkanoates (PHAs) such as poly(3-hydroxybutyrate) (PHB) and its copolymers are notable examples. While poly(caprolactone) (PCL) and poly

**Fig. 1** Different groups of plastics based on the origin of the raw material and environmental fate [7]. Copyright 2024. Reproduced with permission from Elsevier Ltd (butylene adipate-*co*-terephthalate) (PBAT) are synthesized from fossil-based resources. Such polymers offer controlled degradation rates and tuneable properties, making them suitable for various applications, including medical devices and packaging. Figure 1 shows the origin of different types of plastics especially bioplastics [7].

Thermal degradation is a critical factor influencing the processing and performance of biodegradable polymers. During melt processing, such as extrusion, injection moulding, or 3D printing, these polymers are subjected to elevated temperatures, which can lead to chain scission and a consequent reduction in molecular weight. This degradation not only diminishes the mechanical properties of the polymer but also affects its viscosity, making it challenging to achieve desired processing conditions and final product quality. Understanding thermal degradation in the melt state is thus crucial for several reasons. Detailed knowledge of thermal degradation kinetics allows for the optimization of processing parameters such as temperature, shear rate, and residence time. This helps in minimizing degradation, thereby preserving the polymer's molecular integrity and mechanical properties. By studying the thermal degradation behaviour, researchers can develop strategies to enhance the thermal stability of biodegradable polymers. This includes



the use of stabilizers, antioxidants, or blending with more stable polymers, leading to materials with improved performance in end-use applications [4, 8, 9]. For applications where durability is critical, such as in automotive or construction, understanding thermal degradation is essential. It ensures that the biodegradable polymer-based products maintain their structural integrity and functionality over their intended lifespan. Studying thermal degradation in the melt state provides insights into the long-term behaviour of biodegradable polymers under various environmental conditions. This information is crucial for predicting the lifespan and degradation timeline of products, particularly in biomedical and packaging applications. Rheology, the study of the flow and deformation of materials, plays a pivotal role in characterizing the thermal degradation of biodegradable polymers [10, 11]. Rheological analyses provide real-time data on the viscoelastic properties of polymers, offering a comprehensive understanding of their behaviour under thermal stress [12–15]. The characterization of thermal degradation in biodegradable polymers using rheological methods is essential for optimizing their processing and enhancing their performance. By providing detailed insights into the viscoelastic properties and degradation kinetics, rheological analyses enable the development of strategies to improve the thermal stability of these polymers. This, in turn, facilitates

the production of durable and high-performance biodegradable products, contributing to the broader goal of sustainable development and environmental protection. There are several rheological methods that are described as follows.

#### 1.1 Time sweep tests

Time sweep test is one of the most critical rheological methods used to monitor the stability of polymeric structures under constant conditions and environments [15, 16]. This method involves subjecting the polymer to a continuous oscillatory shear at a fixed frequency and strain while recording the material's response over time. The primary objective of time sweep tests is to observe changes in the storage modulus (G'), loss modulus (G''), and complex viscosity ( $\eta^*$ ), which provide insights into the material's structural stability, degradation behaviour, and time-dependent mechanical properties. Time sweep tests have been frequently used in numerous studies to determine critical parameters such as gelation time, crosslinking behaviour, and thermo-oxidative degradation [14, 17–19]. Figure 2 demonstrates the storage modulus of linear low-density polyethylene (LLDPE) processed at different temperatures as a function of 1 h time evolution at 190 °C [12].



**Fig. 2** Elastic (storage) *G'* moduli of neat and processed LLDPE at a frequency of 0.1 rad/s, strain amplitude of 0.5%, and temperatures of 190 °C under air atmosphere [12]. Copyright 2017. Reproduced with permission from Elsevier Ltd

It is discussed that the increase in G' with higher processing temperatures is primarily due to thermo-oxidative degradation, which initiates cross-linking reactions in the polymer chains. As the LLDPE is extruded at higher temperatures (220 °C, 250 °C and 260 °C), there is a more significant occurrence of cross-linking during the extrusion process. Cross-linking stiffens the polymer matrix, increasing its elastic response, reflected by the higher G' values observed at elevated temperatures. This result highlights the usefulness of time sweep test in realizing the thermooxidative behaviour of LLDPE over time, especially when considering its thermal history and its effect on the degree of branching during the experiment. These tests are invaluable for pinpointing the gelation point in polymers, which is the time at which the material transitions from a liquid-like to a solid-like state. By analyzing the increase in G' during time sweeps, researchers can accurately identify the onset of gelation, which is essential for applications requiring precise control over material curing and setting times [20–22]. Moreover, time sweep tests are widely employed to study crosslinking behaviour [23, 24]. By monitoring the evolution of viscoelastic properties over time, these tests provide insights into the formation of crosslinked networks within polymers. This information is crucial for understanding how crosslinking agents and conditions affect the mechanical strength and stability of the final product. Additionally, time sweep tests are extensively used to assess thermo-oxidative degradation, which is a critical aspect of polymer stability under thermal and oxidative conditions [12, 15, 19]. By conducting time sweeps at elevated temperatures in the presence of oxygen, researchers can observe the rate of degradation and identify the thermal limits of biodegradable polymers. This data is essential for developing materials that maintain their integrity and performance over their intended lifespan. Alternatively, in the context of biodegradable polymers time sweep tests can be useful in understanding how biodegradable polymers degrade under thermal stress, which is crucial for optimizing processing conditions and ensuring the stability of the final product. These tests simulate long-term usage conditions, providing valuable information on how biodegradable polymers will perform over extended periods. Moreover, they can reveal the kinetics of thermal and hydrolytic degradation, aiding in the development of more stable biodegradable materials.

#### 1.2 Frequency sweep tests

Small amplitude oscillatory shear (SAOS) tests are powerful tools to investigate the viscoelastic properties of polymers and their thermal degradation behaviour. In such tests, the polymer is subjected to a small oscillating shear strain typically within the linear viscoelastic region, while the response is recorded over a range of frequencies. This allows for the characterization of both the elastic (solid-like) and viscous (fluid-like) components of the material, as represented by the storage modulus (*G'*), loss modulus (*G''*), and complex viscosity ( $\eta^*$ ) [25–27]. To account for the influence of temperature on the degradation process, time–temperature superposition (TTS) is often employed. By shifting the data collected at different temperatures to a reference temperature, a master curve is generated, which represents the combined effects of time and temperature on the degradation process. The shift factors used in TTS can also be described by the Williams–Landel–Ferry (WLF) equation, providing insight into how polymer properties change with temperature and degradation [28].

#### 1.3 High shear rate tests

High shear rate tests are another critical rheological method for analyzing the thermal degradation of polymers, particularly under conditions that closely simulate real-world processing environments like extrusion or injection moulding. These tests involve subjecting the polymer to high shear rates, often significantly higher than those used in small amplitude oscillatory shear (SAOS) tests, to assess how the material's viscosity and flow behaviour change under intense shear forces. The insights gained from high shear testing are invaluable for understanding the thermal stability and degradation characteristics of polymers, particularly in processing scenarios. By simulating these conditions in high shear tests, it is possible to predict how a polymer will behave during processing and assess the extent to which processing conditions might lead to degradation [29].

