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Polylactide Used as Filament in 3D Printing – Part 2: TG-DTG, DSC and DRIFT Investigations

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Abstract

In this second part of the article, we delve deeper into the research area initiated in the first part, focusing on the critical exploration of polylactide (PLA) modification to enhance thermal and mechanical properties in PLA-based materials, building upon the insights obtained from comprehensive structural and thermal analyses utilizing analytical methods such as infrared spectroscopy (FTIR), diffuse reflectance infrared spectroscopy (DRIFT), and thermoanalytical research (DRIFT, TG-DTG). A series of structural and thermal analysis research (TG-DTG, DSC, DRIFT) were performed for samples of polylactide (PLA), which is commonly used in additive technologies as a structural material. In total, four materials were considered, including two containing dyes with different colors, a material made of PLA recyclate and a graphene-modified PLA material. It was noted that PLA material reinforced with graphene phase (GRAFYLON®) retains the best thermal properties (TG-DTG), which results in its wider potential for processing, including further modification and usability in manufacturing vehicle structural elements. Recycled PLA material (ALFA+W) was characterized by a higher melting point (T_p) by more than 20°C than other samples (DSC analysis), so it can be more useful in the production of structural elements operating and used at elevated temperatures.

Keywords:

polylactide, graphene, recycling, 3D printing technology, thermal degradation, TG-DTG, DSC, DRIFT

1. INTRODUCTION

3D printing technology is widely used in the design and manufacturing process of vehicle structural components. Production changes that are currently being implemented are mainly related to the diversification of manufacturing methods and techniques, while reducing waste and sourcing recycled materials. Between 2018 and 2021, approx. 20% of Gartner's Global Top 100 companies have used additive manufacturing methods to produce customized products. It Is predicted that by 2025, expenditure on 3D printing technologies is expected to grow at a compound annual growth rate of 15.5%. With this growth, the market is expected to double up in the value over the next four years. It is also projected that there will be a 100% increase in the use of 3D printing for the automotive and aerospace industries during this time [1, 2].

The dynamic development of the 3D printing industry has led manufacturers of materials used in 3D printing to introduce significant improvements in the technologies applied. Material modifications are being carried out in this area, e.g. composites of polymeric materials are being produced, which are largely based on the addition of recyclates. Companies invest substantial funds in R&D departments that develop innovative materials used in additive manufacturing. A trend that is currently underway is based on the production of biodegradable materials derived from natural sources, as well as those from recyclable waste) [3].

This research represents the next stage of work on the verification of polylactide-containing materials for their ultimate use as a base material in the production of new filament. Nowadays, composites and plastics containing poly(lactic acid) called polylactide (PLA) are widely used engineering materials, also in the automotive industry) [4–6]. Therefore it is important to recognize the physicochemical properties of such commercial materials in detail, also in view of undertaking our own research on PLA modification or creating new composite materials with its participation. In the first part of the publication, a comprehensive thermoanalytical analysis (FTIR, DRIFT, TG-DTG) was performed. It allowed us to determine the temperature range in which commercially available polylactide does not undergo thermal degradation, but it only takes reversible transformations so it does not lose its functional properties. Based on the obtained results in our first part of article [7], PLA was found to be thermally stable in the temperature range of 25–300°C. Thus, the operating temperature of a typical 3D printer, in which the processing of polylactide occurs, is not exceeded (extrusion temperature is not exceeded) [7, 8].

PLA is a biodegradable polyester and is most often made from renewable raw materials. The properties of PLA depends on the constituent isomers, processing temperature, annealing time and molecular weight. PLA homopolymers have a very narrow processing window. A method to improve processing properties involves: lowering the melting temperature by adding randomly small amounts of enantiomers of lactide with opposite configuration into the polymer, e.g. adding D-lactide to L-lactide to obtain PDLLA. Unfortunately, as a consequence, lowering the temperature leads to a significant decrease in the strength of PLA products. High molecular weight poly(lactic acid) is a colorless, glossy, rigid thermoplastic polymer with similar properties to polystyrene. It is not soluble in water, but it is in dichloromethane and dimethylformamide [9–11].

PLA is increasingly being used in the automotive industry, but it has not been easy due to the increased cost of manufacturing. Ford and Toyota were the first automotive corporations to use PLA in their vehicles and mass production with polylactide based components was initiated by the Japanese brand Mazda. Polylactide is used in the production of seat upholstery, car mats, headliner surfaces, dashboards. PLA is UV resistant which makes it a good replacement for common plastics such as polypropylene (PP), poly(ethylene terephthalate) (PET), or acrylonitrile-butadiene styrene terpolymer (ABS). An additional advantage is that it is eco-friendly [12–14].

PLA filament is not very sensitive to temperature changes and has excellent surface quality. It works well for printing complex structural components. The printing process can be carried out in a low temperature range but PLA is more brittle than ABS and less flexible compared to polymer fibres. On the other hand, it is susceptible to painting with primer and to bonding by gluing with a wide range of adhesives, including cyanoacrylates, yet care must be taken during the hot bonding process to avoid the melting of the material [13, 14]. Table 1 summarizes the general characteristics of PLA.

