Thermomechanical improvement of glycerol plasticized maize starch with high loading of cellulose, flax and talc fillers

Thermo-mechanical improvement of glycerol plasticized maize starch (TPS) with high loading of cellulose, flax and talc fillers

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Abstract

For the purpose of extending the applicability fields of thermoplastic starch (TPS), a study on their properties with high filler loadings were performed. Two different organic natural reinforcement (cellulose and flax) and a typical mineral filler (talc) were incorporated in TPS using melt blending. The resulting composites were observed on fragile fracture surfaces by Scanning Electron Microscopy to study the fillers/matrix adhesion. Magnifications revealed good TPS-fiber interfacial interaction with limited debonding. The thermo-mechanical properties by Dynamo-Mechanical Thermal Analysis (DMTA) and the correlation with the filler amount (from 10 to 50 wt.-%) were deeply investigated at 50 % of relative humidity and 23 °C. The tests evidenced a huge increase of composite storage moduli (E') of more than 200 % with respect to the neat matrix. Moreover, the resulting DMTA experimental data were interpolated with Cox-Krenchel micro-mechanical model. To this aim, the necessary measure of the filler dimensions were calculated after the extrusion process on water dissolved residues using an optical microscope. This model was able to rightly follow the experimental results also at the high filler loadings.

Keywords(5): Thermoplastic starch; bio-composites; Dynamic mechanical thermal analysis; Extrusion; natural fillers.

Introduction

Biodegradable bio sourced plastics minimise the environmental impact and increase plastics sustainability. Starch-based thermoplastic polymers are relatively cheap and are manufactured using an annually renewable source as raw material. Unfortunately, starch degrades before melting because it has an high number of intermolecular and intramolecular hydrogen bonds of hydroxyl groups. Thus it is not truly a thermoplastic polymer [1]. This problem is partially overcome by the use of plasticizers (such as water, glycerol, sorbitol, etc.). In presence of plasticizers at high temperatures (90–180 °C) and under shear, starch crystalline structure dissolves and becomes suitable for use as an injection, extrusion or blow moulding material, similarly to most conventional synthetic thermoplastic polymers. This is the so-called thermoplastic starch (TPS) [1,2]. Polyols such as: glycerol [3-6], glycol [5-6], sorbitol and sugars [7-8], amide [9-10], isosorbide [11] were usually used as plasticizers.

Unfortunately, TPS properties do not fulfil requirements for applications such as packaging, for a great moisture sensitivity and rather weak mechanical properties despite a lot of effort in the study of the fittest plasticizer agent [12-14]. To overcome these weaknesses, during the last decades, different strategies were elaborated:

- chemical starch modification has been carried out, since the first half of the twentieth century [15] till nowadays [16-17], but it generally implies the use of solvents and process not environmental friendly.
- the association of TPS with other biodegradable compounds to obtain compostable multiphase materials of starch/polymer blends [18-24], but the mechanical properties of

blends remain far below the ones of the main polymer matrix and the advantage of low cost is partially lost;

- addition of reinforcement fillers to TPS matrix to make a composite with different types of fibers or microfibrils [25-31] or silicates [32-36].

In the last few years a lot of effort have been dedicated to study filler addition, with a corresponding increase in research papers. Some examples of the bio-based reinforcements used in these composites are cellulose and nano cellulose [37,38]. However, most nanocomposites were obtained by the casting method limiting a possible industrial exploitation [39]. On the other hand, when conventional melt processing methods were used, only a low amount of fillers were added, reaching in some cases great improvement in the mechanical properties [40]. Generally speaking, results show that incorporation of bio-based nano or micro reinforcements in TPS improves mechanical properties [41] and the improvements are proportional to the filler loading.

Furthermore, also the incorporation in the TPS matrix of a common mineral filler such as talc in low amount reached interesting final properties [42] opening the way for further investigations.

The aim of the present research is to investigate benefits and drawbacks of the addition of two selected natural filler, flax and cellulose, on TPS. These effects were also compared with a classical mineral filler (talc). In doing so, different filler loadings were tested till the maximum percentage that could be introduced in the extrusion process was reached obtaining, anyway, a processable composite. Such high filler amounts were not much investigated however could be a good strategy to enhance the properties having more benefits than drawbacks. In addition, a micro-mechanical model (Cox-Krenchel) was applied to assess the results fitting the dynamo-mechanic experimental data. An additional parameter to the model is used to take in consideration also the temperature.