## 2 Evaluation of thermal degradation by time sweep methods

#### 2.1 Effect of environment

Several studies explored the thermal degradation of PLA using time-sweep tests. In a comprehensive study on the degradation kinetics of PLA in the molten state, both rheological properties and thermal degradation kinetics were thoroughly examined to provide insights into material behaviour under processing conditions [25]. PLA, a biodegradable polymer, is highly sensitive to both thermal and hydrolytic degradation, which significantly impacts its rheological properties and processability. The research utilized dried and undried PLA samples, subjected to rheological testing using a rotational rheometer in a cone-plate configuration under a dry nitrogen atmosphere. Measurements of  $\eta^*$  were performed over a range of processing temperatures (180–220 °C) to observe the effects of residence time and drying conditions. The findings demonstrated that dried samples maintained a

more stable viscosity over time compared to undried samples, where a notable decrease in viscosity was observed. especially at higher temperatures. This reduction in viscosity was attributed to the degradation-induced decrease in molecular weight. To model the observed viscosity changes, the study employed a relationship between zero-shear rate viscosity and molecular weights. For dried samples, thermal degradation followed a first-order reaction with kinetic constants derived from fitting the experimental data. In contrast, the undried samples required consideration of both hydrolysis and thermal degradation, with initial water content and hydrolytic degradation kinetics identified through a fitting process. The kinetic constants for both degradation mechanisms increased with temperature, exhibiting an Arrhenius-type dependence. A key aspect of the research was the extrapolation of the degradation model to lower temperatures, close to the glass transition temperature of PLA. At these lower temperatures, thermal degradation became negligible and hydrolytic degradation dominated. The model's predictions were consistent with literature data, indicating its robustness despite being primarily tuned to higher temperature conditions. Similarly, Lin et al. [26] studied the PLA degradation using time-sweep tests. The study provided critical insights into the degradation behaviour of PLA, emphasizing the significant role of both thermal and hydrolytic factors in determining its rheological properties and stability during processing. The developed model successfully described the viscosity changes and degradation rates, offering a valuable tool for optimizing processing conditions and enhancing material performance in industrial applications. The rheological analysis conducted in the study corroborated the findings from Raman spectroscopy, demonstrating that the  $\eta^*$  of PLA decreased over time under various thermal degradation conditions [26]. This decrease in viscosity was more pronounced at higher temperatures and in the presence of oxygen (Fig. 3C), indicating accelerated chain scission and thermal degradation. The results showed that under a nitrogen atmosphere (Fig. 3A), PLA exhibited a more stable viscosity, highlighting the protective effect against thermal degradation. These rheological results align with the kinetic models developed from Raman spectral data, confirming the significant influence of temperature and atmospheric conditions on the thermal degradation of PLA. When comparing the results of Lin et al. [26] to those of Speranza et al. [25], several key similarities and differences emerge regarding the thermal degradation kinetics of PLA. Both studies utilized rheological analysis to investigate thermal degradation, finding that higher temperatures significantly accelerate PLA degradation and that a nitrogen atmosphere mitigates oxidative degradation. However, Lin et al. [26] focussed primarily on thermal degradation, using real-time Raman spectroscopy to study the effects of different atmospheres (nitrogen, air, and oxygen), and provided detailed activation energies, highlighting the significant impact of oxygen in accelerating degradation. In contrast, Speranza et al. [25] examined both thermal and hydrolytic



Fig. 3 Time evolution of complex viscosity for degraded samples under different degradation conditions, A nitrogen atmosphere, B air atmosphere, C oxygen atmosphere [26], Copyright 2020. Reproduced with permission from Wiley-VCH. (D) effect of residence time

on viscosity at each temperature for dried samples, and (E) undried samples [25]. Copyright 2014. Reproduced with permission from Elsevier Ltd

degradation, emphasizing the role of hydrolysis in undried samples and incorporating both mechanisms into their kinetic model. Lin et al.'s real-time monitoring approach offered dynamic insights into degradation processes, while Speranza et al. [25] provided a comprehensive view by considering multiple degradation pathways. Together, these studies enhance the understanding of PLA stability under various conditions, with one emphasizing atmospheric effects and real-time monitoring, and the other offering a broader perspective on degradation mechanisms. Figure 3 shows time evolution of  $\eta^*$  for degraded PLAs under different degradation conditions [25, 26]. Figure 3A-C demonstrates the change of  $\eta^*$  as a function of time at temperatures of 180-220 °C under nitrogen, air and oxygen environments respectively. While Fig. 3D, E shows how  $\eta^*$  changes at temperatures of 180 to 220 °C when PLA is either dried (D) or undried (E).

In the study by Daly et al. [30], the thermal degradation kinetics of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (Nodax) were investigated using rheological time sweep tests. The dynamic time sweep tests demonstrated a significant decrease in the  $\eta^*$  over time at temperatures ranging from 155 to 175 °C, indicating the progressive thermal degradation of Nodax (Fig. 4a). This decrease in viscosity was more pronounced at higher temperatures, reflecting the accelerated chain scission and molecular weight reduction due to increased thermal energy. The study found that the rate of viscosity decrease followed a first-order decay process, consistent with the random chain scission model. The degradation rate constants were derived from the linear relationship observed in the plots of the inverse of viscosity versus time, indicating that thermal degradation kinetics could be adequately described by this model (Fig. 4b). The apparent activation energy for thermal degradation was determined to be  $189 \pm 5$  kJ/mol, suggesting a substantial energy barrier for chain scission in Nodax.

Time sweep results provided a comprehensive understanding of the thermal degradation behaviour of Nodax, highlighting the critical impact of temperature and mechanical forces on the stability of this biodegradable polymer.

In a comparative study Qiao et al. [31] revealed a more dramatic change in complex viscosity of PHB at different fixed temperatures as opposed to PLA (Fig. 5a).

It was evident that PLA loses nearly 20% of its viscosity after 400 s at all temperatures, while PHBV exhibited 40, 70 and 90% loss of viscosity at 175, 185 and 195 °C, respectively. Alternatively, this was mirrored by a more tangible reduction in molecular weight of PHBV compared to PLA as shown in Fig. 5b [31]. Specifically, PHBV showed 42.6% loss in number average molecular weight ( $M_n$ ) at 195 °C, whereas PLA showed 26.4% loss at the same temperature.