Table 1
Characteristics of the basic PLA filament used in 3D printing [15]

Density [kg/m^3]	1200–1240
Glass transition temp. [°C]	55.0–60.0
Coefficient of linear thermal expansion [1/°C]	8.5×10^{-5}
Process shrinkage [%]	0.3–3.0
Tensile stress [MPa]	25.0–41.0
Young's modulus [GPa]	3.5–3.6
Shore hardness [ShD]	85.0–97.0
Min. continuous operating temperature [°C]	50.0–87.0
Printing temperature [°C]	190–230
Automotive application	instrument panels, dashboards, decorative for interior, headliner

2. METHODOLOGY

2.1. Materials

The following polylactide filament samples were used in this study:

- PLA1 – pure polylactide based filament, color: transparent, density: 1.24 g/cm^3, diameter: 1.75 mm (manufacturer: AGH);
- PLA7 – commercial PLA filament, color: blue, density: 1.24 g/cm^3, diameter: 1.75 mm (manufacturer: Fiberlogy);
- ALFA+W – commercial polymeric filament based on PLA, color: silver, density: 1.30 g/cm^3, filament diameter: 1.75 mm, base material is polylactide produced from recycled materials containing above 80% of recyclate (manufacturer: FILOALFA);
- GRAFYLON® – commercial polymeric filament based on PLA matrix (composite of graphene and PLA), color: graphite, density: 1.23 g/cm^3, diameter: 1.75 mm; filament is reinforced with graphene phase in the form of pure graphene nano-flakes (manufacturer: FILOALFA and Directa Plus).

2.2. Thermal analysis by TG-DTG-DSC

TG-DTG test were performed in accordance with PN-EN ISO 11358-1:2014-09 [16] using TGA/SDTA 851e thermogravimeter from Mettler-Toledo. The following parameters were used: temperature range: 25–900°C, heating rate: 10°C/min. The analysis was performed in an atmosphere of synthetic oxygen of 99.9992% purity. The gas flow through the furnace was set on: 60 ml/min. Aluminum oxide (Al_2O_3) crucible pots were used for this study. The temperature value of the center point of the T_c distribution was take as the temperature value of the maximum peak of the DTG curve. The initial weights of the samples were as follows: PLA1 – 14.164 mg; PLA7 – 14.594 mg; ALFA+W – 14.443 mg; GRAFYLON® – 14.986 mg.

DSC analysis was performed according to PN-EN ISO 11357-1:2016-11 [17] and PN-EN ISO 11357-2:2020-09 [18]. The temperature and enthalpy of melting and crystallization were also determined using a Mettler-Toledo DSC 822e differential scanning calorimeter. The test was performed according to the test standard PN-EN ISO 11357-3:2018-06 [19]. The following test parameters were used: temperature range: 0–180°C. For the ALFA+W samples, a higher temperature range 0–210°C was used. Analysis carried out up to the final measurement temperature of 180°C did not allow the extrapolated value of the melting end to be determined. Heating and cooling rate used: 10°C/min, duration of isometric segments: 5 min. A synthetic oxygen atmosphere of 99.9992% purity with 60 ml/min flow rate was used, an Al – pure aluminum crucible 40 µl with perforated lid. Initial samples massed: PLA1 – 9.04 mg, PLA7 – 9.03 mg, ALFA+W – 9.44 mg, GRAFYLON® – 8.75 mg.

2.3. Thermal analysis by diffuse reflectance technique (DRIFT)

DRIFT investigations were performed using a Bruker "Vertex 70V" vacuum spectrometer operating in the mid- and far-infrared in the wavenumber range of 8000–370 cm^{-1} and

700–30 cm^{-1}. Spectra were recorded in the temperature range 20–500°C and wave number range 4000–500 cm^{-1} with a preset resolution of 4 cm^{-1}. Interferograms consisted of 64 scans, which were averaged into one spectrum.

Test sample preparation involved grinding the test materials in an agate mortar (200 mg KBr and 2 mg polymer plastic samples). The powdered materials were directly placed in the measuring crucible. The ceramic crucible was placed inside the dome in the spectrometer. The windows of the dome were made of zinc selenium ZnSe. The spectrometer operated in coupling with "Opus Operator" software, which recorded the received spectra from the analytical instrument. Measurements were made at a rate of 10°C/min.

3. RESULTS AND DISCUSSION

3.1. Thermal analysis

Figures 1a–d show the TG-DTG results for polylactide samples. Thermal decomposition of both PLA1 sample (Fig. 1a), PLA7 sample (Fig. 1b), ALFA+W (Fig. 1c) and GRAFYLON® (Fig. 1d) started at the same moment (after reaching the temperature of 300°C).