Materials and methods

Materials

The starch used was the maize starch CERESTAR RG 03408 purchased from Cargill that was mixed with glycerol as plasticizer purchased from Aldrich. Cellulose (CreaTech Alpha Cellulose Fibers from Creafill Fibers Corp.), pelletized flax fibers with polymeric binder (industrial wastes) and talc (HTP1 from Imifabi) were used as TPS fillers.

The starch was dried for 5 hours at 120 °C in a vacuum oven, reaching 4000 ppm of water content. At the same time, all the fillers were dried at 80 °C for 5 hours before blending, reaching less than 400 ppm of water content for talc and 20000 ppm for cellulose and flax. Moisture was checked for all materials using a Karl-Fischer titration.

Thermoplastic starch preparation

TPS based on glycerol (TPSG) was obtained by a co-rotating twin screw extruder LEISTRITZ ZSE 18 / 40D (Φ=18 mm L/D=40). Dried starch was mixed manually with glycerol, then directly put by a gravimetric feeder in the main hopper of the extruder placed at the beginning of the screw. During the extrusion process a temperature profile from 115 to 150 °C, a screw speed of 150 rpm and an extrusion output of 1kg/h was maintained. The ratio of the plasticizer in the dry starch was 30 wt.-%.

Thermoplastic starch-based composites preparation

The composites containing the three fillers were prepared using a co-rotating twin screw micro extruder DSM Xplore 15 ml Microcompounder. Residence time was fixed for all runs at 10 minutes. The screw speed was maintained at 100 rpm for the melt mixing and the heating temperature fixed at 160 °C. The compositions of obtained samples are listed in

Table 1. The maximum loading with a processable material were 20, 50 and 40 wt.-% for cellulose, flax and talc, respectively. For each filler higher concentrations were tested but revealed too viscous to be extruded.

Specimens preparation

The specimens for analysis were prepared by compression moulding with 5 MPa at 160 °C for 3 minutes obtaining 60x60x1 mm^3 specimens.

The fibers for optical analyses were collected from the dissolution in hot water at 80 °C and under sonication for 2 h of the filled plasticized starch. The fibers and particles were separated from the solution by centrifugation at 4000 rpm for 5 min. These residues were dispersed in distilled water and a drop of this solution was deposed on a microscope glass, dried and finally observed with optical microscope.

Analyses

The chemical structure of flax and cellulose was evaluated by Attenuated Total Reflectance (ATR) coupled with infrared spectroscopy (FTIR). ATR spectra were recorded at room temperature in the range 4,000–400 cm^{-1} (16 scans and 4 cm^{-1} resolution), using a Perkin-Elmer Frontier FT-IR/FIR spectrophotometer, equipped with a diamond crystal.

Scanning Electron Microscope (SEM) magnifications were taken with LEO 1400 VP Series on the cross section surface of samples obtained by a fragile fracture in liquid nitrogen. The samples were metallized with gold and pinned on conductive holders before observations.

Dynamic-mechanical thermal experiments (DMTA) were performed using a DMA TA Q800 with tension film clamp. The analyses were made on 6 mm width, 26 mm height and 1 mm thick samples prepared by compression moulding. The temperature range set was from 30 °C

to 120 ºC with a heating rate of 3 ºC/min and a frequency of 1 Hz in strain-controlled mode with 15 µm of amplitude. All the sample were conditioned at 23 °C and 50 % RH, in a climate-controlled chamber Binder BFK240.

Optical Microscope images were taken with Nikon ECLIPSE LV100D. For each sample several photographs were taken in different areas at two magnifications (10x and 50x). For each photograph was evaluated the length and the diameter of the fillers through the program ImageJ. The program also calculated the mean, standard deviation, minimum and maximum value of the two parameters.

Micro-mechanic model calculations

To fit and estimate the effect of the filler type and content in the prepared composites, Cox-Krenchel model [43] was used.

From Cox studies, Young's modulus of a short fibre reinforced composite is determined by a modified Voigt model (**Equation 1**).

$$E_c = \eta_\vartheta \eta_f V_f E_f + \left(1 - V_f\right) E_m$$

Equation 1.

where E_f, E_m, and V_f are the Young's modulus of the fibre, the matrix and the volume fraction of the fibre in the composite, respectively and η_f, η_θ are efficient factors of fibre length and orientation.