Similarly, Helminen et al. [32] investigated the thermal degradation kinetics of biodegradable poly(ester-urethane) (PEU) at various temperatures (100 °C, 120 °C, and 140 °C). The time sweep results indicated that PEU samples exhibited significant thermal degradation at elevated temperatures. At 100 °C, the *G'* decreased by one order of magnitude after 28 min, indicating a substantial reduction in the material's rigidity. This degradation was even more pronounced at higher temperatures; at 120 °C, *G'* decreased within 1 min, and at 140 °C, the decrease occurred in less than one minute. This rapid reduction in *G'* and  $\eta^*$  highlighted the severe thermal instability of PEU at temperatures above 100 °C. The data also showed that the thermal degradation of PEU is



Fig. 4 a The reduced complex viscosity of Nodax at a frequency of 10 rad/s as it varies with time and temperature, b plots of  $1/\eta^{\alpha}$  as a function of time at the frequency of 10 rad/s [30]. Copyright 2005. Reproduced with permission from Wiley-VCH





tions. For instance, PLA E@195 °C represents the PLA extruded at

195 °C and PLA R@195 °C represents rheological measurement of

PLA was at 195 °C [31]. Copyright 2022. Reproduced with permis-

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**Fig. 5 a** Normalized complex viscosity of PLA and PHB as a function of time (20 min) acquired at different temperatures of 175, 185 and 195 °C, under strain amplitude of 5% and frequency of 1 rad/s. **b** Molecular weights of PLA and PHBV measured after different condi-

associated with the formation of small degradation products, such as lactide. These products acted as lubricants within the polymer matrix, significantly lowering the measured viscosities and moduli. The terminal splitting mechanism, where chain ends react to form cyclic by-products like lactide, was confirmed by an increase in lactide content detected through 13C-NMR.

#### 2.2 Effect of molecular structures

At this stage, it should be noted that degradation rate could be also proportional to the molecular structure of the biodegradable polymers too. It is known that permeability of PLA could be different depending on the crystallinity, as such crystallinity can affect the rate at which PLA could undergo thermal degradation. Thus, Atalay et al. [11] investigated thermal degradation behaviours of amorphous PLA (aPLA) and semicrystalline PLA (cPLA) using rheological properties obtained through time sweep tests. It was shown that the thermal degradation behaviours differed significantly between the two types of PLA. At temperatures below 190 °C, both aPLA and cPLA showed a relatively modest decrease in viscosity over time, indicating minor thermal degradation. Specifically, the viscosity of both PLAs dropped by approximately 20% after 40 min at 190 °C. As the temperature increased beyond 190 °C, the degradation rate of both aPLA and cPLA increased dramatically. At 210 °C, 230 °C, and 250 °C, the viscosity reductions were more pronounced, with both PLAs exhibiting drops of 27%, 45%, and 57%, respectively, after 40 min. This indicated that higher temperatures significantly accelerated the thermal degradation of PLA, likely due to increased chain scission and molecular weight reduction. While both aPLA and cPLA exhibited increased degradation rates at higher temperatures, aPLA, due to its amorphous nature, demonstrated a more substantial decrease in viscosity compared to cPLA. The semicrystalline structure of cPLA, with around 50% crystallinity, provided better resistance to thermal degradation. The crystalline regions in cPLA likely acted as physical crosslinks, which helped maintain the molecular integrity of the polymer chains to some extent. This agrees with the recent study of Velghe et al. [33] where they also found higher D-isomer content (more amorphous) degraded the PLA faster. In this study, a parallel plate rheometer was used to investigate the melt-phase degradation of PLA under various processing conditions. This allows the control and isolation of key parameters, including moisture content, temperature, residence time, and shear stress, to systematically assess their effects on the molecular weight of three different PLA grades namely PLA4043D, PLA4032D and PLA2500HP, which differ in their amorphous content, with PLA4043D having the highest and PLA2500HP the lowest. The rheological properties were then correlated with the molecular weight decrease of the polymer, providing a quantitative assessment of degradation. Four factors were considered in the study: D-content, moisture level, residence time, and shear stress. The D-isomer content in PLA played a significant role, especially in the presence of moisture, where higher D-content led to faster degradation due to increased hydrolytic susceptibility in the amorphous regions. Moisture content was identified as the most critical factor, with dried PLA samples showing minimal degradation and high-moisture samples suffering significant molecular weight loss due to hydrolytic degradation. Residence time also had a noticeable effect; longer residence times exposed the PLA to elevated temperatures for longer durations, further promoting thermal and hydrolytic degradation. However, shear stress was found to have an insignificant effect under the conditions tested, likely due to the linear viscoelastic region being maintained in the rheometer, where the polymer chains were not significantly aligned or stretched.

Figure 6 highlights the correlation between rheological behaviour and degradation. During the rheometer measurements, the molecular weight decreased more significantly during the initial preparation phase than during the measurement phase itself. This result suggests that most degradation occurred while the material was being melted and trimmed for testing, with a 13% decrease in molecular weight during preparation and only an additional 5% loss during the 10-min testing phase. This reveals the importance of minimizing the initial exposure of PLA to high temperatures to reduce degradation before the actual processing begins. The data emphasize the importance of controlling both moisture content and temperature during sample preparation to minimize degradation prior to testing.

In the study by Partini et al. [34] the thermal degradation kinetics of two aliphatic polyesters, poly(ethylene dodecanedioedioate) (polymer L) and poly(tetramethylene dodecanedioate) (polymer H), were investigated using transient dynamic time sweep rheological tests. The time-sweep experiments revealed significant changes in the  $\eta^*$  of the polymers at

various temperatures (140 °C, 160 °C, and 180 °C), indicating the impact of thermal degradation on their molecular structure. The initial phase of the time-sweep tests demonstrated a marked reduction in viscosity for both polymers, attributed primarily to hydrolytic degradation. For instance, at 180 °C, the viscosity of polymer H decreased to about 90% of its initial value, while polymer L showed a more pronounced reduction to 70%. This decrease in viscosity reflects the chain scission caused by hydrolysis, which leads to a lower molecular weight and reduced mechanical strength. Following the initial drop, an increase in viscosity was observed at all tested temperatures, which was more pronounced at higher temperatures. This rise in viscosity was attributed to the esterification reaction, where the hydrolysisgenerated carboxylic and hydroxyl end groups recombine to form ester linkages, effectively increasing the molecular weight and viscosity. Notably, dried samples exhibited a faster and more significant increase in viscosity compared to undried samples, highlighting the crucial role of moisture content in the degradation and reformation processes. The study also included temperature ramp tests, where the temperature was gradually increased or decreased. These tests showed consistent viscosity changes that aligned well with the isothermal test results, indicating high reproducibility. In decreasing temperature ramp tests (DTRT), the viscosity increased more rapidly at lower temperatures following high-temperature exposure, suggesting that prior thermal history influences the degradation kinetics. Conversely, in increasing temperature ramp tests (ITRT), the viscosity



**Fig. 6** Correlation between molecular weight degradation and different stages of rheological testing for PLA 2500HP. The figure shows the percentage decrease in molecular weight during different stages of the parallel plate rheometer test. The preparation phase (steps 1–4), which includes melting and trimming the sample, accounts for

approximately 13% of the total molecular weight decrease, while the actual measurement phase (steps 4–5) contributes an additional 5% over 10 min [33]. Copyright 2024. Reproduced with permission from Elsevier Ltd

changes were delayed, confirming the impact of temperature transitions on the degradation and reformation dynamics.