Thermal degradation of the PLA1 sample occurred in the temperature range 353–466°C, and the total mass loss was 99.9%, which indicated its virtually complete degradation. For the PLA7 material, the degradation pattern was similar to that recorded for PLA1. However, in the case of PLA7, the degradation took longer, up to the temperature of about 466°C, the sample actually degraded completely. ALFA+W sample made of recycled material showed the highest thermal stability, the first weight loss was only 84.1% in the temperature range of 25–351°C. On the other hand, the sample modified with graphene nanoplatelets showed higher thermal stability than the polylactide PLA1 and PLA7 samples.

In Figures 2–5 the recorded DSC curves for the considered filament samples are shown.

Based on the analysis of the DSC curves, it can be concluded that the polylactide has a relatively low glass transition temperature (T_g) oscillating at 60°C. Material recycling and reinforcement has no significant effect on T_g value. Highest T_g value was determined for PLA7 polymer (T_g = 60.16°C). On the other hand, the filament ALFA+W produced from the recyclate had the lowest T_g value (T_g = 60.07°C). The melting point (T_p) of the polymeric materials which indicates the moment when the material undergoes the complete transition to the liquid state was also determined. Highest value of T_p was obtained for ALFA+W polymeric filament (T_p = 175.89°C). It can be caused by reuse of recyclate already used, which were remelted and regranulated and additionally could consist of modified materials. Rest of the materials had similar melting point valued in the range of 150–155°C. The results of the glass transition temperature and melting point temperature for PLA samples are shown in Table 2.