Fiber volumetric fraction (V_f) is determined from the fiber weight fractions (W_f) calculated using the density (ρ) of each component obtained from the literature, or data sheets (reported in **Table 2**) following **Equation 2**. The density of the matrix was calculated with the rule of mixtures with the density of the single component in the nominal ratio (30 wt.-% of glycerol).

$$V_f = \left(1 + \frac{\rho_f}{\rho_m}\frac{1 - W_f}{W_f}\right)^{-1}$$

Equation 2.

Going into details, the efficient factor for the fiber length η_f is given [44-45] by the **Equation 3**.

$$\eta_f = 1 - \frac{(\tanh\frac{1}{2}\beta L)}{\frac{1}{2}\beta L} \; ; \; \beta = \left(\frac{2G_m}{E_f r_f^2 ln(R/r_f)}\right)^{\frac{1}{2}}$$

Equation 3.

where r_f and R are the radius of the fibre and the interval among fibres, respectively, L is the length of the fibers and G_m is the shear modulus of the matrix. Thus, from Equation 3 the Young's modulus of the composite decreases with decreasing the fibre length L.

To effectively use the efficient factor some hypotheses and simplifications are introduced. Firstly, if the distribution of the fibres is homogeneous, in an ideal packing square composite R is given by **Equation 4**.

$$R = \frac{r_f}{2}\sqrt{\frac{\pi}{V_f}}$$

Equation 4.

Then, the shear modulus G_m, assuming that the composite is isotropic, is given by **Equation 5**.

$$G_m = \frac{E_m}{2(1+\nu_m)}$$

Equation 5.

where ν_m is the Poisson's ratio of the matrix that is assumed 0.3.

The second efficiency factor η_θ in the modified Voigt equation, due to the fiber orientation, was introduced by Krenchel [46] and was assumed 0.27 [47] (0.2 for random 3D and 0.375 for random 2D orientation).

Result and Discussion

Chemical characterization of flax fiber and cellulose

The chemical composition of the natural fibers was investigated with FT-IR apparatus and the spectra were reported in **Figure 1**.

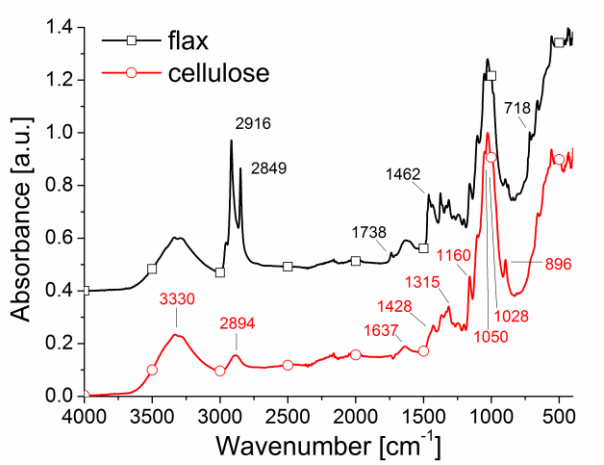


Figure 1. ATR spectra of flax and cellulose

The spectrum of cellulose has the expected peaks [38,41] ν(OH) at 3,330, ν(CH_2) at 2894, δ(OH) at 1637, δ(CH_2) at 1428, δ(CH) at 1367 and 1315, pyranose ring skeletal vibrations involving C–O and C–C groups at 1160, 1050, 1028 and 896 were detectable and evidenced (**Figure 1**). However, also weak peaks at 1742 cm^{-1} and 1246 cm^{-1} due to hemicelluloses were visible [38,41].

Typically, natural fibers such as flax have the same characteristic peaks of cellulose with the addition of others that could be attributed to hemicellulose, lignin, protein, sugars, wax or oils. In the case flax fibers used, the ATR analysis revealed peaks principally due to the cellulose with the presence of polymeric binder. The peaks at 2953, 2916 and 2849 cm^{-1} in combination with peaks at 1462, 1375 and 718 cm^{-1}, assigned to CH_2 and CH_3 and the peak at 1738 due to stretching CO and stretching C-O-C of esters and 1245 cm^{-1} indicate that the

binder is ethylene vinyl acetate. In addition, the complete absence of the peak around 1520 cm^{-1} in the spectrum of flax confirm the lack of lignin.

