

PREPARATION AND THERMAL PROPERTIES OF THERMOPLASTIC COMPOSITES FILLED WITH SPARTIUM JUNCEUM L. FIBRES

Emi GOVORČIN BAJSIĆ, Mario MEHEŠ, Ljerka KRATOFIL KREHULA, Ana PERŠIĆ,
Veljko FILIPAN, Igor SUTLOVIĆ

University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia, EU,
egovor@fkit.unizg.hr

<https://doi.org/10.37904/nanocon.2023.4812>

Abstract

The increasing environmental awareness, depletion of non-renewable petroleum resource and growing demand on sustainable product development, plant fibres are actually assigned to more technical applications through the development of polymer/ natural fibre composites. Indeed, owing to their important advantages, such as low density, renewability and biodegradability, plant organic fibres represent a viable alternative to inorganic fillers or synthetic fibres in composite materials. *Spartium junceum L.* is a small shrub that belongs to the leguminosae family and grows in all countries around the Mediterranean Sea. In this work the effect of Spartium junceum L. (SJL) fibers content on the thermal properties of polypropylene/Spartium junceum L. (SJL) fibers (PP/SJL), polycarbonate/Spartium junceum L. (SJL) fibers (PC/SJL) and thermoplastic polyurethane/Spartium junceum L. (SJL) fibers (TPU/SJL) composites were studied. Composites were prepared by reinforcing thermoplastic polymers (PP, PC and TPU) with randomly oriented, short Spartium junceum L. fibres in Brabender mixer and hydraulic press. The neat PP, TPU and PC as well as their composites were characterized by DSC and TGA techniques. The results confirm that the Spartium junceum L fibres can be used as reinforcement to produce composites with properties suitable for automotive applications.

Keywords: Thermoplastic polymers, Spartium junceum L. (SJL), composites, thermal analysis

1. INTRODUCTION

Most plastics are not degradable, and burning them will produce a lot of toxic substances. Therefore, the environmental awareness attracted researchers to develop new composites with addition reinforcement from natural resources, such as natural fibre/natural fibre or natural fibre/nanofiller from organic sources as an alternative to synthetic fibres. Natural fibres are renewable bio-based materials source in nature and can be utilized as potential substitutes for synthetic fibres to reinforce polymer matrix. Lignocellulosic fibres have been used as reinforcing or filling materials for the past 3000 years, in association with polymeric materials. Biofibres are used in thermoplastic composites because of their low cost, sustainability, lower density, and significant biodegradability [1,2]. The low processing costs is another advantage of thermoplastic matrix composites, and also the design flexibility and easy of moulding the complex parts. The chemical composition of natural fibres greatly depends on the type and nature of fibre, these fibres are mainly made of cellulose, hemicelluloses, lignin, pectin and a small quantity of extractives [3]. Cellulose is a semicrystalline polysaccharide responsible for the fibres hydrophilic nature whereas hemicellulose is an amorphous polysaccharide of lower molecular weight when compared to cellulose. Lignin is a macromolecule present in many lignocellulosic materials. Fibre variability, crystallinity, strength, dimensions, defects, and structure are the important factors governing the properties of different natural fibres. The most important matters in the development of natural fibre reinforced composites are (i) surface adhesion characteristics of the fibres, (ii) thermal stability of the fibres, and (iii) dispersion of the fibres in the case of thermoplastic composites. Natural fibres have different origins such as wood, pulp, cotton, bark, nut shells, bagasse, corncobs, bamboo, cereal straw, and vegetable (e.g., flax, jute,

hemp, sisal, ramie, flax, kenaf, abaca pine cone and *Spartium Junceum*). The cost of synthetic fibers keeps increasing, while the natural fibres are inexpensive and do not cause allergic reactions in the human body. *Spartium junceum L.* (SJL) is a shrub-like plant from the family of legumes and the only species in the genus *Spartium*. *Spartium junceum L.* grows 1-1.5m tall and the only old examples grow into smaller trees of 4-5m tall and 15-20 cm thick and produces intensively yellow flowers between May and July. Its fibers have been used as reinforcement for several polymer matrices. This study demonstrates the influence of the SJL fibres content on the thermal properties of polypropylene/*Spartium junceum L.* fibres (PP/SJL), polycarbonate/*Spartium junceum L.* fibres (PC/SJL) and thermoplastic polyurethane/*Spartium junceum L.* fibres (TPU/SJL) composites.