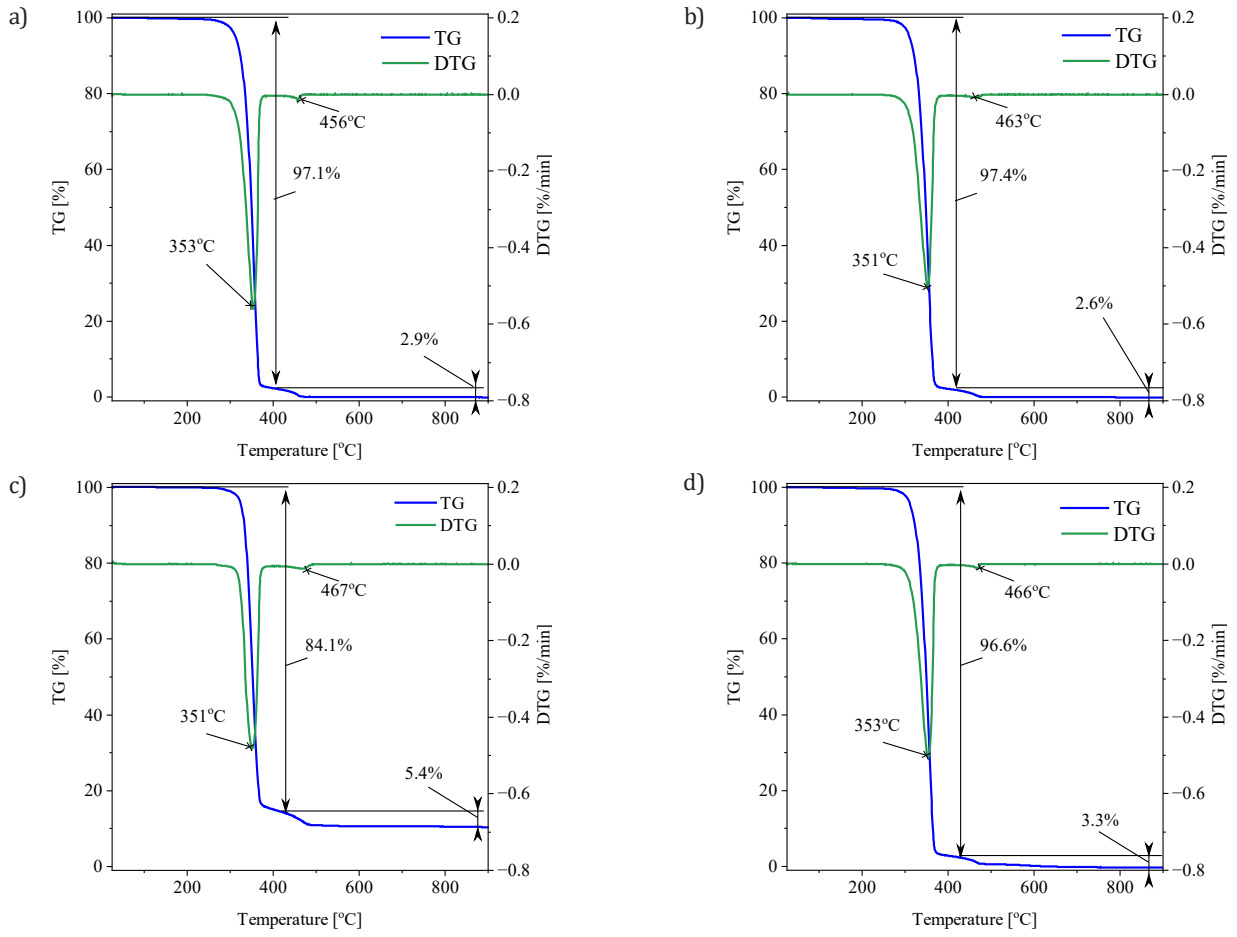

Fig. 1. TG-DTG curves of: a) PLA1; b) PLA7; c) ALFA+W; d) GRAFYLON®

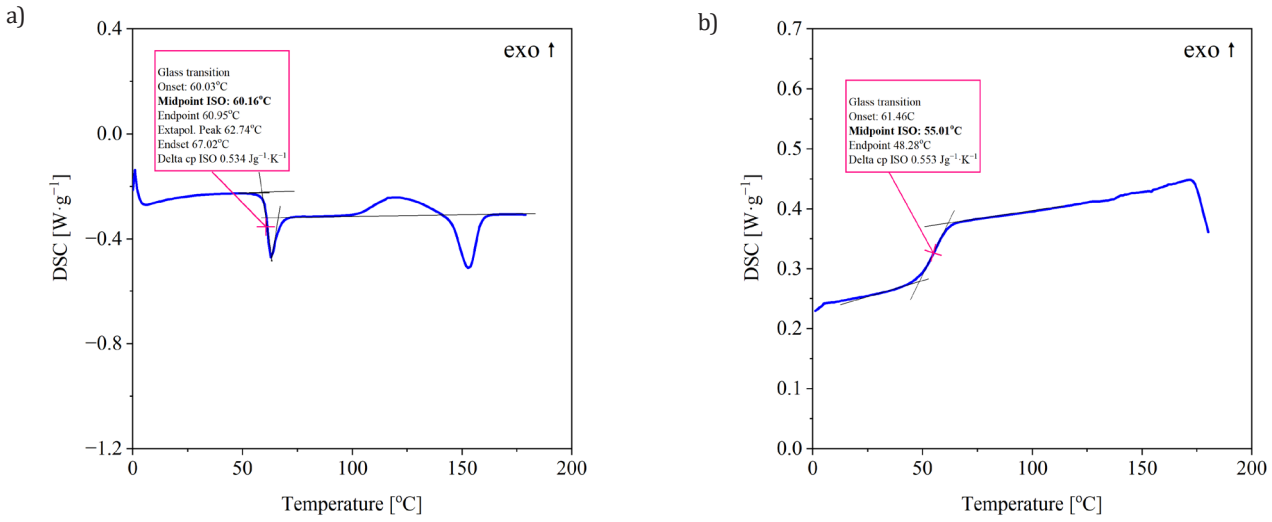

Fig. 2. DSC curves of PLA1: a) heating; b) cooling

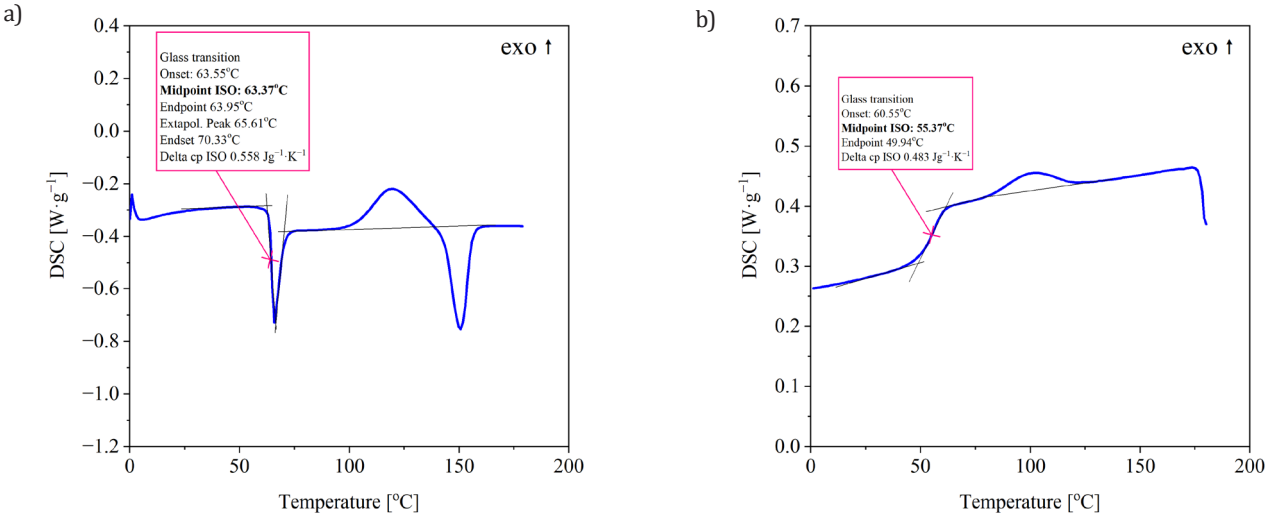

Fig. 3. DSC curves of PLA7: a) heating; b) cooling