#### 2.3 Effect of fillers/additives

It was revealed that degradation mechanism can be directly influenced by molecular structure at various environmental conditions. It is, therefore, mandated to enhance the durability of biodegradable polymers across wider temperature ranges and for longer durations. One approach is to incorporate external fillers or additives which can act as reinforcing agents against imposed harsher conditions and thus improve their resistance against higher temperatures. In this context, the rheological analysis of PLA-based nano-biocomposites revealed that the incorporation of layered double hydroxides (LDHs) intercalated with organic acids significantly mitigates the decrease in viscosity over time, attributed to thermal and hydrolytic degradation [35]. Specifically, LDHsuccinic acid demonstrated the most substantial protective effect, maintaining higher viscosity levels during processing. This indicates that the thermal degradation of PLA is effectively slowed down by the presence of these intercalated LDHs, thereby enhancing the material's stability and processability. The study by Lin et al. [36] incorporated New Zealand jade (pounamu) particles into PLA to enhance the composite's properties, including its thermal stability and degradation behaviour. Rheological time sweep tests at 215 °C showed that the addition of jade particles accelerated the thermal degradation of PLA, as indicated by the more rapid decrease in the  $\eta^*$  over time (Fig. 7) [36]. The presence of jade particles led to a significant reduction in molecular weight, suggesting enhanced thermal degradation kinetics.

In another study by Yikelamu Jilili et al. [37], the creation of photo-induced atom transfer radical polymerization (ATRP) modified hectorite (Hec-g@PS) through a novel surface modification of hectorite using photocatalytic ATRP was conducted. Subsequently, PLA/Hec-g@PS nanocomposite films were produced by incorporating Hec-g@PS as an additive through the blown moulding process. They investigated the thermal degradation kinetics of PLA/Hec-g@PS nanocomposites by monitoring the G' over time at various temperatures (190 °C, 200 °C, 210 °C, 220 °C, and 230 °C). The study revealed that the G' of both pure PLA (PLA0) and PLA3 composites (PLA3=0.5 wt.% Hec-g@PS) decreased significantly with increasing temperature and time. This decrease in G' is indicative of the accelerated chain scission and molecular weight reduction at higher temperatures. The area under the G' curve,  $A_{actual}$ , was used to quantify the extent of thermal degradation over time. The integration of G' over the degradation time from t = a to t = b provided a measure of the material's structural stability. The results showed a progressive decrease in  $A_{actual}$  values with rising



**Fig. 7** Normalized complex viscosity  $\eta^*(t)$  of PLA composites as a function of time at 215 °C [36]. Copyright 2023. Reproduced with permission from MDPI

temperatures, highlighting a direct correlation between higher temperatures and increased thermal degradation.

$$A_{\text{actual}} = \int_{a}^{b} f(G) \mathrm{d}t.$$

The  $A_{ratio}$ , defined as the ratio of  $A_{actual}$  to an idealized, non-degraded G' area ( $A_{ideal}$ ), further quantified the degradation extent. Higher  $A_{ratio}$  values were observed at elevated temperatures, confirming greater degradation. The comparison between PLA0 and PLA3 showed that PLA3 consistently had lower  $A_{ratio}$  values, indicating that Hec-g@ PS effectively mitigated thermal degradation by enhancing intermolecular interactions and promoting crystallinity.

$$A_{\text{ratio}} = \frac{A_{\text{actual}}}{A_{\text{ideal}}} = \frac{\int_{a}^{b} f(G) \, \mathrm{d}t}{t \, \text{degradation} \times G'}$$

Figure 8 indicates the results of G' with degradation time, the  $A_{\text{actual}}$ , and  $A_{\text{ratio}}$  values of PLA0 and PLA3 [37].

These findings demonstrate that the presence of Hec-g@PS significantly improves the thermal stability of PLA by reducing the degradation rate as opposed to jade particles used in previous study [36], where evidenced by the smaller decrease in G' and lower  $A_{ratio}$  values compared to pure PLA.

As such, Arza et al. [38] also investigated the impact of various additives on the thermal degradation of PHB at 180 °C. The results showed that neat PHB exhibited a significant decrease in the dynamic shear modulus, dropping by about 94% after 40 min, indicating extensive thermal degradation. This reduction in modulus correlated with a 77% decrease in the weight-average molar mass, as confirmed by size exclusion chromatography (SEC). Various additives were tested for their effectiveness in improving the thermal



**Fig.8** a Variation of PLA0 and PLA3 G' with degradation time; b A<sub>ideal</sub> and A<sub>actual</sub> of PLA0 and PLA3; c A<sub>ratio</sub> of PLA0 and PLA3 [37]. Copyright 2024. Reproduced with permission from Elsevier Ltd

stability of PHB. The addition of bis(3,4-epoxycyclohexylmethyl) adipate (BECMA), 2,2'-bis(2-oxazoline) (BOX), and trimethylolpropane tris(2-methyl-1-aziridinepropionate) (PETAP) resulted in a further decrease in the dynamic shear modulus compared to neat PHB, indicating that these additives negatively impacted the thermal stability (Fig. 9a–c) [38]. In contrast, triarylphosphites (TPP and TNPP) showed no significant effect on the thermal stability of PHB (Fig. 9d, e) [38].

However, the incorporation of polycarbodiimide (PCDI) and poly (methyl methacrylate-*co*-glycidyl methacrylate) (GMA.MMA) led to minor improvements in melt stability. For instance, PHB with 1 wt% PCDI exhibited an increased modulus of 15.9 kPa after 40 min, compared to 10.6 kPa for neat PHB. Similarly, GMA.MMA significantly enhanced the dynamic shear modulus, reaching a peak value of 31.3 kPa at 10 wt%, indicating a stabilizing effect due to possible chain extension reactions. In general, the study demonstrated that while some additives could potentially improve the thermal stability of PHB, others might exacerbate degradation. The findings indicate the complex interactions between additives

and polymer chains during thermal processing, highlighting the need for careful selection of stabilizers to optimize the thermal performance of biodegradable polymers like PHB.