2. EXPERIMENTAL

2.1 Materials

Polypropylene (PP) Daplen EG107HP-9590, MFI 22 g/10min at 230°C, $\rho = 0.9 \text{ g cm}^{-3}$ supplied from the Borealis, Austria, polycarbonate (PC) Makrolon 2805 MFI 10 g/10min at 230°C, and thermoplastic polyurethane (TPU), Desmopan 588E, $\rho = 1.2 \text{ g/cm}^3$, supplied from the Bayer, Germany served as polymer matrix for the preparation of the composites. *Spartium junceum L.* fibres were obtained from the *Spartium junceum L.* plant which was harvested in the area of town Šibenik, Croatia. The fibres were obtained by microwave maceration process in order to increase the effectiveness of composite material production (lower use of water and energy).

2.2 Preparation of composites

Composites were prepared by reinforcing thermoplastic polymers (PP, PC and TPU) with randomly oriented, short *Spartium junceum L.* fibres in Brabender mixer and hydraulic press. Preparation of composites is shown in **Figure 1**.

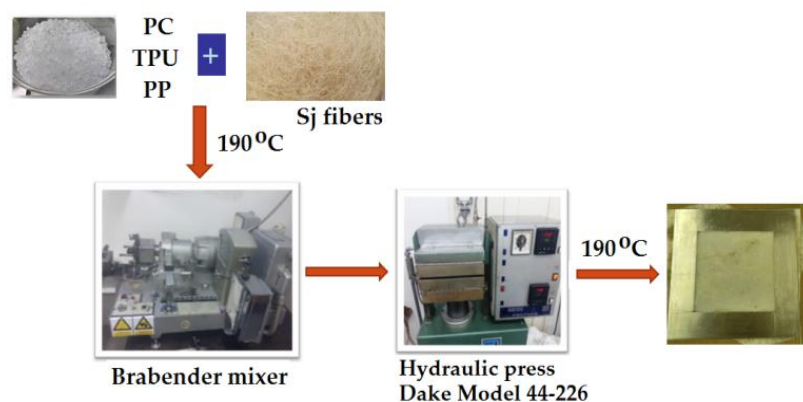


Figure 1 Composite preparation

2.3 Characterization

Differential scanning calorimetry (DSC) analysis was performed in a Mettler DSC 822e differential scanning calorimeter (Mettler Toledo, Greifensee, Switzerland) with purged dry nitrogen gas flow ($40 \text{ mL} \cdot \text{min}^{-1}$), previously calibrated with indium. The samples (each ca. 10 mg) were heated to 190°C and maintained at this temperature for 5 min. Then they were cooled from 190°C to -100°C at a rate of 10°C/min (cooling cycle), held for 5 min at this temperature and then heated again to 190°C at a rate of 10°C/min (heating cycle). All experiments were performed under nitrogen atmosphere.

To evaluate the thermal stability properties of the composites, **thermogravimetric analysis (TGA)** was carried out on a TA Q500 system analyzer (TA Instruments, New Castle, DE, USA). Samples of approximately $10 \pm 0.5 \text{ mg}$ was heated from 25°C to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere (60 ml/min). The initial temperature of 5% loss of weight ($T_{5\%}$) and temperature of maximum weight loss (T_{max}) were measured.

3. RESULTS AND DISCUSSION

3.1 PP/SJL composites

Polymer composites with a PP matrix and SJL fibres were studied in DSC experiments. The DSC curves related, to the 2nd heating / cooling cycle of neat PP and PP/ SJL composites are shown in **Figure 2**. The melting (T_m), and crystallization (T_c) temperatures and the enthalpy of melting (ΔH_m) were determined from the DSC curves. The degree of crystallinity (χ_c) of the PP was obtained by using the relationship:

$$\chi_c = \left(\frac{\Delta H_m^0}{\Delta H_m^{100} \times \left(1 - \frac{\%w_{SJL}}{100}\right)} \right) \times 100 \quad (1)$$

where for 100% crystalline PP the heat of fusion $\Delta H_m^{100}=165 \text{ Jg}^{-1}$ [4] was taken, and w is the content of SJL in the composite.