Morphological characterization of TPS composites

SEM analysis was used to investigate the morphology of TPS composites. For sake of brevity only one loading of each filler-matrix samples are reported. Secondary electrons images obtained from cross section of TPSG (**Figure 2a**) show the formation of a homogeneous structure.

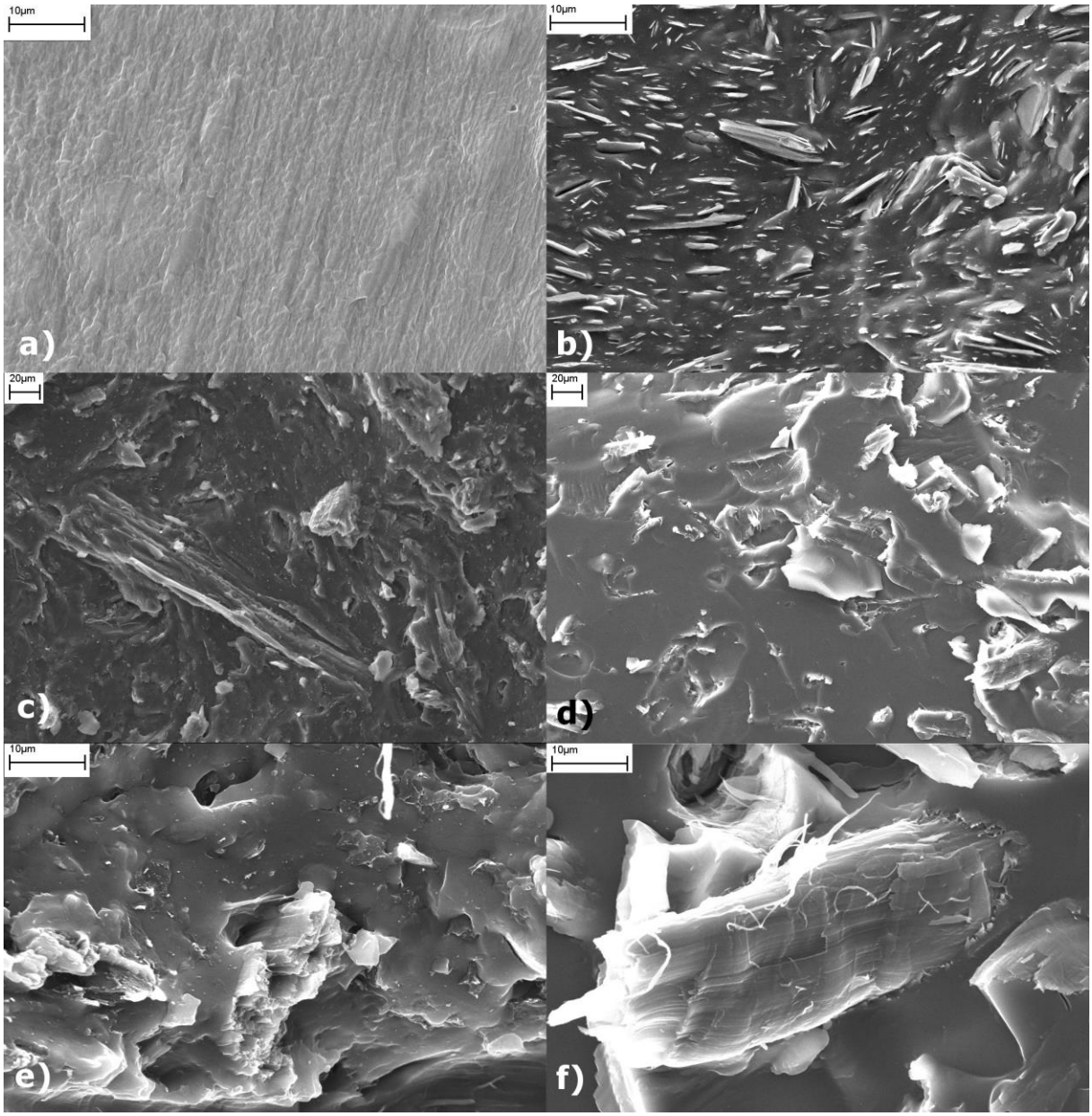


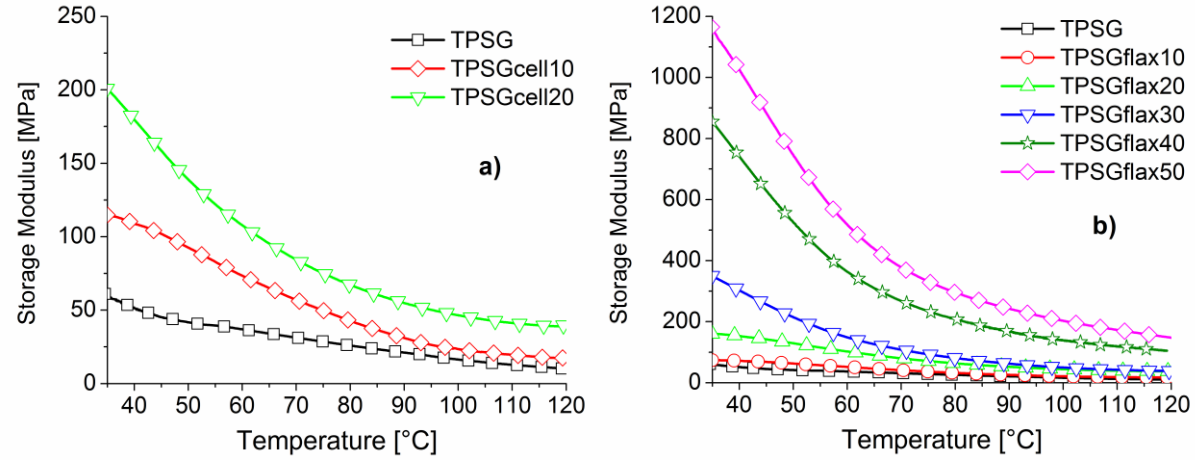
Figure 2. Cross section SEM analysis of: TPSG (a), TPSGtalc30 (b), TPSGflax30 (c) and (e), TPSGcell20 (d) and (f).

As far as TPSG composite cross sections are concerned, visible gaps cannot be found between the fibers and matrix, (**Figure 2b,c,d,e,f**) suggesting good interfacial adhesion. However, fibers partially emerged from the matrix breaking surface, indicating some slippage. This phenomenon seems to be more evident with cellulose. In **Figure 2f** it is possible to clearly distinguish a single fiber exit from the fracture surface. In the case of talc composites, even if

in some cases it was possible to observe some little spaces near lamellas or some lamellas lack in **Figure 2b**, substantially, the adhesion seemed quite good. The micrograph of this last composite also shows the particle preferential orientation in the matrix during thermo-compression processing. Indeed, a preferential horizontal orientation can be observed in the **Figure 2b**.

Resuming, plasticized starch appears to be compatible matrix for these natural fillers. The reasons are due to the remarkable intrinsic adhesion of the fibers–matrix interface caused by the chemical similarity of such thermoplastic and the plant fibres filler. For what concern the talc, good results were already registered by Castillo et al. [42] in a previous work with nanoparticles. They report a good adhesion of talc–TPS interfaces indicating a good compatibility between particles and matrix, even for an unmodified surface mineral. This findings are confirmed also with micrometric talc.