# 3 Evaluation of thermal degradation by frequency sweep tests

#### 3.1 Effect of measuring temperature

López Arraiza et al. [39], modelled the degradation process of PCL and poly(L-lactide) (PLLA) using Saito's model. Saito's equation is based on the concept of random chain scission, where the degradation of a polymer occurs through the random breaking of molecular chains, leading to a reduction in molecular weight. The model is particularly useful for characterizing the degradation kinetics of polymers that degrade predominantly through chain scission processes. It describes the time-dependent decrease in molecular weight and the corresponding increase in the number of chainends due to the breaking of polymer chains. The thermal



**Fig. 9** Dynamic shear modulus of neat PHB and PHB containing **a** BECMA, **b** BOX, and **c** PETAP as a function of time, at 180 °C and at  $\omega = 62.8$  rad s<sup>-1</sup> and **d** PHb + TPP and **e** PHB + TNPP as a func-

tion of time, at 180 °C and at  $\omega = 62.8$  rad s<sup>-1</sup> [38]. Copyright 2015. Reproduced with permission from Wiley-VCH

degradation of PCL was found to be complex, involving multiple concurrent reactions: post-polymerization, loss of structural regularities, and random chain scissions. The degradation curve for PCL decomposed into three elementary first-order components, each representing different degradation mechanisms: initial viscosity increase due to post-polymerization, chain scissions due to structural irregularities, and random chain scissions primarily in crystalline zones. PLLA, on the other hand, exhibited linear degradation kinetics with a simpler mechanism limited to depolymerization. The activation energy for PLLA's degradation process was determined, illustrating its rapid degradation at temperatures above 230 °C, hence, indicating a narrower processing window compared to PCL.

Later, Cuadri and Martín-Alfonso [40], extensively examined the thermomechanical degradation of poly PLA using

frequency sweep tests to understand the impact of different degradation conditions on the material's rheological properties. The frequency sweep tests were conducted at 180 °C, 200 °C, and 220 °C under nitrogen (thermal degradation) and air (thermo-oxidative degradation) atmospheres. The results revealed that both G' and G'' decreased significantly with increasing degradation time and temperature, indicating a predominately viscous behaviour (G'' > G'). This behaviour is characteristic of the terminal zone for polymers and suggests extensive chain scission phenomena. At lower frequencies, a Newtonian plateau was observed, followed by shear-thinning behaviour at higher frequencies. The decrease in zero-shear viscosity ( $\eta_0$ ) with degradation time was used to estimate the weight-average molecular weight  $[\eta_0 = 5.5 \times 10^{-15} \times M_W^{3.4}]$ , which decreased from  $1.33 \times 10^5$ to  $8.58 \times 10^4$  after 60 min of thermo-oxidative degradation (Fig. 10) [40].

This reduction in  $(\eta_0)$  and molecular weights revealed the extensive chain scission occurring under oxidative conditions. Additionally, the relative modification index (R.M.I.), calculated from  $(\eta_0)$  values at time-zero  $\eta^*_{0@t=0}$  and after *n*min of degradation  $\eta^*_{0@t=n}$  quantified the extent of chain scission. Higher R.M.I. values at higher degradation temperatures and longer times indicated more severe degradation. The discrete relaxation spectrum further corroborated these findings, showing shorter relaxation times with increasing degradation, reflecting shorter chain lengths due to scission.

R.M.I. = 
$$\frac{\eta_{0@t=0}^*}{\eta_{0@t=n}^*}$$
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Fig. 10 Changes in A the storage modulus (G') and loss modulus (G''), and **B** complex viscosity with frequency for samples degraded in an air atmosphere at 180 °C, analyzed over different degradation times [40]. Copyright 2018. Reproduced with permission from Elsevier Ltd

Similarly, Choong and De Focatiis [28] employed relaxation spectra to analyze the thermal degradation of PLDLA from the isothermal frequency sweep tests at temperatures ranging from 160 to 220 °C. The results showed that as the degradation time increased, the cross-over frequency (where the G' equals the G'') shifted to higher frequencies, indicating a decrease in the relaxation time (Fig. 11A) [28]. This shift is a clear sign of thermal degradation, as it suggests a reduction in the molar mass of the polymer chains due to chain scission and depolymerization. To quantify the effect of temperature and degradation on the relaxation time, the researchers employed time-temperature superposition (TTS) principles. The temperature dependence of the shift factors was described using the Williams-Landel-Ferry (WLF) equation, with parameters optimized to fit the experimental data. The relaxation times at different temperatures were then horizontally shifted to a reference temperature (170 °C), creating a master curve that demonstrated the combined effects of temperature and degradation over time (Fig. 11B) [28].

The degradation kinetics were further characterized by plotting the relaxation times against the degradation time for each temperature, which were then normalized using an Arrhenius-type equation. This approach revealed an activation energy of 131 kJ/mol for the thermal degradation process, consistent with values reported for similar biodegradable polymers. The master curve constructed from the normalized relaxation times allowed the researchers to propose a mathematical function that accurately described the degradation behaviour across the studied temperature range.

The applied rheological analysis can provide insights relevant to understanding the thermal degradation of other



Degradation temperature:180 °C ; Atmosphere: air





**Fig. 11 A** Evolution of the characteristic relaxation time with degradation time for temperatures ranging between 160 and 220 °C [28]. **B** Relaxations times  $\tau^*$  measured for a range of temperatures at a ref-

erence temperature  $T^* = 170$  °C [28]. Copyright 2016. Reproduced with permission from Elsevier Ltd



Fig. 12 a Complex viscosity  $\eta^*$  and b elastic modulus G' of PHBH measured at different temperatures of 160, 180 and 200 °C and nitrogen atmosphere [42]. Copyright 2024. Reproduced with permission from MDPI

biopolymers such as PHBV [41]. Rheological characterization of PHBV at various temperatures (177-190 °C) were exploited. The frequency sweep tests revealed that higher temperatures led to a significant decrease in  $\eta^*$ , indicating the onset of thermal degradation. The viscosity curves for temperatures of 188 °C and 190 °C were notably lower than those for lower temperatures, illustrating substantial thermal degradation at these higher temperatures. At lower temperatures, the viscosity curves exhibited a more stable profile, with a pronounced zero shear viscosity at low frequencies, indicating minimal thermal degradation. This was particularly evident at 178 °C, which was identified as the minimum suitable temperature for rheological measurements without significant degradation. The rheological properties measured provided the basis for developing master curves at a reference temperature of 180 °C. Similarly, comparable results were found for poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBH), with a significant drop in viscosity and elastic modulus at higher temperatures, as shown in Fig. 12. However, an increasing trend in viscosity was observed at lower frequencies and high temperatures [42], which is attributed to trans-esterification reactions and branching occurring at elevated temperatures.

#### 3.2 Effect of fillers/additives

In the study by Mazzanti et al. [43], the thermal degradation kinetics of PLA reinforced with short hemp fibres were investigated using consecutive frequency sweep tests (Fig. 13). It was intended to understand how small amounts ( $\leq 3 \text{ wt\%}$ ) of hemp fibres influenced the stability of PLA in the molten state. The frequency sweep tests revealed that the  $\eta^*$ , G' and G'' viscous modulus (progressively decreased during testing, with the reduction being more pronounced in the PLA/hemp composites compared to pure PLA. This indicated that the presence of hemp fibres accelerated the degradation of the PLA matrix. These results are reminiscent of Lin et al.'s [35] findings, where similarly, jade particles accelerated the degradation of PLA, although their study relied on the results of time sweep tests. The study by Mazzanti et al. [43] attributed this accelerated degradation primarily to hydrolytic degradation facilitated by residual water bound to the fibres, which remained even after the processing steps.