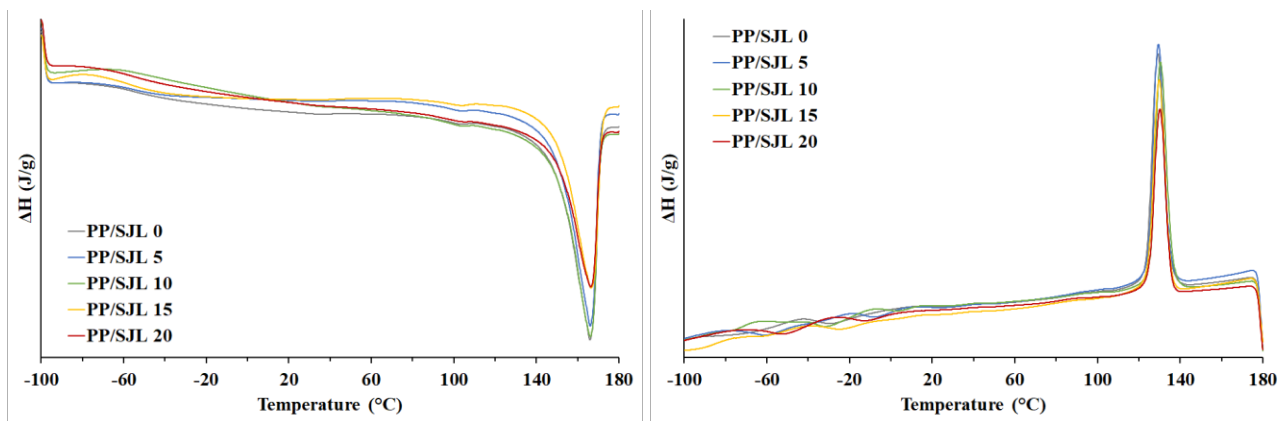


Figure 2 DSC curves of 2nd heating/cooling cycle of neat PP and PP/SJL composites

The DSC curves of 2nd heating scan of PP and PP/SJL composites reveal one melting peak which temperature for the neat PP taken at the maximum is 166 °C (**Figure 2**, **Table 1**), which is a typical characteristic of a α -crystallization form in the PP matrix. [5]. The PP cooling curve exhibit an exothermic peak presenting a maximum at 130 °C (**Table 1**). It is clear that the incorporation of SJL fibres in the PP matrix has no significant impact on the value (**Table 1**) nor on the shape (**Figure 2**) of the melting or crystallization peaks. From the results in the **Table 1**, it is observed that the degree of the crystallinity χ_c was lower than the PP matrix with increasing SJL fibres content. The decrease of χ_c indicated that the SJL fibres play a significant role in heterogeneous nucleating of PP. This can be explained by the nucleating ability of the cellulosic filler, which alter the kinetics of crystallization of the PP matrix [6,7]. TGA and DTG curves of of the neat PP and the different PP/SJL composites are presented in **Figure 3**. The neat PP has a decomposition process in a single step and begins at 438.5 °C (**Table 1**) due to the rupture of the C-C bonds of the main chain [8,9]. The composites clearly show two step decomposition. The first step is the decomposition of the SJL fibres between 235 and 400 °C (decomposition of the cellulose), and the second step corresponds to that of the PP matrix (between 400 and 507 °C). Adding SJL fibres reduces the thermal stability of PP. However the thermal stability of the PP/SJL composites increased as the SJL fibres content increased (as is reported in **Table 1**). In general, increasing amount of fibres in polymer matrix results in decreasing of thermal stability of polymer composites as the thermal stability of the fibres being lower than that of the polymer, the degradation of the fibre can accelerate the decomposition of the polymer [8].

