



# Article **Filament Extrusion and Its 3D Printing of Poly(Lactic Acid)/Poly(Styrene-***co***-Methyl Methacrylate) Blends**

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**Abstract:** Herein, we report the melt blending of amorphous poly(lactide acid) (PLA) with poly(styrene-*co*-methyl methacrylate) (poly(S-*co*-MMA)). The PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends were made using amorphous PLA compositions from 50, 75, and 90wt.%, namely PLA<sub>50</sub>/poly(S-*co*-MMA)<sub>50</sub>, PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub>, and PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub>, respectively. The PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blend pellets were extruded into filaments through a prototype extruder at 195 °C. The 3D printing was done via fused deposition modeling (FDM) at the same temperature and a 40 mm/s feed rate. Furthermore, thermogravimetric curves of the PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends showed slight thermal decomposition with less than 0.2% mass loss during filament extrusion and 3D printing. However, the thermal decomposition of the blends is lower when compared to amorphous PLA and poly(S-*co*-MMA). On the contrary, the PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blend has a higher Young's modulus (*E*) than amorphous PLA, and is closer to poly(S-*co*-MMA), in particular, PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub>. The PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends proved improved properties concerning amorphous PLA through mechanical and rheological characterization.

**Keywords:** amorphous poly(lactide acid); poly(styrene-*co*-methyl methacrylate); polymer blends; filament extrusion; 3D printing

# 1. Introduction

Additive manufacturing or 3D printing makes it possible to produce exceptional architecture with different complexity grades [1,2]. Additionally, additive manufacturing has several advantages, such as formability, variability, practicability, mass delivery, and surface property designs [3]. Various technologies of additive manufacturing for polymers have been developed, e.g., fused deposition modeling (FDM), bioprinting, selective laser sintering, selective heat sintering, digital light projection, and laminated object manufacturing [4,5]. The polymeric materials employed in these technologies are pellets, polymerizable resins, powders, gels, dispersed solutions, and filaments. Furthermore, the FDM limitations are the high-temperature manufacturing of polymeric filaments prior to 3D printing, exclusivity for thermoplastic polymers, and the lack of polymeric filaments available at the industrial level with mechanical properties suitable for 3D printing [1,6]. The filament extrusion conditions have a few reports in this field [7–9]. For example, Mirón et al. [8] produced uniform filaments extruded with a nozzle diameter of 2.85 mm and a temperature range from 175 to 180 °C for semi-crystalline PLA. Similarly, Kariz et al. [9] obtained PLA-wood filaments at a higher temperature (230 °C) with a nozzle of 0.4 mm. Finally, the additive manufacturing applications cover diverse areas, specifically biomedical fields such as scaffolds [10–13], drug delivery systems [14], surgical tools, and implantable devices [15,16], among others.

Moreover, PLA has been reported for additive manufacturing [16–21]. For instance, Zuniga et al. [16] replicated an amputee's finger through FDM using PLA/copper nanoparticle

composites. Chacón et al. [19] printed semi-crystalline PLA under the following conditions: Temperature = 210 °C, feed rate = 20 mm/s, and a filament diameter of 1.75 mm. For polymethyl methacrylate (PMMA), Nagrath et al. [22] reported printing parameters as follows: Temperature = 275 °C, print speed = 10 mm/s, and a nozzle diameter of 0.4 mm.

Notwithstanding, PLA can be mixed with other (co)polymers, natural or synthetic, as poly(S-*co*-MMA), producing polymer blends with specific characteristics or properties for a given application [23]. In addition, semi-crystalline PLA, PMMA, and polystyrene (PS) have been studied, with potential applications in orthopedics, scaffolds, and tissue engineering. The semi-crystalline PLA focus has been on cell proliferation, vascularization, shape-memory, and mechanical properties [15,24–30]. PLA can be biodegraded under natural body conditions [31]. However, new scaffold architectures can be designed by delaying or anticipating the amorphous PLA biodegradation when PLA is blended with non-biodegradable polymers. In contrast, traditionally commercially available prepolymers of PMMA, PMMA-*co*-PS, or their mixtures, constitute the main component of acrylic bone cement [32]. Therefore, PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends can open new opportunities for device production through additive manufacturing [15,17]. Additionally, the polymer blends containing PS, PMMA, or both have had several reports concerning miscibility and compatibility between materials [33,34]. Contrarily, few authors support PS/PMMA blend immiscibility [35,36].