Yikelamu Jilili et al. [37] also performed frequency sweep tests to analyze the rheological properties of neat PLA0 and PLA composites (PLA3) after thermal degradation. The G', G", and  $\eta^*$  were measured across a range of frequencies to understand the material's viscoelastic behaviour. The  $\eta^*$  of PLA0 and PLA3 decreased with increasing frequency, transitioning from a Newtonian fluid behaviour at low frequencies to shear-thinning behaviour at higher frequencies. This shift is characteristic of polymer degradation, where molecular chain scission leads to a reduction in molecular weight and viscosity. The study noted that PLA3 retained higher  $\eta^*$  values than PLA0 across all temperatures, indicating a higher residual molecular weight and less severe degradation. The relative degradation index (R.M.I.) was calculated to assess the extent of molecular chain breakage after degradation. Higher R.M.I. values at the same degradation temperature indicated more significant chain cleavage. PLA0 exhibited higher R.M.I. values compared to PLA3, reinforcing that Hec-g@PS mitigated thermal degradation by maintaining higher molecular weights and structural integrity. The activation energy for thermal degradation was determined using the Arrhenius equation  $\left[-\ln k = \frac{E_a}{PT} - \ln A\right]$ ,

where the rate constant (*k*) was derived from the frequency sweep data. PLA3 exhibited a higher activation energy ( $E_a = 107,963.47$  J/mol) compared to PLA0 (54,702.12 J/ mol), indicating a greater energy barrier for degradation due to the stabilizing effect of Hec-g@PS. Figure 14 shows alterations in *G'*, *G''*, and  $\eta^*$  pre- and after degradation [37].

These findings show that Hec-g@PS enhances the thermal stability of PLA by maintaining higher storage modulus,  $\eta^*$ , and activation energy, thus reducing the overall rate of thermal degradation. The frequency-sweep tests further supported these findings by showing a consistent decrease in the G' and  $\eta^*$  across various frequencies as degradation time progressed [36].

#### 3.3 Effect of processing conditions

To understand the impact of melt processing conditions on the PLA's stability, thermal degradation kinetics were evaluated using frequency sweep tests [44]. The study focussed on the effects of different extruder types (twin screw extruder, TSE, and quad screw extruder, OSE), screw configurations, screw speeds, and feed rates on the degradation behaviour of PLA. The frequency sweep tests conducted at 180 °C provided critical insights into the viscoelastic properties of PLA under various processing conditions. The results showed that both the G' and G'' decreased with increasing frequency, indicating typical viscoelastic behaviour. The  $\eta^*$ also decreased with increasing frequency, showcasing the shear-thinning nature of PLA. One of the significant findings was that the  $\eta^*$  of processed PLA samples was lower than that of virgin PLA, indicating degradation. This reduction in viscosity was more pronounced in the samples processed using the QSE compared to the TSE. The study attributed this to the greater free volume in the QSE, which resulted in



Fig. 13 Complex viscosity  $\eta^*$  (solid triangle), elastic G' (empty square) and viscous modulus G" (empty circles) a PLA and b PLA/hemp composites, collected from consecutive frequency sweep tests over 2 h. [43]. Copyright 2020. Reproduced with permission from Elsevier Ltd



**Fig. 14** Changes in rheological properties following degradation at various temperature ranges: **a** changes in storage modulus relative to frequency; **b** changes in loss modulus relative to frequency; **c** changes

in complex viscosity relative to frequency; **d** changes in R.M.I.; **e** Arrhenius equation fitting curves for PLA0 and PLA3 [37]. Copyright 2024. Reproduced with permission from Elsevier Ltd

lower shear and viscous dissipation, leading to higher degradation rates due to longer residence times. Moreover, the zero-shear viscosity ( $\eta_0^*$ ) and relaxation time ( $\lambda$ ) were determined using the Carreau–Yasuda model. Figure 15 shows how the *G'*, *G''*, and  $\eta^*$  vary with angular frequency for PLA processed under various conditions [44].

The virgin PLA exhibited a zero-shear viscosity of 5672 Pa·s, while processed PLA showed reduced zeroshear viscosities, with the QSE and screw configurations with kneading blocks (KB) producing greater reductions. This reduction in  $(\eta_0^*)$  was attributed to the higher shear applied by the kneading blocks and the three intermeshing zones of the OSE, as well as the increased residence time. The study also revealed that higher screw speeds (1000 rpm) resulted in higher zero-shear viscosities compared to lower screw speeds (400 rpm), indicating reduced degradation due to shorter residence times. The weight-average molecular weight of PLA, calculated from the zero-shear viscosities, showed significant reductions for both extruder types and screw configurations. The QSE exhibited lower molecular weight values than the TSE, with reductions ranging from 5.31 to 9.42% for the OSE and 1.81 to 7.47% for the TSE. The presence of kneading blocks and lower screw speeds further reduced molecular weight, emphasizing the impact of shear and residence time on thermal degradation.

In the study by Tesfaye et al. [45], the thermal degradation kinetics of PLA and PLA/silk nanocrystal (SNC) bionanocomposites were investigated using frequency sweep tests at 190 °C, with measurements taken over a range of frequencies from 0.1 to 600 Hz. This study focussed on the influence of repetitive extrusion processes on the thermal and rheological properties of these materials. It was shown that the  $\eta^*$ , G', and G'' of neat PLA (NPLA) decreased significantly

with each reprocessing cycle, indicating severe thermal degradation. Specifically, the viscosity of NPLA dropped dramatically, with a 67% decrease observed by the third reprocessing cycle and an additional 58% decrease by the fourth cycle at the lowest frequency (0.1 Hz). This trend was attributed to the molecular weight reduction and chain scission induced by high-temperature processing. Conversely, the PLA/SNC nanocomposites demonstrated improved thermal stability compared to neat PLA. The presence of SNCs mitigated the degradation effects, as evidenced by the more stable values across the reprocessing cycles (Fig. 16) [45]. For example, the viscosity of the SNC-PLA nanocomposites decreased by only 15% between reprocessing cycles, indicating that SNCs effectively reduced the rate of thermal degradation. The improved stability was further confirmed by the relatively constant zero shear viscosity and power law index (n) values for SNC-PLA, suggesting that the SNCs acted as a stabilizing agent, preserving the molecular weight distribution.

The study revealed the role of SNCs in enhancing the viscoelastic properties of PLA. The G' of SNC-PLA remained relatively stable at low frequencies across the reprocessing cycles, unlike the significant decrease observed in NPLA. This indicated that SNCs helped in maintaining the structural integrity of the polymer matrix, preventing excessive molecular degradation.