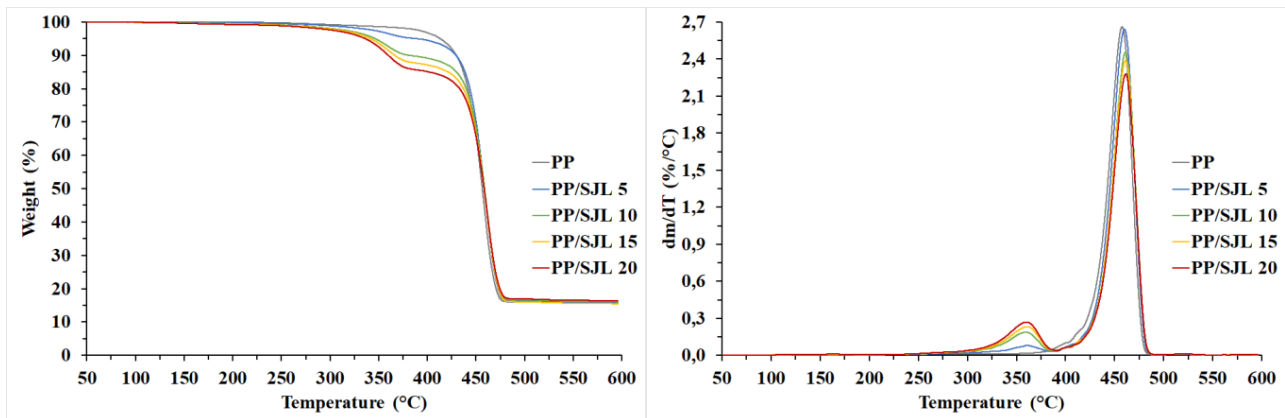


Figure 3 TG and DTG curves of neat PP and PP/SJL composites

Table 1 DSC and TGA results of the neat PP and PP/SJL composites

Sample	T_m (°C)	T_c (°C)	ΔH_m (Jg ⁻¹)	χ_c (%)	$T_{5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	R/600°C (%)
PP	166	130	57.22	34.7	438.5	-	457.7	15.7
PP/SJL 95/5	166	130	53.66	32.5	318.6	361.3	459.9	15.9
PP/SJL 90/10	166	131	52.50	31.8	323.7	360.6	461.0	16.1
PP/SJL 85/15	166	131	47.37	28.7	327.6	360.9	461.3	15.5
PP/SJL 80/20	166	131	41.40	25.1	323.6	360.3	461.2	16.4

3.2 PC/SJL composites

The DSC curves of 2nd heating / cooling cycles for the neat PC and PC/SJL composites are presented in **Figure 4**. The thermal characteristics including: glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c) obtained from DSC curves are summarised in **Table 2**. The T_g of the neat PC was 146 °C, as the content of SJL fibres was increases the T_g decrease up to 20 wt. % of SJL. The most important factor affecting T_g is the flexibility of the molecular chain. The higher the flexibility of the main chain, the lower the T_g ; the higher the rigidity of the main chain, the higher the T_g . That means as SJL content increased, the mobility of polymer chains increased, and T_g decreased subsequently.