In the present study, we reported the processing conditions for filament extrusion and additive manufacturing for PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends, as well as their mechanical, thermal, and rheological properties. The key question of this research was whether a polymer blend could be made between amorphous PLA and poly(S-*co*-MMA) to improve on the processability of PLA during polymeric filament extrusion and 3D printing, but preserving physicochemical properties of PLA.

## 2. Materials and Methods

#### 2.1. Materials

PLA Ingeo 4060D, D-lactide 12%, with an average molecular weight of 190 kg/mol,  $\rho = 1.24$  g/cm<sup>3</sup>, and glass transition temperature T<sub>g</sub> = 55–60 °C from NatureWorks LLC, USA. Poly(S-*co*-MMA), SMMA NAS<sup>®</sup>30,  $\rho = 1.090$  g/cm<sup>3</sup>, T<sub>g</sub> = 103 °C, MFI = 2.2, from Ineos Styrolution Group GmbH, Germany. In addition, the styrene and methyl methacrylate content on Poly(S-*co*-MMA) ranged from 70 to 90wt.% and 10 to 30wt.%, respectively [37].

## 2.2. Melt Blending

The amorphous PLA and poly(S-*co*-MMA) were dried at 60 °C for 8 h. The blending was done through a Brabender internal mixer (BB) [DDRV501, C.W. Brabender Instruments Inc., Hackensack, NJ, USA], at 50 rpm, and at a temperature of 195 °C. The blend compositions are shown in Table 1. Afterwards, the bulk sample of PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends were ground through a blade mill to obtain PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blend pellets.

Samples	PLAx/poly(S-co-MMA)y (wt.%)		
	x	у	
Neat PLA	100	0	
Neat poly(S-co-MMA)	0	100	
PLA <sub>50</sub> /poly(S-co-MMA) <sub>50</sub>	50	50	
PLA <sub>75</sub> /poly(S-co-MMA) <sub>25</sub>	75	25	
PLA <sub>90</sub> /poly(S-co-MMA) <sub>10</sub>	90	10	

Table 1. PLA<sub>x</sub>/poly(S-co-MMA)<sub>y</sub> blends compositions.

## 2.3. Filament Extrusion

The filaments were produced through a single-screw extruder using  $PLA_x/poly(S-co-MMA)_y$  blend pellets. A temperature of 195 °C was set. The  $PLA_x/poly(S-co-MMA)_y$  blend filaments had a 1.75+/-0.1 mm average diameter. A moto-reducer with 1.6 A, 15.6 N-m of torque, and 12 V DC was used.

## 2.4. 3D Printing

The adequate properties for additive manufacturing were proved through a CTC 3D printer at 195 °C. The specific parameters are shown in the Table 2. The nozzle diameter was 0.4 mm.

Parameter	Value	Units
Object infill (%)	10	%
Layer Height (mm)	0.25	mm
Number of shells	3	
Feed rate (mm/s)	40	mm/s
Travel feed rate	35	
Print temperature (°C)	195	°C

Table 2. 3D printing parameters of PLA<sub>90</sub>/poly(S-co-MMA)<sub>10</sub> blend.

# 2.5. Characterization

## 2.5.1. Mechanical Properties

The mechanical testing for PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends, neat PLA, and neat poly(S-*co*-MMA) was performed using a 3382 Floor Model Universal Testing System from Instron, USA. A 5 mm/min velocity was set. The tensile mode was selected, and five probes were evaluated. The probes were manufactured in a hot press molding machine 4122 Bench Top manual press model, from Carver<sup>®</sup>, USA. The compression molding was in two stages, as follows: First, a zero load for 1 min was applied, and second, a maximum load of 2.75 tons for 3 min was used. Both stages were performed at a temperature of 225 °C. The probe's dimensions are based on ASTM D638 type IV.