DMTA analysis of TPS composites



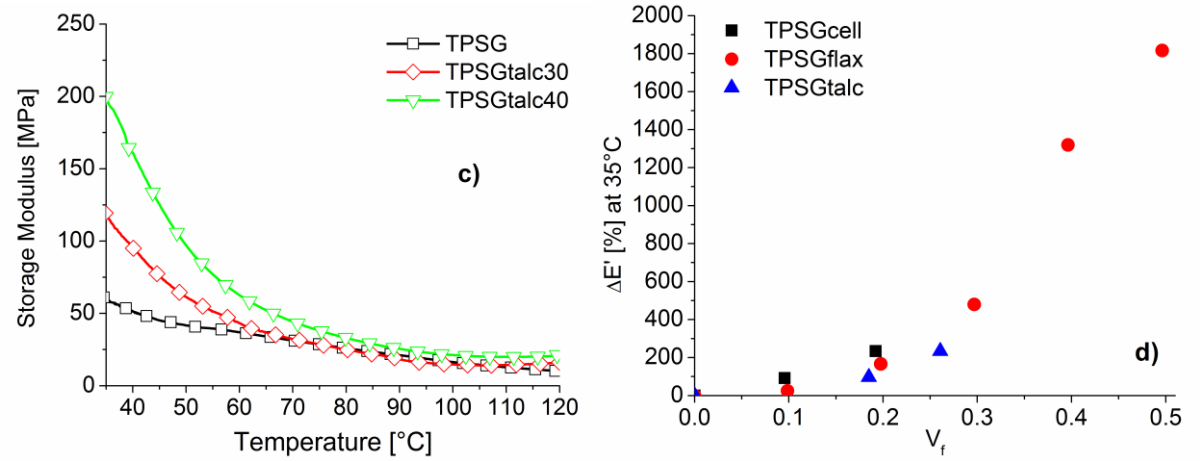


Figure 3. Storage modulus as a function of temperature of thermoplastic starch and composites after 15 days: TPSG-cellulose composites (a), TPSG-flax composites (b), TPSG-talc composites (c) and storage modulus increase of TPSG-based composites at 35 °C (d).

The mechanical properties of samples were evaluated using DMTA analysis after 15 days of conditioning at 23 °C and 50 % RH. The curves divided for each filler type are reported in **Figure 3a, b, c**. Generally speaking, independently of the filler type, a substantial increase of the storage modulus E' was observed for the composites under study. This increase shifts the curves to higher modulus values for all the temperature range.

In order to deeply understand and compare the behavior of different fillers, the data obtained at three temperatures (namely 35,55 and 85 °C) were reported in **Table 3** for all the formulations and the percent increase (ΔE') were calculated with respect to the storage modulus of the neat matrix. Furthermore, a resuming plot of this percent increase at 35°C was presented in **Figure 3d**. As is possible to read from the **Table 3**, the reference storage modulus (E') of neat TPSG was 60, 39 and 23 MPa at 35, 55 and 85 °C, respectively. These values are very low and unsuitable for plastic practical use, confirming that one of the main drawbacks of TPS material are the poor mechanical properties. A good solution to this problem seems to be the addition of cellulose in TPSG matrix that results in a storage modulus increase of about 100 % with 10 wt.-% and 200 % with 20 wt.-%. The same

behaviour is achieved adding flax in a greater amount: indeed 20 wt.-% of flax has lower effect than 20 wt.-% of cellulose. Nevertheless, in the case of flax, is possible to load the composite with a greater amount of filler, thus better performances could be achieved. Indeed, the high filler content of flax gave a progressive dramatic increase of storage modulus. This increase is probably also due to the fiber-fiber interactions not negligible at so high loading.

The addition of 50 wt.-% of flax leads to modulus increase of about 1800 % and 1000 % at 35 °C and 85 °C, respectively. Better results (increase of modulus 15 times with 30 wt.-%) were obtained by Cao et al. [37] with the use of nanocrystals that are extremely smaller than fibers but need chemical treatments to extract from the flax. Also Martins et al. [40] found the Young Modulus 30 and 17 times higher than that of the unfilled TPS at a fiber content of 5wt.-% of bacterial and vegetal cellulose, respectively. Newly, the filler is highly efficient but the composition adopted by authors start from a TPS with a very low modulus for the high plasticizer content. Thus also the final modulus is still too low (20 MPa) for a lot of practical applications.

For what concern talc, it is important to notice that talc density value (**Table 2**) is higher than all other component, thus weight percentage and volume percentage differ substantially. To correctly correlate the results, in this case, volume fraction (V_f data in **Table 3** and **Figure 3d**) is used for discussion. A lower storage modulus E' improvement than those obtained with cellulose or flax is reached with talc at similar volume fraction at 35 °C (**Figure 3d**). This behaviour is confirmed by temperature, indeed, talc is revealed quite ineffective to increase the modulus at 85 °C (**Table 3**).

One of the key factor for the differences highlighted during the DMTA for talc and natural fibers could be the dimension of filler inside the matrix. For this reason an evaluation of the filler dimension is hereafter presented.