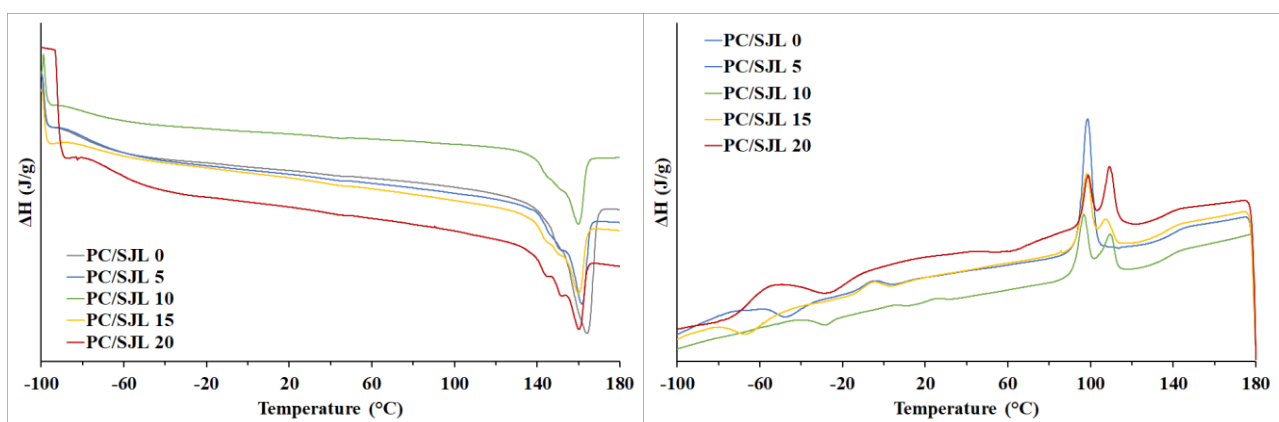


Figure 4 DSC curves of 2nd heating/cooling cycle of neat PC and PC/SJL composites

After 2nd heating cycle the melting peak at about 164 °C was observed for the neat PC [10]. This melting peak can be attributed to the melting of PC. In the PC/SJL composites T_m decreased and the values are the same

in all composites. Also, two exothermic peaks were observed for the PC/SJL composites (**Figure 4**). This result suggests that SJL fibres induced PC crystallization. The reason may be that during the cooling process, SJL fibres played the role of nucleating agents, promoting the formation of crystal nuclei of composites. According to that in the DSC measurements, the crystal grains had time to grow into crystal planes, thereby forming a crystalline structure.

From TGA curves of neat PC and PC/SJL composites, as seen in **Figure 5**, one decomposition peak observed at around 440-520 °C for the neat PC.