## 2.5.2. Rheological Properties

A rotational rheometer (Physica MCR 501, Anton Paar) was used. The conditions were as follows: Oscillatory mode, parallel plate geometry with a 25 mm plate diameter, and a 1 mm gap. The analysis was achieved at a temperature of 195  $^{\circ}$ C.

## 2.5.3. Differential Scanning Calorimetry Analysis

Thermal studies were carried out in a DSC Q2000 differential scanning calorimeter from TA Instruments, USA. Samples of about 10 mg were sealed in standard aluminum pans under the following conditions: At a 10 °C/min heating rate and a -10-200 °C temperature range. Argon atmosphere was used in all samples.

#### 2.5.4. Thermogravimetric Analysis

Thermal degradation was measured under air atmosphere with an SDT Q600 from TA Instruments, USA. The PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends, neat PLA, and neat poly(S-*co*-MMA) were heated at a rate of 10 °C/min up to 800 °C. Approximately 16 mg of polymeric material was placed in a platinum crucible.

# 3. Results and Discussion

Briefly, poly(S-*co*-MMA) used in this research is a commercial material with random copolymer architecture. Furthermore, poly(S-*co*-MMA) copolymer has improved ultimate strength and elongation

at break than PS, and has better thermal properties regarding PMMA. Similarly, this thermal property is one advantage over PMMA on heat transfer and melt processing [37]. In other words, this polymeric material has advantages over neat PS and PMMA.

## 3.1. Mechanical Properties

# 3.1.1. Young's Modulus

Figure 1 shows E of neat PLA, random copolymer, and the  $PLA_x/poly(S-co-MMA)_y$  blends. The *E* values were 1.57, 1.58, and 1.60 GPa for PLA<sub>50</sub>/poly(S-*co*-MMA)<sub>50</sub>, PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub>, and  $PLA_{90}$ /poly(S-co-MMA)<sub>20</sub> blends, respectively. The increasing E of blends can be due to compatibility between the polymer and random copolymer. The term "compatibility" refers to the blend behavior in terms of mechanical properties, and the "miscibility" is related to a homogeneous system formation at a molecular level. Usually, a miscible mixture is compatible; however, a compatible mixture is not necessarily miscible. The compatibilization of polymer blends containing PLA has been reported. For example, Quitadamo et al. [38] produced PLA/high-density polyethylene blends obtaining an optimal E = 1.88 GPa for PLA<sub>50</sub>/HDPE<sub>50</sub>. In another study, Balakrishnan et al. [39] improved the flexibility and E (2.2 GPa) of a PLA/low linear density polyethylene (LLDPE) blend when adding up to 15wt.% of LLDPE. Additionally, the PMMA *E* has been reported around 3.3 GPa, a higher value than the poly(S-co-MMA) used in the present investigation [40]. It is essential to mention that amorphous PLA has a lower *E* than semi-crystalline PLA, with values close to 2 GPa [31,41]. In addition, the *E* reported in the literature is a function of processing conditions for amorphous and semi-crystalline PLA [27]. A further example, an amorphous PLA processed (4060D from Nature Works<sup>®</sup>) at 160 °C for 10 min, in an internal mixer at 100 rpm, yielded 1.79 GPa of *E* [41].



**Figure 1.** Young's modulus, elongation at break, and ultimate strength of (**a**) PLA<sub>50</sub>/poly(S-*co*-MMA)<sub>50</sub>; (**b**) PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub>; (**c**) PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub>; (**d**) neat poly(S-*co*-MMA); (**e**) neat PLA; and (**f**) overall.

Contrary to *E*, a decreasing effect on the elongation at break was observed in the blends (Figure 1). When poly(S-*co*-MMA) content was reduced from 50 to 10wt.% in the PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends, the elongation at break improved. The blend PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> had the highest value of 3.84%. This same effect was observed on PLA/PS blends [42]. The polystyrene elongation at break was reported in other research, and it was about 4.3%, a closer value to the present result [43]. An interesting issue is that the elongation at break overrode the neat poly(S-*co*-MMA) by just adding 10wt.% of poly(S-*co*-MMA) into the PLA matrix. Finally, the poly(S-*co*-MMA) content in the blends decreases the elongation at break.