Fillers analysis of extruded TPS composites

The adhesion of fibers was estimated empirically from SEM photographs and the modulus of the composites measured by DMTA but to correlate reinforcement with presence of fibers, it is important to know the length and diameter of the fillers, as described by the Cox-Krenkel model. The work presented in this paragraph makes possible to evaluate if there is a correspondence between the storage modulus of materials and the length / section of the fibers inserted. The optic microscope images and the calculated distribution of size of fibers are reported in **Figure 4**, while in **Figure 5** are presented for the talc. Furthermore, **Table 4** report the main data calculated by the ImageJ program as minimum (Min), maximum (Max) and mean (Mean) values of the measured fiber as well as the standard deviation (SD). As is possible to deduce from the SD values, the distribution of size of cellulose and flax fibers are very wide. Indeed, cellulose fibers longer than 600 μm are visible, 20 times larger than the finer one that measure below 15 μm (**Figure 4a**). As far as flax fibers are concerned, the size varies between 13-700 μm with an average at around 80 μm. (**Figure 4b**). Thus these two fillers are very similar in the distribution of fiber length after the extrusion process. It seems that flax fiber are longer with a diameter lower than cellulose fiber.

On the other hand, talc has a much narrower distribution with particles between 2.5 and 20 μm and an average platelet size of around 7.5 μm (**Figure 5, Table 4**). These results are in agreement with the distribution reported by the producer in the technical specifications.

In this latter case the size is one order of magnitude less than the case of fibers but, obviously, is extended in two dimensions with an irregular polygonal shape and the thickness sub micrometric.

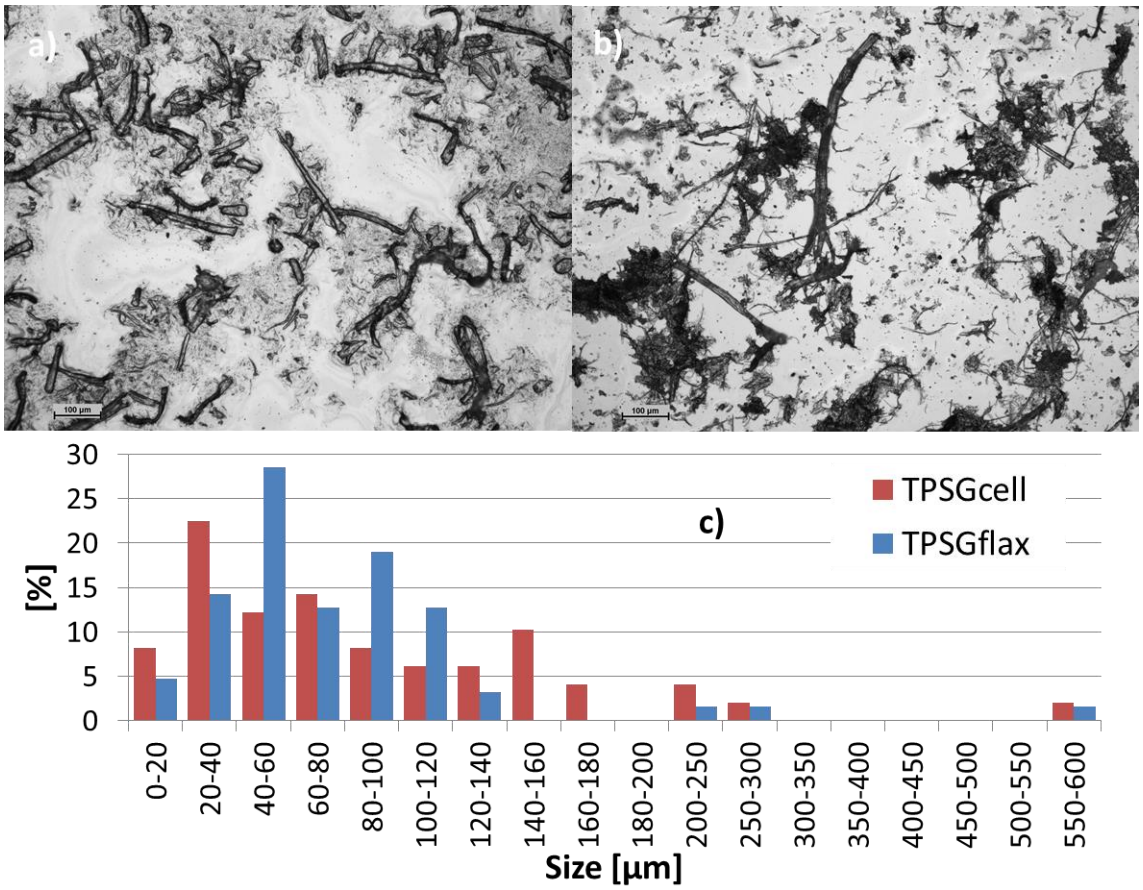


Figure 4. Optical microscopy observation of filler from TPSG20cell (a), TPSG30flax (b) and length size distribution (c).