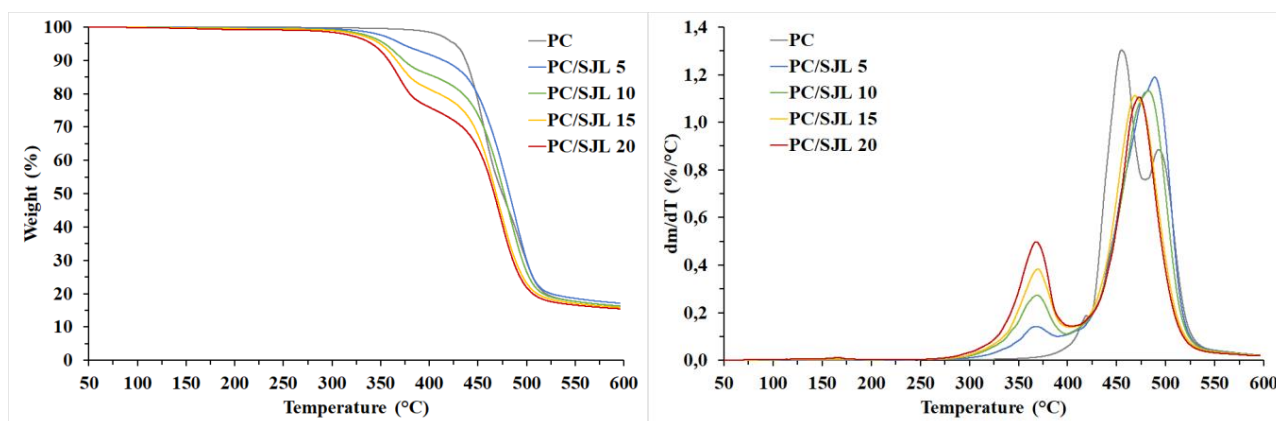


Figure 5 TG and DTG curves of neat PC and PC/SJL composites

Based on the DTG curves three distinct decomposition steps can be seen for the PC/SJL composites (**Figure 5**). The first and the second step is the decomposition of the SJL fibres and the third step corresponds to that of the PC matrix. The first step below 200°C °C is attributed to water loss in the form of absorbed moisture in the fibres. The second step (the temperature range of the decomposition is between 200°C and 400°C) was related to the thermal decomposition of hemicellulose, cellulose and lignin present in the fibres. The temperature at which 5 wt % is degraded ($T_{5\%}$) is given in **Table 2**. The $T_{5\%}$ date of the PC/SJL composites showed that the thermal stability of the PC/SJL composites was lower than the thermal stability of neat PC. This result can be explained by the fact that the addition of SJL fibres decreases the thermal stability of the composites as the thermal stability of the SJL fibres being lower than that of the PC, consequently the degradation of the SJL fibres can accelerate the decomposition of PC. The temperature at maximum PC degradation decreased after introduction of SJL fibres.

Table 2 DSC and TGA results of the neat PC and PC/SJL composites

Sample	T_g (°C)	T_m (°C)	T_{c1} (°C)	T_{c2} (°C)	$T_{5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	R/600°C (%)
PC	146	164	118	100	426.2	-	493.8	16.3
PC/SJL 95/5	142	161	-	99	371.5	369.5	460.0	17.2
PC/SJL 90/10	141	160	110	97	354.3	368.9	489.6	16.4
PC/SJL 85/15	139	160	108	98	349.4	370.1	483.7	16.0
PC/SJL 80/20	141	160	112	109	342.9	368.8	468.7	15.6

3.3 TPU/SJL composites

DSC curves of neat TPU and TPU/SJL composites are shown in **Figure 6**, characteristic thermal parameters are listed in **Table 3**. In the DSC curve of neat TPU after 2nd heating cycle a T_g of soft segment obtained at -32 °C. It was observed that in the TPU/SJL composites the T_g decreased for 1°C with SJL fibre content. It is

suggested that with increasing fibre content, the polymer chains have higher mobility. The DSC curves of neat TPU and TPU/SJL composites show the existence of two different melting peaks. The melting peaks appear at 65 and 124 °C, the T_m at 124 °C related to the long chain hard segments, while the lower T_m (65 °C) correspond to the short chains and partial disordered hard segments. With increasing SJL fibre content the position of the peaks no change. During the 2nd cooling cycle (**Figure 6**), the DSC curve of neat TPU show a peaks at 55 and 108 °C attributed to its crystallization temperature ($T_{c1,2}$). The crystallization peaks temperature (T_{c1} and T_{c2}) slightly increased with increasing SJL fibres content (**Table 3**). This behavior shows that TPU/SJL composites started to crystallize sooner than the neat TPU, which is an indication that the presence of SJL fibres can act as nucleating agent on the crystallization of TPU.

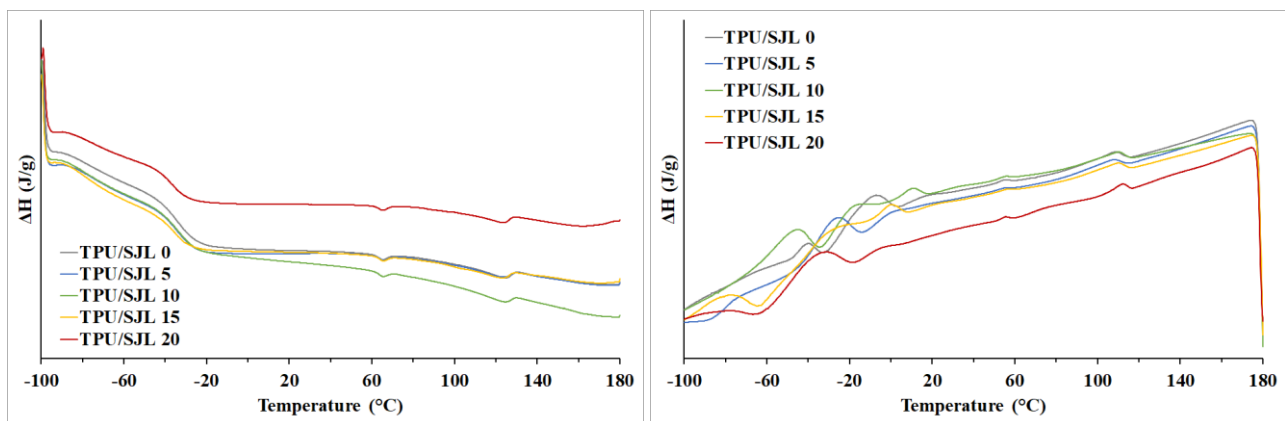


Figure 6 DSC curves of 2nd heating/cooling cycle of neat TPU and TPU/SJL composites