## 3.1.3. Ultimate Tensile Strength

The PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends also showed compatibility in tensile strength (Figure 1). In general, it is observed that blend PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> presented the highest value (56 MPa), which even surpassed the neat PLA value (52 MPa). The PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub> blend had a lower value than poly(S-*co*-MMA) copolymer with 45 MPa and 46 MPa, respectively.

The PLA, in some cases, can be used to increase the ultimate tensile strength for specific blends, for instance, PLA/PS blends. This improvement was attributed to low interfacial tension and high-stress transfer parameters [42]. Similarly, PLA<sub>70</sub>/HDPE<sub>30</sub> blends showed an increasing effect for the ultimate tensile strength of about 49 MPa [38]. In the same manner, the PLA<sub>85</sub>/LLDPE<sub>15</sub> blends displayed a maximum value of 43 MPa [39]. Table 3 displays the mechanical properties of PLA, PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends, and poly(S-*co*-MMA).

Sample	Young's Modulus (GPa)	Elongation at Break (%)	Ultimate Tensile Strength (MPa)
Neat PLA	1.16	6.00	52
PLA <sub>50</sub> /poly(S-co-MMA) <sub>50</sub>	1.57	3.23	48
PLA <sub>75</sub> /poly(S-co-MMA) <sub>25</sub>	1.58	3.17	45
PLA <sub>90</sub> /poly(S-co-MMA) <sub>10</sub>	1.60	3.84	56
Neat poly(S-co-MMA)	1.68	3.00	46

Table 3. Mechanical properties of neat PLA, PLA<sub>x</sub>/poly(S-co-MMA)<sub>y</sub> blends, and neat poly(S-co-MMA).

#### 3.2. Rheological Properties

The miscibility of the binary blends was studied through the Han and Cole–Cole plot analysis because of the improvement in *E* concerning PLA. First, the Han plot was used to identify the polymer blend miscibility or composite materials at different temperatures and compositions [30]. The Han plots of the PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends, neat poly(S-*co*-MMA), and neat PLA analyzed at 195 °C are displayed in Figure 2. A significant characteristic concerning the Han plot (log G' vs. log G") is that a slope of 2 must be observed in the terminal region or low frequency if a blend is regarded as truly homogeneous [44,45]. The slope of the PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> blend is the highest of all the mixtures with 1.85, while PLA<sub>50</sub>/poly(S-*co*-MMA)<sub>50</sub> is the lowest, 1.62. In other words, the miscibility is present in the PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends as a function of the PLA content obtaining adequate mechanical properties.



**Figure 2.** Han plots of (**a**) PLA<sub>50</sub>/poly(S-*co*-MMA)<sub>50</sub>; (**b**) PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub>; (**c**) PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub>; (**d**) neat poly(S-*co*-MMA); and (**e**) neat PLA; (**f**) Cole–Cole plot of neat PLA, PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>v</sub> blends, and neat poly(S-*co*-MMA).

Additionally, Figure 2b illustrates the Cole–Cole plots of neat PLA, neat poly(S-co-MMA), and PLA<sub>x</sub>/poly(S-co-MMA)<sub>v</sub> blends. In particular, all samples present information about the relaxation process occurring in polymeric blends. These diagrams, in particular, form or become one semicircle when they indicate miscibility; on the contrary, immiscibility is attributed when more than one semicircle appears [46]. The Cole–Cole diagrams revealed the homogeneity of amorphous PLA, showing a smooth semicircular arc. A deviation from this smooth semicircular arc was observed in the case of poly(S-co-MMA) neat copolymer, with a more opened arc and tail. The PLA<sub>50</sub>/poly(S-co-MMA)<sub>50</sub> blend displayed a non-closed semicircular arc accounting for immiscibility. Otherwise, the PLA<sub>75</sub>/poly(S-co-MMA)<sub>25</sub> and PLA<sub>90</sub>/poly(S-co-MMA)<sub>10</sub> had a similar smooth semicircular arc to the amorphous PLA, which explains the miscibility and homogeneity of these last blends [47,48]. Similarly, the Cole–Cole plots were used by Ding et al. [49] reporting two relaxation behaviors in immiscible PLA/PBAT blends, the left arc explains the polymer chain relaxation, and the right arc accounts for the droplet relaxation. Thus, Singla et al. [50] reported excellent compatibility and homogeneity for PLA/ethyl-vinyl acetate (EVA) blends for a maximum EVA content of 30wt.%. In addition, Maroufkhani et al. [51] observed a tail at the end of the curves in Cole–Cole plots, confirming phase separation between PLA and acrylonitrile butadiene rubber (NBR). In the same way, Adrar et al. [52] studied the effect of adding epoxy functionalized graphene to PLA/PBAT blends, in which a semicircular shape was observed showing positive miscibility.