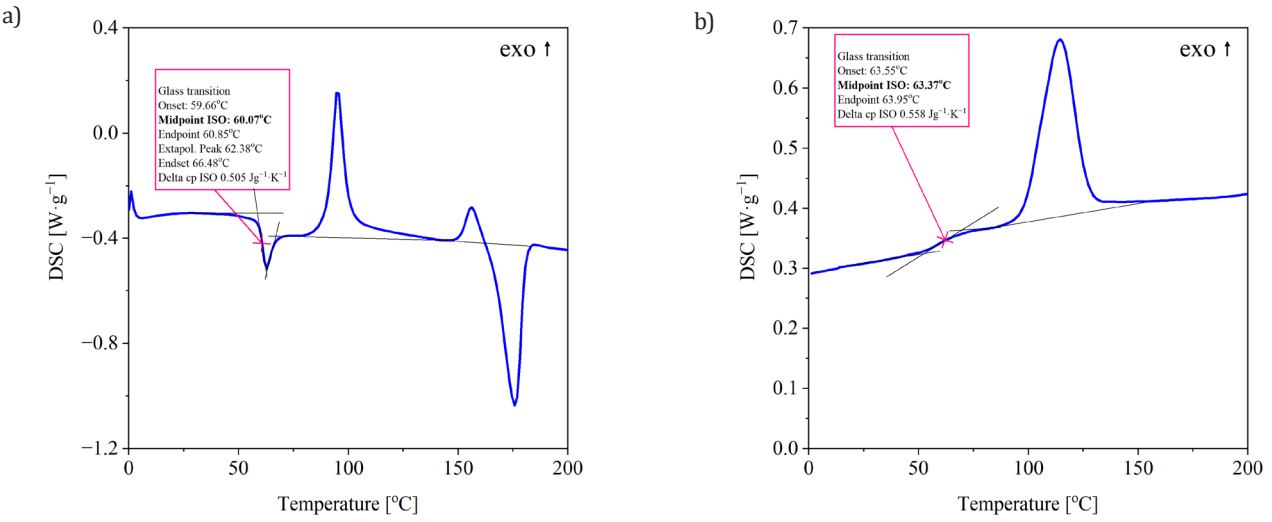

Fig. 4. DSC curves of ALFA+W: a) heating; b) cooling

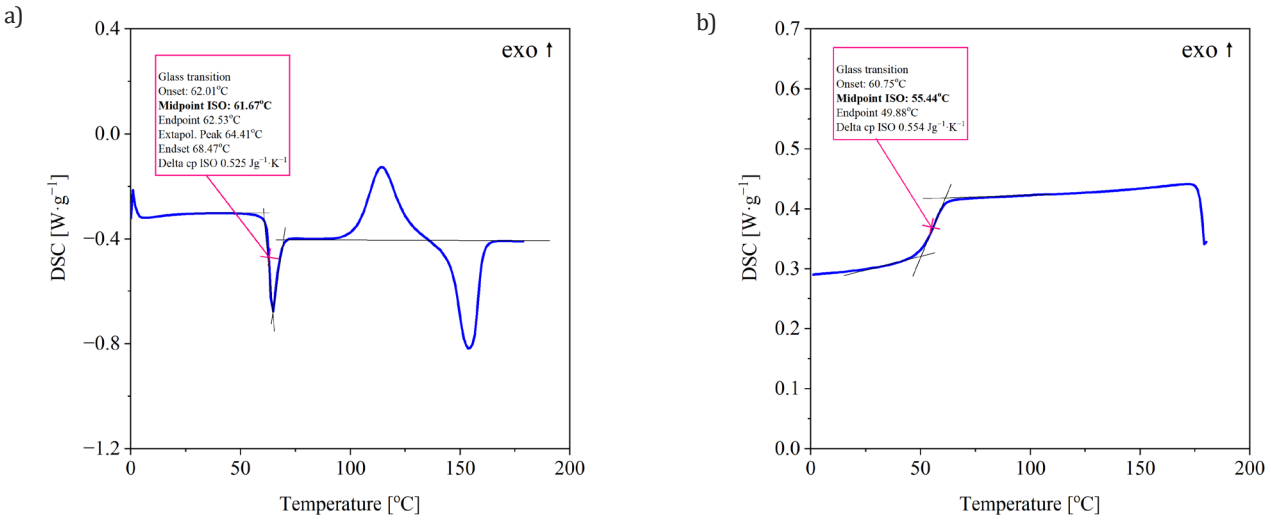

Fig. 5. DSC curves of GRAFYLON®: a) heating; b) cooling

Table 2
Glass transition and melting point temperature for PLA1, PLA7, ALFA+W and GRAFYLON®