The thermal stability of TPUs is dependent to a great extent on the chemical structure of their backbone chains that consist of various hard segments and soft segments. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves are presented in **Figure 7**. The TG curve of neat TPU has two distinct regions of weight loss, implying at least two steps of degradation occur in TPU. Segmented polyurethane (PU) copolymers consist of hard and soft segments. The soft segment built with polyols provides flexibility, while rigid segment built with isocyanate and chain extender contributes toward mechanical and physical properties. The hard segments are generally urethane groups reacted with aromatic diisocyanate and the chain extenders are diols with low molecular weight or urea groups that reacted with aromatic diisocyanate and the chain extender is diamine with low molecular weight. The degradation of the first step (step I) and the second step (step II) was around 250-350 °C and 350-430 °C, respectively, reflected in two peaks in the DTG curve in **Figure 7** at 332.0 °C and 389.9 °C (**Table 3**).

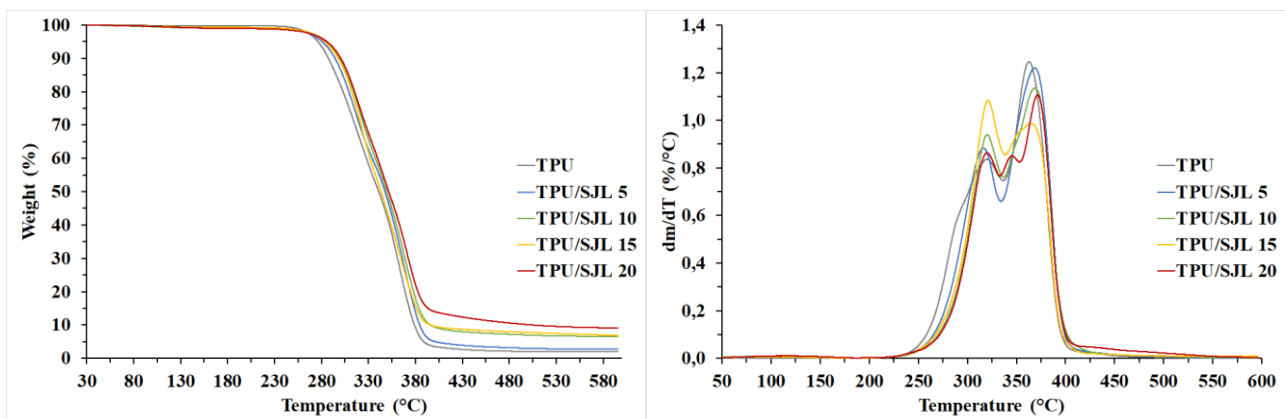


Figure 7 TG and DTG curves of neat TPU and TPU/SJL composites

The initial degradation in step I is primarily the decomposition of the hard segment, which involves the dissociation of urethane to the original isocyanate which then to form a primary amine, alkene and carbon dioxide. The consequent step II proceeds by the depolycondensation and polyol degradation mechanisms [11,12]. It can be stated that thermal decomposition of prepared TPU/SJL composites occurs in two steps, where first one is related to the degradation of SJL fibres and hard segment of TPU, while the second one is connected to the thermal decomposition of TPU. Based on the TGA results the thermal stability of the TPU/SJL composites increased as the SJL fibers content increased up to 20 wt.% SJL.