In a similar study, Zhang et al. [46] investigated the effect of recycling on poly (butylene succinate) (PBS). Mechanical recycling of PBS was simulated using a lab-scale twin-screw extruder to mimic industrial processes. Virgin PBS pellets were subjected to multiple extrusion cycles under controlled conditions, with varying extrusion temperatures (120 °C and 140 °C) and screw speeds (30 rpm and 100 rpm). The



Fig. 15 The impact of screw speed and screw design on the rheological properties, depending on the angular frequency, of PLA processed with a TSE and QSE: a G' and G'', and b  $\eta^*$  [44]. Copyright 2022. Reproduced with permission from MDPI



Fig. 16 a, b Storage modulus G' of a PLA and b SNC-PLA nanocomposite, c, d loss modulus G'' of c PLA and d SNC-PLA nanocomposites, collected after multiple reprocessing cycles [45]. Copyright 2017. Reproduced with permission from Elsevier Ltd

material was fed into the extruder, and a closed-loop system was employed to internally recirculate the PBS within the extruder. This method simulated multiple recycling generations by adjusting the extrusion time, which ranged from 3 to 24 h. To further mimic real-world recycling, the PBS samples were processed in different closed-loop cycles to simulate extended mechanical recycling. This allowed the researchers to observe how prolonged exposure to mechanical shearing and elevated temperatures would affect the polymer's rheological and molecular properties. The resulting recycled PBS (rPBS) was subsequently analyzed through rheological tests to assess changes in its flow behaviour, molecular weight distribution, and overall degradation over time. This approach provides a comprehensive understanding of how different recycling conditions (such as residence time, temperature, and screw speed) impact the material's performance. The study found that increasing extrusion time and screw speed led to significant degradation of molecular weight, which was reflected in the reduction of zeroshear viscosity and relaxation times. Higher shear rates caused greater molecular chain scission, resulting in lower molecular weight and viscosity, indicating severe degradation. In contrast, extrusion temperature had a lesser effect within the range tested. Figure 17 illustrates the clear correlation between molecular weight reduction and extrusion time, showing that long processing times and high screw speeds (100 rpm) drastically decreased molecular weight and broadened molecular weight distribution. The molecular weight decreases by a factor of 3, while viscosity decreases by a factor of 100 after prolonged extrusion, indicating substantial degradation due to polymer chain scission. Increased screw speed leads to further degradation, with a 97% reduction in viscosity and 64% decrease in molecular weight, highlighting the critical influence of shear stress on polymer degradation during mechanical recycling. These findings reveal the critical role of controlling mechanical recycling conditions to maintain PBS's rheological and mechanical integrity.

#### 3.4 Effect of blending

Qiao et al. [31], explored the thermal degradation kinetics of PLA and PHBV blends using frequency sweep tests. The frequency sweep tests revealed significant changes in the viscoelastic properties of PLA/PHBV blends with varying compositions. The tests were conducted at different temperatures (175 °C, 185 °C, and 195 °C) to monitor the changes in G', G", and  $\eta^*$  over a range of frequencies. The results showed that both G' and G'' decreased with increasing frequency, indicating a typical viscoelastic behaviour transitioning from a solid-like to a more fluidlike state at higher frequencies. The blends exhibited a pronounced decrease in  $(\eta^*)$  with increasing temperature, highlighting the thermal degradation of the polymer chains. This degradation was more severe in PHBV-rich blends, as PHBV has a lower thermal stability compared to PLA. Additionally, the results from the frequency sweep tests indicated that the  $\eta^*$  of the blends decreased more rapidly at higher temperatures, confirming the accelerated degradation kinetics. The data from the small-amplitude oscillatory shear (SAOS) measurements were used to calculate the activation energy of thermal degradation for both neat polymers and their blends. The activation energy was lower for PHBV, further confirming its susceptibility to thermal degradation. The study also explored the effects of molecular weight changes due to thermal degradation using size exclusion chromatography (SEC). The molecular weight distribution shifted towards lower values with increased processing time and temperature, particularly for PHBV-rich blends. This shift was consistent with the rheological findings, indicating significant chain scission and molecular weight reduction due to thermal degradation.

Although, as the results of this study indicate, the polymer composition plays a significant role in degradability since one polymer, such as PHBV, may be much more prone to degradation than the other in immiscible polymer blends, other factors such as coalescence and breakup of polymer phases, driven by weak interfacial tensions, can also play a crucial role. Therefore, in such conditions, and given the unique complexities of these blends, conclusions based solely on composition may not be very accurate. For instance, a (80/20) PLA/PBAT blend with a fixed composition can exhibit different rheological properties solely due to differences in particle geometries and localization, due to affecting the interfacial tension (Fig. 18) [18].

#### 4 High shear rate tests

Leroy et al. [47] focussed on the rheological characterization of PHBV bioplastic under high shear rate conditions, examining its thermal degradation kinetics. Utilizing an inline rheometrical device mounted on an injection moulding machine allowed for dynamic viscosity measurements at shear rates up to  $50,000 \text{ s}^{-1}$  with residence times in the melt state as short as a few seconds. This setup mimicked real processing conditions more closely than traditional methods. The high shear rate results demonstrated a rapid decrease in viscosity associated with thermal degradation, even at temperatures close to PHBV's melting point. For example, at 175 °C, the viscosity decreased significantly with increasing residence time in the melt state, indicating that PHBV undergoes substantial molecular weight reduction due to chain scission. The study found that the apparent viscosity at 600 s<sup>-1</sup> shear rate nearly halved over an 85-s period, showing the material's poor thermal stability under





**Fig. 17** Impact of extrusion time and screw speed on the molecular weight and zero-shear viscosity of recycled PBS. **a** Relative changes in zero-shear viscosity  $(\eta_0/\eta_0^0)$  and molecular weight  $(M_W/M_W^0)$  as a function of extrusion time at 120 °C and 100 rpm, showing signifi-

cant reductions after 12 h of recycling. **b** Comparison of zero-shear viscosity and molecular weight at different screw speeds (30 rpm vs. 100 rpm) after 12 h of extrusion at 120 °C [46]. Copyright 2024. Reproduced with permission from Elsevier Ltd





phene oxide GO [18]. Copyright 2020. Reproduced with permission from WileysVCH

high shear conditions. The study demonstrated the significant impact of processing conditions on the stability and mechanical properties of bioplastics, emphasizing the need for optimized processing parameters to mitigate degradation. These findings are crucial for improving the industrial application of bioplastics, ensuring their viability as sustainable alternatives to conventional polymers.

(80/20) PLA/PBAT blend and its nanocomposites filled with 1 wt.% of Cloisite C30B Nanoclay, silica, carbon nanotube CNT and gra-

In the study by Lin et al. [48], the thermal degradation kinetics of biodegradable poly (propylene carbonate) (PPC) during melt processing were examined using a combination of rheological analysis and population balance modelling.