Parameter	Sample			
	PLA1	PLA7	ALFA+W	GRAFYLON®
Extrapolated temperature of onset of glass transition ($T_{ei,g}$) [°C]	60.03	63.55	59.66	62.01
Extrapolated temperature end of glass transition ($T_{ef,g}$) [°C]	67.02	70.33	66.48	68.47
Glass transition temp. (T_g)[°C]	60.16	63.37	60.07	61.67
Extrapolated initial melting point temp. ($T_{ei,m}$) [°C]	144.91	142.94	165.89	144.76
Melting point temp. ($T_{p,m}$) [°C]	154.97	150.55	175.89	153.87

3.2. Structural analysis

DRIFT spectra for the samples were recorded in the temperature range of 20–500°C, indicating that with increasing temperature the shape as well as the position and intensity of particular bands changed. Some of them intensified and some of them disappeared completely, which indicates the progressive degradation of the polymer chain due to the temperature. New bands were also formed during the temperature increase, which was indicated in the sample structure. DRIFT spectra of PLA are shown in Figures 6–9.

Recorded spectra for three samples: PLA1, PLA7 and ALFA+W at 20°C, contained characteristic bands originating from the vibrations group of atoms found in the PLA structure (Table 3). It was also observed that the spectra contained additional bands throughout the range of wave numbers, whose vibrational energy was often close to the vibrational energy of the bonds of atoms present in PLA. These vibrations come from the introduced additives to the base material of polylactide i.e., dyes and graphene. For the GRAFYLON® sample, a significantly reduced intensity of the bands was found across the considered range of wave numbers. This is probably due to the fact that the sample contains a significant amount of graphene, for which the detection of the vibrational energy of individual bonds is not possible in the mid-infrared range. It was found that the characteristic bands did not change up to a temperature of around 360°C.

Above the temperature of 360°C on the spectra of the examined samples in the region of wavenumbers 4000–2800 cm^{-1} a slow decrease in the intensity of particular bands is observed, which indicates progressing degradation of the samples. It is noteworthy that at 500°C, in the region of 1700 cm^{-1} characteristic bands of carbonyl group (>=C=O) are present and even an increase in intenisty of this band is observed. Additionally, the bands below 1450 cm^{-1} characteristic for C-C vibrations did not disappear, it confirms that all of the samples under consediration have not yet completely decomposed. In the case of the GRAFYLON® sample, no band in the region of wavenumbers 3600–3700 cm^{-1} was observed. It proves a lack of a tendency for water adsorption on the surface. Based on the analysis of DRIFT spectra, it can be concluded that the least thermostable filament is PLA1 material, and the most stable is GRAFYLON®. The thermostability of PLA7 and ALFA+W samples, on the other hand, is similar and proves the validity of manufacturing felt using recycled materials.