Table 3 DSC and TGA results of the neat TPU and TPU/SJL composites

Sample	T _g (°C)	T _{m1} (°C)	T _{m2} (°C)	T _{c1} (°C)	T _{c2} (°C)	T _{5%} (°C)	T _{max1} (°C)	T _{max2} (°C)	R/600°C (%)
TPU	-32	65	124	55	108	297.2	332.0	389.9	1.9
TPU/SJL 95/5	-33	65	122	55	109	300.1	335.5	381.4	3.0
TPU/SJL 90/10	-34	65	123	56	110	303.8	343.3	384.3	5.0
TPU/SJL 85/15	-35	65	122	58	111	309.0	345.3	394.7	6.8
TPU/SJL 80/20	-37	65	123	61	112	307.1	346.4	397.2	9.0

4. CONCLUSION

DSC analysis measurements illustrates that the addition of SJL no effect on T_m and T_c of PP/SJL composites while the values of the T_m slightly increased in TPU/SJL composites. The T_g in PC/SJL composites shifted to lower temperatures compared to the neat PC due to the amorphous structure of lignin. Based on the TGA results the thermal stability of the PP/SJL and TPU/SJL composites increased as the SJL fibres content increased. TGA results showed that the thermal stability of PC/SJL composites decreased.

ACKNOWLEDGEMENTS

The research in this work was supported by grant no.121142 University of Zagreb, Croatia.

REFERENCES

- [1] VAN DE VELDE, K.; KIEKENS, P. Biopolymers: overview of several properties and consequences on their applications. *Polymer Testing*. 2002, vol. 21, pp. 433-442 .
- [2] CAULFIELD, D.F.; CLEMONS, C.; JACOBSON, R.E.; ROWELL, R.M. Wood thermoplastic composites. *Handbook of wood chemistry and wood composites*. New York: Taylor and Francis, 2012.
- [3] MOHANTY, A.K.; MISRA, M.; DRZAL, L.T. Surface modifications of natural fibres and performance of the resulting biocomposites: an overview. *Composite Interfaces*. 2001, vol. 8, pp. 313-343.
- [4] WUNDERLICH, B. *Macromolecular Physics*. New York: Academic Press, 1980.
- [5] FIORE, V.; SCALICI, T.; VALENZA, A. Characterization of a new natural fiber from Arundo Donax L. as potential reinforcement of polymer composites. *Carbohydrate Polymers*. 2014, vol. 106, pp. 77-83.
- [6] LUZ, S.M.; GONCALVES, A.R.; DEL'ARCO, A.P.; FERRAO, P.M.C. Composites from Brazilian natural fibers with polypropylene: mechanical and thermal properties. *Composite Interface*. 2008, vol. 15, no. 7-9, pp. 841-850.
- [7] XIAN, J.; HE, Z.; LI, M.; LIN, Z.; CHEN, J.; YANG, Q.; XIAO, L.; LI, W. Preparation and properties of coral/ β -polypropylene biocomposites. *Journal of Thermal Analysis and Calorimetry*. 2015, vol. 122, pp. 1005-1011.
- [8] DOAN, T.T.L.; BRODOWSKY, H.; MADER, E. Jute fibre/polypropylene composites II. Thermal, hydrothermal and dynamic mechanical behaviour. *Composite Science and Technology*. 2007, vol. 67, pp. 2707-2714.
- [9] NACHTIGALL, S.M.B.; CERVEIRA, G.S.; ROSA, S.M.L. New polymeric-coupling agent for polypropylene/wood-flour composites. *Polymer Testing*. 2007, vol. 26, pp. 619-628.

- [10] LIAO, X.; LI, G.; SUN, X.H.; HE, J.S. Effect of supercritical CO₂ and cosolvent on the crystallization and melting behavior of bisphenol-A polycarbonate. *Acta Chimica Sinica*. 2003, vol. 61, no. 10, pp.1697-1699.
- [11] LAGE, L.G.; KAWANO, Y. J. TG and DTG Study of Decomposition of Commercial PUR Cellular Materials. *Journal of Applied Polymer Science*. 2001, vol. 70, pp. 910-919.
- [12] LEE, H.K.; KO, S.W. Structure and thermal properties of polyether polyurethane urea elastomers. *Journal of Applied Polymer Science*. 1993, vol. 50, pp. 1269-1280.