Figure 3a displays the complex viscosity results,  $\eta^*$ , of neat PLA, neat poly(S-*co*-MMA), and PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends. In particular, the PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub> and PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> samples presented a broad plateau in comparison to the poly(S-*co*-MMA) copolymer. However, at high frequencies, all materials converged on similar  $\eta^*$  values at approximately 30 Hz. Equally important, the amorphous PLA effect on the blends is in the  $\eta^*$  stabilization as a frequency function. Conversely, a poly(S-*co*-MMA) disadvantage is its high  $\eta^*$ , and a small plateau at low frequencies, which has a shear thinning behavior. It should be noted that the PS and PMMA present a similar  $\eta^*$  curve compared to poly(S-*co*-MMA), although more identical to the PS caused by a more significant number of styrene monomer units according to the random copolymer composition [53].



**Figure 3.** (a) Complex viscosity of neat PLA, neat poly(S-*co*-MMA), and PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends; (b) Storage modulus of neat PLA, neat poly(S-*co*-MMA), and PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends.

Additionally, the increase or decrease in  $\eta^*$  is the result of changes in structure when compared to starting materials. For instance, the composites present an increased  $\eta^*$  based on the filler content in the polymer blends [54–57]. On the other hand, in this study PLA and poly(S-*co*-MMA) presented differences in their  $\eta^*$  ascribable to their molecular weight, resulting in polymer mixtures with behavior between the frontier of the neat polymers. In summary, the PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends do not show changes in structure, specifically with a physical interaction between the PLA and poly(S-*co*-MMA).

Figure 3b shows the storage module (G') graph versus square frequency of polymer blends, PLA, and poly(S-*co*-MMA). In general, PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends converge at high frequencies; however, at low frequencies, the blends showed a predominant elastic behavior. The PLA showed the lower G' at low frequencies, while the poly(S-*co*-MMA) had a high value in the same range.

From 7 Hz to the highest frequency,  $PLA_{75}/poly(S-co-MMA)_{25}$  presented a higher modulus than  $PLA_{50}/poly(S-co-MMA)_{50}$ . For  $PLA_{90}/poly(S-co-MMA)_{10}$ , there was a similar situation at approximately 30 Hz. The G' decreased with PLA concentration in the  $PLA_x/poly(S-co-MMA)_y$  blends. The G' decreased at low frequencies according to the rheological behavior of unlinked polymers when small molecules are in the polymer structure [58].

Moreover, blend miscibility can be analyzed in the oscillatory rheology through the storage module plot versus the frequency where the behavior should be closer to a neat homopolymer. For example, this same behavior was observed in PLA-EVA [50] and PEO/PMMA blends [54]. Additionally, the PVDF/PMMA blends showed an increase in G' compared to the neat PMMA; however, it was lower than the neat PMMA when the temperature changed [55]. Similarly, Mao et al. [56] observed an increase for G' in the PMMA/PCE blends at low and high frequencies. These results were attributed to the short time for chain relaxation. Equally, Suresh et al. [57] reported a decrease in the rheological parameters (G' and G'') of PVC/PMMA/rubber nitrile blends as a consequence of the flexibility provided by the rubber nitrile.