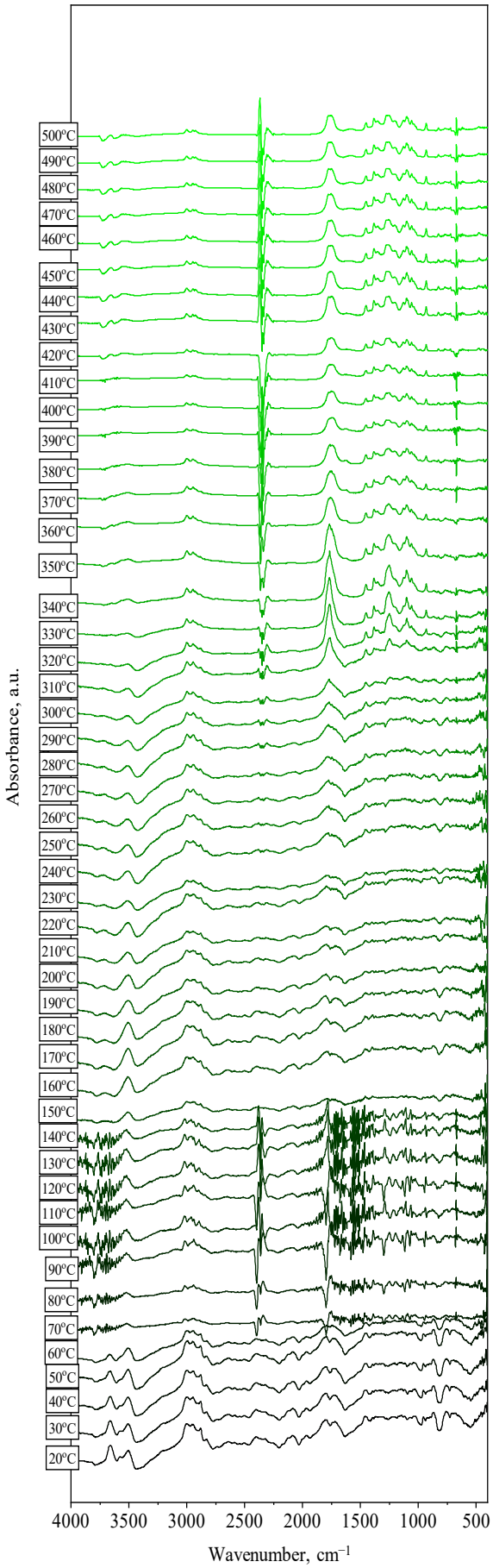

Fig. 6. DRIFT spectra of PLA1

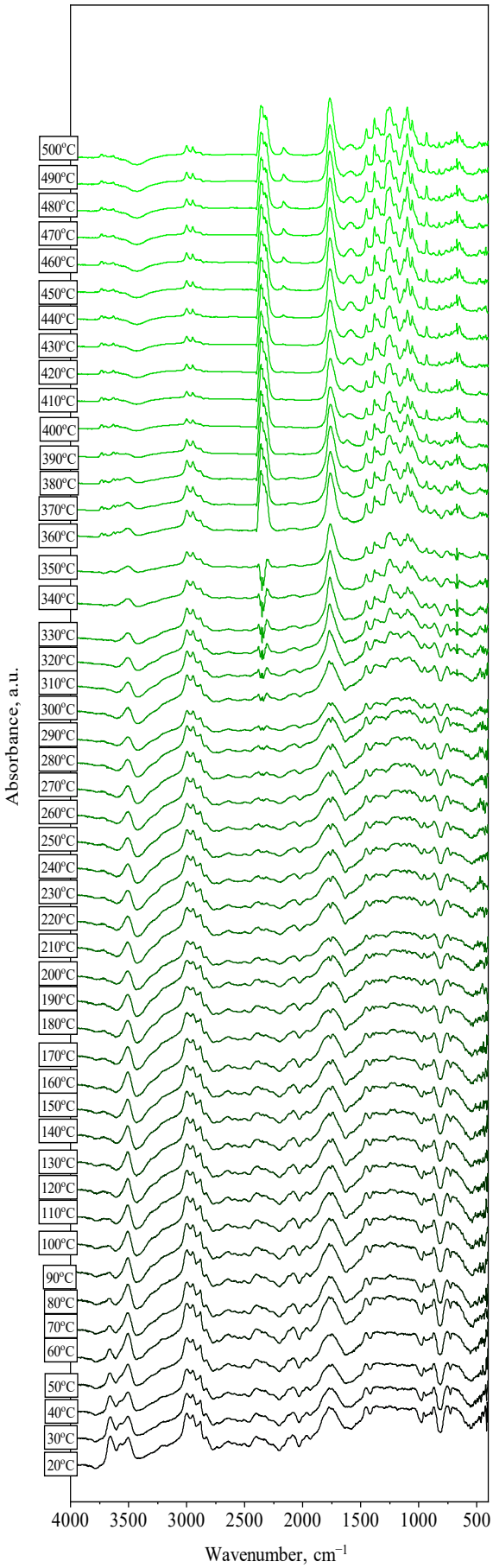

Fig. 7. DRIFT spectra of PLA7

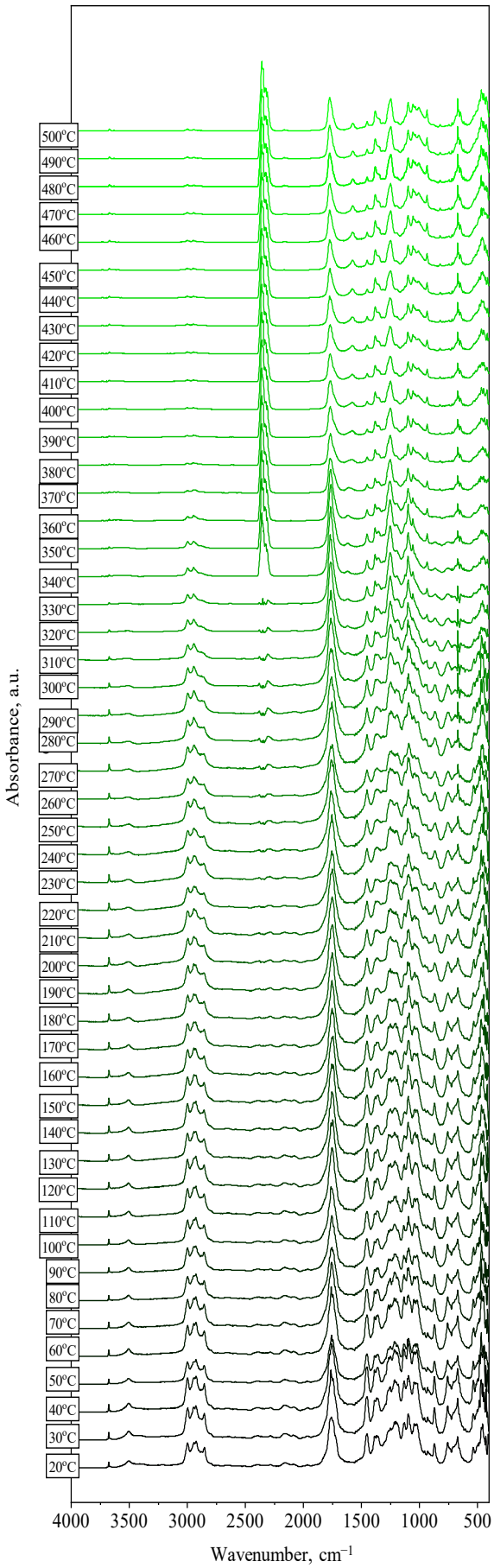

Fig. 8. DRIFT spectra of ALFA+W

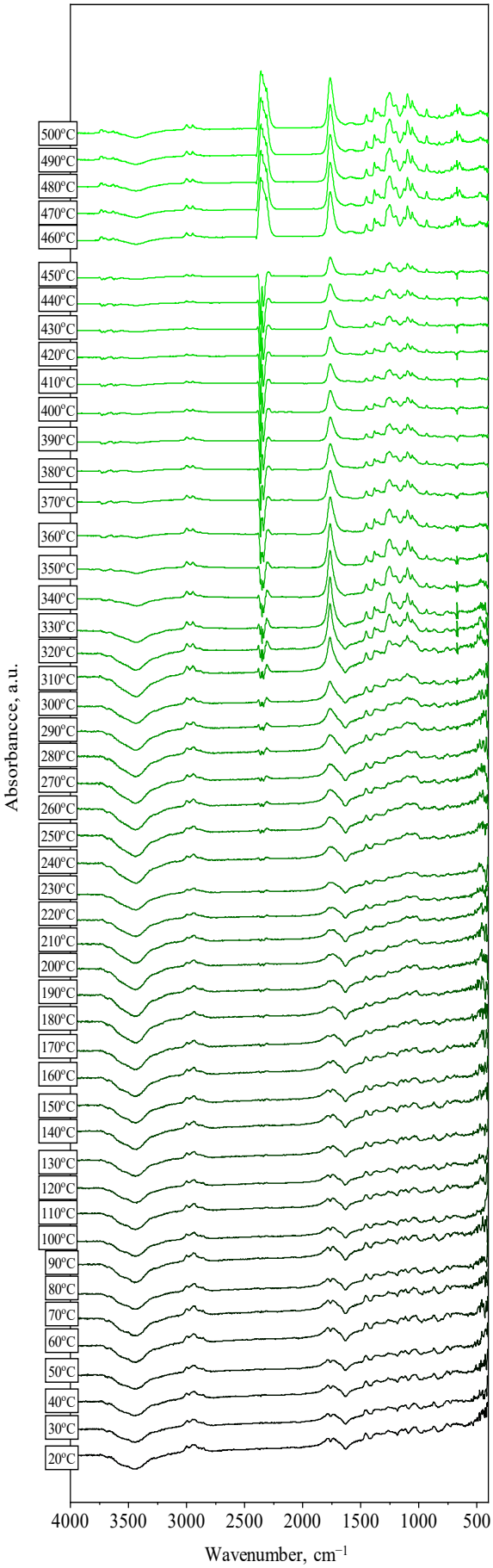

Fig. 9. DRIFT spectra of GRAFYLON®

Table 3
Characteristic absorption bands on the DRIFT spectra of PLA samples

Wavenumber [cm^{-1}]	Assignment	Remarks
3500–3400	*v*-OH	Band of free OH group (water adsorption)
2945–3000	*v*-C–H *v*(CH_2)	Stretching vibrations asymmetric and symmetric
1750–1760	v_s-C=O	Stretching vibrations of carbonyl group
1450–1455	β(CH_3)	In-plane bending vibrations
1380	δ-CH–	Deformation vibrations asymmetric and symmetric
1250–1220	–C=O	Bending vibrations
1170–1175	*v*-C–O–	Stretching vibrations
1030–1040	*v*-OH	Stretching vibrations
860–890	–C–C–	Stretching vibrations

4. CONCLUSIONS

Based on the thermal analysis of TG-DTG, it was confirmed that the degradation of the considered samples of PLA material begins around the temperature of 350°C. This fact indicates the possibility of their use in 3D printing processes. It has been shown that, among the tested samples, the material reinforced with graphene phase (GRAFYLON®) retains the best thermal properties, which results in even wider possibilities of its processing, including further modification, and wider usability for structural elements of vehicles with its participation. Moreover, the glass transition temperature for the supplied samples was determined by the DSC method. It was found that recycling and modification with graphene had no significant effect on the T_g value. The melting point and change to the melting enthalpy (ΔH_p) was also determined. The material from recyclate (ALFA+W) was characterized by a higher T_p value than the other samples by more than 20°C, hence it may be more suitable for use in the production of structural components operating at increased temperature. It has been shown that the most important structural changes under the influence of temperature begin above the temperature of 360°C. Conclusions from these studies find practical applications in determining the suitability of a given material for use in 3D printing technologies. It can be concluded that the tested materials exhibit adequate thermal stability for their use in the 3D printing process.

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