High shear rate rheological tests were conducted to understand the degradation behaviour under practical processing conditions. The results revealed significant insights into the thermal stability and degradation mechanisms of PPC. The rheological time sweep tests demonstrated that the viscosity of PPC decreased markedly with increasing temperature and shear rate, indicating substantial thermal degradation. This reduction in viscosity was attributed to both random chain scission and chain end scission processes occurring simultaneously. The study employed a miniature conical twin-screw extruder to perform degradation experiments at

various temperatures and rotational speeds, analyzing the molecular weight and molecular weight distribution (MWD) of PPC samples through gel permeation chromatography (GPC). The study found that at temperatures above 160 °C, random chain scission dominated the degradation process, with an activation energy of approximately 120 kJ/mol. This was evident from the significant shift in MWD curves towards lower molecular weights with increased processing time. The model predictions based on random chain scission aligned well with the experimental data, particularly at higher temperatures, confirming that this mechanism was predominant under these conditions. Additionally, the study introduced a novel method that combined population balance equations (PBEs) with rheological measurements to determine degradation kinetics directly from the torque data during melt processing. This approach proved effective in capturing the degradation kinetics without the need for extensive molecular weight measurements. The kinetic parameters obtained from the torque measurements were consistent with those derived from traditional extrusion experiments, validating the reliability of this method.

The study by Nekhamanurak et al. [49] examined the thermal degradation kinetics of PLA composites filled with micro- and nano-sized calcium carbonate (CaCO<sub>3</sub>) particles, focussing particularly on the behaviour under high shear rates. The use of a capillary rheometer allowed for the investigation of PLA composites at shear rates ranging from 100 to  $2500 \text{ s}^{-1}$ , simulating the conditions experienced during extrusion processes. The presence of fatty acid treatment on CaCO<sub>3</sub> particles facilitated the trans-esterification reaction with PLA, accelerating thermal degradation. This was evident from the reduction in viscosity and molecular weight of the composites, as the fatty acid promoted chain scission under high shear and thermal conditions. The study found that nano-CaCO<sub>3</sub> particles, due to their larger surface area and higher fatty acid content, had a more significant impact on the thermal degradation of PLA compared to micro-CaCO<sub>3</sub> particles. The power law index (n) derived from the shear viscosity versus shear rate data indicated pseudoplastic behaviour (n < 1) across all samples. Neat PLA exhibited a higher sensitivity to shear rate changes compared to extruded PLA, reflecting the influence of thermal degradation during processing. This study provides critical insights into the thermal degradation kinetics of PLA composites under high shear rates, highlighting the dual role of CaCO<sub>3</sub> particles as both reinforcing fillers and catalysts for degradation through fatty acid-mediated transesterification.

Zhang and Zhen [50] investigated the thermal degradation kinetics of PLA composites filled with modified fulvic acid (MFA) under high shear rates. Using a capillary rheometer, the study explored the effects of shear rate and temperature on the viscosity and thermal stability of PLA/MFA composites. Their study highlighted the dual role of MFA in enhancing both the mechanical and thermal properties of PLA composites. The rheological tests under high shear rates revealed that while MFA improves interfacial compatibility and initial viscosity, high shear stress can disrupt these interactions, leading to similar viscosity behaviour between PLA and PLA/MFA composites. The thermal degradation kinetics showed that MFA effectively enhances the thermal stability of PLA, making these composites more suitable for high-temperature applications. The improved thermal stability was attributed to the hydrogen bonds formed between MFA and PLA, which inhibited the thermal decomposition process. Further, Li et al. [29] investigated the thermal degradation kinetics of polyoxymethylene (POM) and PLLA blends, focussing on the behaviour under high shear rates using a capillary rheometer. The rheological analysis revealed significant insights into the impact of shear rate and temperature on the viscosity and thermal stability of these biodegradable blends. The study also highlighted the impact of PLLA content on the activation energy ( $\Delta Ea$ ) for flow, derived from the Arrhenius equation. The activation energy decreased with increasing shear rate for both pure polymers and their blends, reflecting the shear-thinning effect. Interestingly, the  $\Delta Ea$  values for the blends were lower than those for the pure polymers, suggesting that the incorporation of PLLA facilitated molecular motion and reduced the energy barrier for flow. At higher shear rates, the activation energy decreased more significantly for blends with higher PLLA content, indicating that the disentanglement of PLLA macromolecules played a crucial role in reducing flow resistance (Fig. 19) [29]. The study demonstrated that while the incorporation of PLLA into POM blends facilitates processing by reducing viscosity and activation energy for flow, it also introduces complexities in thermal stability due to the lower decomposition temperature of PLLA. These findings highlight the importance of optimizing the blend composition and processing conditions to balance the benefits of enhanced processability with the challenges of maintaining thermal stability.

# **5** Conclusion

In this review article, numerous studies were looked upon where degradation behaviour of biodegradable polymers were the main focus. It was shown that the reduction in molecular weight (MW) emerges as the primary mechanism underlying the thermal degradation of biodegradable polymers. This phenomenon is consistently observed across various studies and is a crucial determinant of the material's mechanical and viscoelastic properties. The selection of appropriate fillers plays a pivotal role in enhancing the thermal stability of these polymers. Fillers such as layered double hydroxides (LDHs) and silk



Fig. 19 a-c Plots of shear viscosity as a function of shear rate for POM/PLLA blends at different temperatures; d flow activation energy of pure POM, PLLA and their blend [29]. Copyright 2019. Reproduced with permission from Elsevier MDPI

nanocrystals (SNB) stabilizers have been shown to effectively slow down the degradation process by maintaining higher molecular weights and improving resistance to chain scission. In contrast, fillers like jade particles and hemp fibres were found to have negatively affected degradation by accelerating the process.

Additionally, the use of the Arrhenius equation in modelling thermal degradation kinetics provides an effective framework for predicting degradation rates and understanding the energy barriers associated with the process. This model allows for a more accurate determination of activation energies, which are critical for optimizing polymer processing conditions to reduce degradation.

Different rheological testing methods also offer distinct insights into the degradation behaviour of polymers. Time sweep tests are particularly valuable for monitoring product stability over extended periods under various environmental conditions, offering a clear picture of how the material evolves in real-time. In contrast, frequency sweep tests provide a deeper understanding of how processing history affects polymer degradation, allowing for the assessment of molecular structure changes and chain scission post-processing. Finally, nonlinear rheological tests at higher shear rates more closely mimic real-world processing conditions, such as extrusion and injection moulding, and offer critical insights into how these high shear environments can accelerate polymer degradation. These tests are essential for understanding the impacts of shear forces on molecular weight reduction and predicting material performance in industrial settings.

The relevance of these studies extends into the recycling of biodegradable polymers. During recycling, multiple reprocessing cycles can exacerbate thermal degradation, leading to significant reductions in molecular weight and mechanical properties. Therefore, careful control of processing conditions, such as temperature and shear rate, is crucial to minimizing degradation. Additives and stabilizers that enhance thermal stability during initial processing can also play a vital role in maintaining polymer integrity during recycling. Understanding the degradation mechanisms through rheological analysis ensures that recycling processes are optimized to preserve the performance and durability of biodegradable polymers in their second life cycle. Together, these approaches form a comprehensive toolkit for understanding and mitigating thermal degradation in biodegradable polymers, ensuring their durability and performance across a wide range of applications.

**Data Availability** No new data were created in this study. Data sharing is not applicable to this article.

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