Figure 4 shows the G' and loss modulus (G") curves against the angular frequency, crossing point, of neat PLA, neat poly(S-*co*-MMA), and PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends. It is well known that, at low frequencies, G' > G' shows a fluid state following a typical linear polymer behavior; however, at high frequencies, G' > G' exhibits a solid-state behavior [59–61]. Furthermore, the crossing point (G' = G'') may change according to the composition or the branch generation due to the melt blending. For the neat PLA and poly(S-*co*-MMA), the crossing points were at 72.91 and 2.06 Hz, respectively. The PLA<sub>50</sub>/poly(S-*co*-MMA)<sub>50</sub> blend presented a crossing point at 23.17 Hz, with a trend closer to the poly(S-*co*-MMA) copolymer. Subsequently, the PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub> crossing point was observed at 28.35 Hz. Finally, the PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> had a crossing point at 57.32 Hz. Therefore, the crossing point of PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends presented displacements, along with frequency, between amorphous PLA and poly(S-*co*-MMA) content.



**Figure 4.** Crossing point of G' and G" modulus. (a) neat Poly(S-*co*-MMA); (b) neat PLA; (c) PLA<sub>50</sub>/poly(S-*co*-MMA)<sub>50</sub>; (d) PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub>; and (e) PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub>.

#### 3.3. Thermal Analysis

## 3.3.1. Differential Scanning Calorimetry

The T<sub>g</sub> dictates the miscibility phenomenon for polymer blends and processing conditions. As a rule, the polymer blend miscibility is associated with the observation of one single T<sub>g</sub> [62]. Nonetheless, a slight T<sub>g</sub> displacement on the PLA/PS blends suggested compatibility for those blends [42]. In other research, a single T<sub>g</sub> for semi-crystalline PLA/PMMA blends was reported with different PMMA compositions on the PLA matrix [63]. In addition, Zhang et al. [62] evaluated the miscibility of PLA/PMMA blends through two methods, as follows: (1) Solution/precipitation, and (2) solution-casting film. The results showed that for solution/precipitation, just one T<sub>g</sub> was observed, but two isolated T<sub>g</sub> were present in the solution-casting film method. Figure 5 shows the curves obtained in differential scanning calorimetry, and Figure S1 displays a zoom-in of poly(S-*co*-MMA)<sub>y</sub> T<sub>g</sub> curves belonging to PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends. In general, all PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends showed a T<sub>g</sub> increasing behavior for both transition temperatures when compared with the polymer and random copolymer alone. These results suggest immiscibility, however, compatibility was observed in the *E*.



**Figure 5.** Heating curves (2nd cycle) of neat PLA, neat poly(S-*co*-MMA), and PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends.

Further processing conditions (such as temperature, torque, and screw speed) for filament production are analogous to conventional extrusion. Specifically, the temperature must be between 15–60 °C above the  $T_g$  or melting point for amorphous, and semi-crystalline polymers, respectively [64].

Furthermore, these PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends have the advantage that the system is amorphous, and therefore require less energy for their transformation. The final  $T_g$  of the PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends varied between 102.1 and 106.5 °C, which determined the melt blending temperature via extrusion at 195 °C.

## 3.3.2. Thermogravimetric Analysis

Figure 6 displays thermogravimetric mass loss and derivative mass loss (DTG) curves of neat PLA, neat poly(S-*co*-MMA), and PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends. Furthermore, a particular behavior was observed in all blends presenting at least two degradation stages regarding a mass loss. For example, the PLA<sub>50</sub>/poly(S-*co*-MMA)<sub>50</sub>, in Figure 6a, presented a first mass loss stage of 96.8% between 321.4 and 420.8 °C, and a second step losing 3.0% over 420.8 until 490 °C. Correspondingly, there are three peaks in the DTG curve; one is located at 351 °C, followed by a second one maximum degradation temperature ( $T_{max}$ ) = 358.6 °C, and lastly, a small peak at 488 °C. Similarly, the PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub> blend in Figure 6b displayed a peak with  $T_{max}$  = 325.1 °C, and two shoulders placed next to the central peak with a mass loss of 16.4% from 343.6 to 400.1 °C, according to DTG and mass loss, respectively. The mass loss in the first event was about 80.8% between 255 and 343.6 °C. A third stage was also observed over 400.1 °C, with a mass loss of 1.8%. Concerning the DTG curve of the PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> blend, Figure 6c shows one peak with  $T_{max}$  at 334.3 °C and another at 368.5 °C. In addition, the first mass loss was observed from 250.1 to 345.6 °C, losing about 87.8%. The next stage of mass loss was of 9.4% between 345.6 and 388.6 °C. The last stage was presented at over 388.6 °C, with a mass loss of 2.0%.



**Figure 6.** Thermogravimetric mass loss and DTG (dm/dT) curves of (**a**) PLA<sub>50</sub>/poly(S-*co*-MMA)<sub>50</sub>; (**b**) PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub>; (**c**) PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub>; (**d**) neat poly(S-*co*-MMA); (**e**) neat PLA.

Additionally, the degradation stages of the  $PLA_x/poly(S-co-MMA)_y$  blends can be attributed to PLA degradation by hydrolysis during the process [65,66]. In addition, the chemical structure of poly(S-co-MMA) can decrease the thermal stability due to the presence of double carbon bonds and

aromatic rings, according to Witkowski et al. [67]. Furthermore, the poly(S-*co*-MMA) had a thermal decomposition stage from 260 to 460 °C and a  $T_{max}$  around 378 °C (Figure 6d). Figure 6e displays a single degradation step for PLA with a  $T_{max}$  at 352.9 °C [50]. On the other hand, these results agreed with other publications that studied blends or composites of PLA, poly(S-*co*-MMA), PS, or PMMA. For instance, Arshad et al. [68] reported an initial decomposition temperature for poly(S-*co*-MMA) at 260 °C. In addition, Buruga et al. [69] reported three thermal decomposition stages from 360 to 474 °C for poly(S-*co*-MMA), owing to individual functional group decomposition. Likewise, it was observed that PLA/PS blends two different stages attributed to the semi-crystalline and amorphous structures for PLA and PS, respectively [70]. Similarly, Teoh et al. [71] studied the thermal decomposition of PLA/PMMA blends with or without flame retardant, finding a displacement in PMMA  $T_{max}$  from 379 °C to 430 °C when the mixture contained flame retardant. However, Mangin et al. [72] decreased the PLA  $T_{max}$  from 362 to 315 °C when incorporating phosphorus as flame retardant (5wt.%) into PLA/PMMA blends. Finally, Anakabe et al. [73] added poly(styrene-*co*-glycidyl methacrylate) P(S-*co*-GMA) to a PLA<sub>80</sub>/PMMA<sub>20</sub> blend improving thermal stability with the copolymer at 3 pph.

Moreover, the blends' thermogravimetric curves established the conditions of thermal stability during the process of filament extrusion and 3D printing. The mass loss percentage at 195 °C for PLA<sub>50</sub>/poly(S-*co*-MMA)<sub>50</sub>, PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub>, and PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> were 0.03, 0.10, and 0.19%, respectively. However, poly(S-*co*-MMA) and PLA presented 0.30 and 0.02% of mass loss, respectively. Likewise, the temperatures for a mass loss at 5% for PLA and poly(S-*co*-MMA) were of 321.7 and 310.4 °C, respectively. Similarly, Cuadri et al. [74] (2018) reported a temperature of 322.4 °C for a mass loss of 5% for semi-crystalline PLA. Concerning poly(S-*co*-MMA), Zubair et al. (2017) reported a temperature of 367 °C for 5% of mass loss [75]. Regarding PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>50</sub>, PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub>, and PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub>, respectively.

#### 3.3.3. Filament Extrusion and 3D Printing

The aim of blending poly(S-*co*-MMA) with amorphous PLA was to evaluate the material under processing conditions for filament production and additive manufacture (see Figure 7). Additionally, the methodology was developed specifically for the amorphous PLA, obtaining blends with improved properties. In general, these blends present similar *E* to the poly(S-*co*-MMA); however, a decrease in the elongation at break and tensile strength were observed. However, the best polymer blend was  $PLA_{90}$ /poly(S-*co*-MMA)<sub>10</sub> concerning the *E*.

Moreover, the three filaments of  $PLA_x/poly(S-co-MMA)_y$  blends were produced via extrusion. The extruder at the prototype level was designed with two heating zones, as follows: The first zone was a pre-heating of the feed polymer blend until 150 °C, and the second had a thermal resistance in the extrusion die at 195 °C to avoid thermal degradation of the blends. The screw speed was established between 20–40 rpm as a limit for obtaining 1.75 mm filament diameter, according to the experimental values reported by Mirón et al. [8]. The filament diameter was 1.75+/-0.03 mm of standard deviation.

The PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> blend was selected to show the 3D printing process in the present research. A uniform 1.75 mm diameter was reached; this size was reported by other authors [24,76]. Nevertheless, another 1.6 mm diameter was reported for PLA-hydroxyapatite filaments [21]. The printing temperature is typically set between 180–240 °C for blends and composites having PLA as the matrix. For example, in a few investigations, 210 °C were used when printing PLA [21,77], but also, a 190 °C lower temperature was set in another analysis [76].



**Figure 7.** Scheme of the filament extrusion and 3D printing process. (**a**) Screw, barrel, and housing manufacture. (**b**) 3D printing.

The proper filament was charged to a CTC 3D printer. Parameters were set (Table 2), such as temperature and feed rate printing, a cube 1 cm × 1 cm × 1 cm for probes. The temperature variable was analyzed from 195 to 210 °C, where at 210 °C, the 3D printing piece presented melted layers with a 35 mm/s feed rate. The behavior at 200 °C was improved in the printing piece. Finally, an optimal piece was obtained at 195 °C, and at a 40 mm/s feed rate. A small 2 cm cube was used as a model (see Figure 8d). In addition, the parts manufactured for mechanical analysis through compression molding, polymeric filament via extrusion, and 3D printing by means of FDM do not undergo changes color whenever compared. Therefore, although there is slight thermal degradation in the blends, the parts do not have yellowing in the final product.



**Figure 8.** Filament extrusion and its 3D printing of PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends. (**a**) Filament extrusion level prototype. (**b**) Scheme of filament extrusion. (**c**) 3D-printing. (**d**) Some parts manufactured through compression molding (probes), filament extrusion, and 3D printing, comparing their color.

## 4. Conclusions

The filament extrusion was obtained through a prototype using conditions resulting from thermal and rheological characterization. The thermal stability of blends at 195 °C established the final design of the prototype, placing the main heating source closer to the die. This modification also allowed filaments to be extruded without apparent changes in color at different process conditions. The filament diameter was 1.75+/-0.1 mm, according to the print head.

The 3D printing (FDM) conditions were based on the PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> blend, as well as being confirmed with the other mixtures. The temperature and feed rate can directly influence 3D printing because it is a thermoplastic polymer. For example, at a high temperature and feed rate, the final product may have a deformation and a color change (thermal degradation). Furthermore, these blends were printed at temperatures from 210 to 195 °C, finding better conditions at 195 °C. Concerning feed rate was set at 40 mm/s.

The amorphous PLA degradation during the mixing process with poly(S-*co*-MMA) produces polymer chains with lower molecular weight than neat PLA, improving compatibility between the poly(S-*co*-MMA) and amorphous PLA. Compatibility was verified in mechanical properties because Young's modulus was improved for the PLA<sub>50</sub>/poly(S-*co*-MMA)<sub>50</sub>, PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub>, and PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> blends. The PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> blend showed the highest value for tensile strength and elongation at break (%) due to a more significant degraded modified polymer generation. On the other hand, the complex viscosity of the blends was improved when compared with neat PLA. However, the complex viscosity of the PLA<sub>90</sub>/poly(S-*co*-MMA)<sub>10</sub> blend showed a broad plateau lower than PLA. Furthermore, the PLA<sub>75</sub>/poly(S-*co*-MMA)<sub>25</sub> blend showed a displacement to the left, almost reaching the neat poly(S-*co*-MMA) crossing point. All PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends had two glass transition temperatures closer to the neat polymer and copolymer, suggesting compatibility in the system. The thermal property of PLA<sub>x</sub>/poly(S-*co*-MMA)<sub>y</sub> blends showed a lower first decomposition temperature when compared with the PLA and poly(S-*co*-MMA).

Finally, mixing amorphous PLA with poly(S-co-MMA) improves processing for the filament extrusion and 3D printing, Young's modulus due to compatibility, and the complex viscosity. In addition, 3D printing of manufactured parts does not produce yellowing, although there is a slight thermal degradation.

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