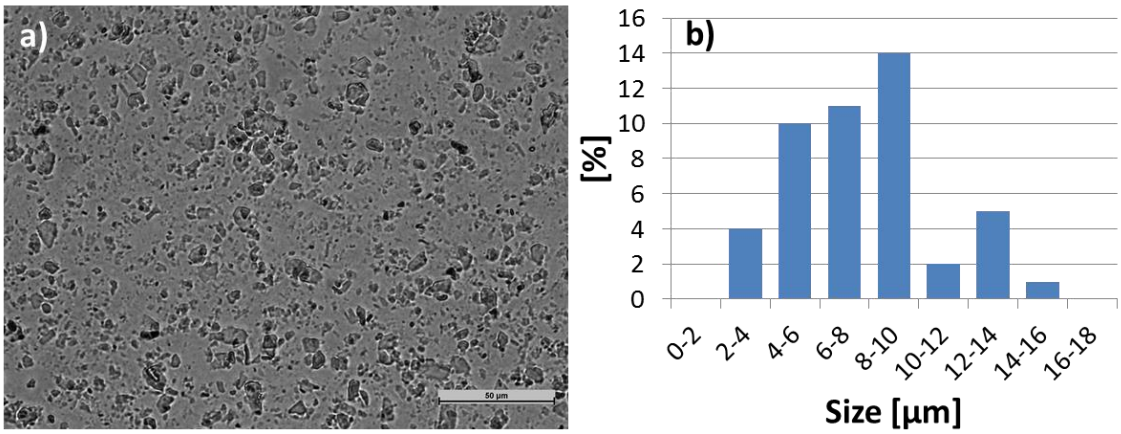


Figure 5. Optical microscopy observation of filler in TPSG30talc (a) and particle size distribution (b).

Application of Cox-Krenchel model

As mentioned in the introduction, Cox-Krenchel model allows the evaluation of the composite modulus (E_c), when those of the matrix (E_m) and of the filler (E_f) are known. To this aim, volumetric fractions (V_f) were calculated following Equation 3, fibre length (L) and radius of the fibre (r_f) were chosen taking into account the observation made in the fillers analysis section (**Table 4**). The other necessary parameters were calculated or assumed as described in the micro-mechanics model calculations part. On the contrary, the evaluation of E_f was quite difficult, since the data reported in the literature show high variability. Thus, the model was used to correctly fit E_c data collected by DMTA changing E_f and r_f parameters. E_f values were selected taking into account the literature, while r_f was chosen in the range gave from optical observations: medium value (Mean line in **Table 4**).

As far as cellulose is considered, Mohanty and coworkers have measured an E_f value in the range 5.5÷12.6 GPa [48] but micro fibrils reach 70 GPa [49]. On the other hand flax E_f range from 28 to 70 GPa stated by Mohanty and Oksman and coworkers [48,50] and talc from 17 to 35 GPa but also till 70 GPa like other silicates [51].

Figure 6 reports Cox-Krenchel model calculations (dotted curves) as a function of the filler content, using E_f, r_f and L values reported in **Table 5**. In the same figure the DMTA experimental data are reported, as well. From experimental data in **Figure 6** can be concluded that examined TPS composites are temperature sensitive materials. Indeed they show a modulus E' variation as a function of temperature. This aspect is considered only in a limited extent in the Cox-Krenchel model through the matrix modulus (E_m) variation. Thus, the composite modulus prediction could be accurate only at one temperature. For this reason, we introduced a new parameter (λ) that correct the E_c calculated with the model at one temperature to a new temperature with a temperature shift ($T-T_0$) as showed in **Equation 6**.

This correction has been already done by other researchers [52] for PP filled with talc with λ empirical coefficient from 0.02 to 0.03.

$$E_c^* = E_c * exp[-\lambda(T - T_0)]$$

Equation 6

With the introduction of this parameter the Cox-Krenchel predictions are consistent also at different temperatures. The calculated and experimental data fit well, taking into account an experimental error of ±10 % (**Figure 6**). Thus, the modified model gives good fit with values in agreement with the literature data for fibers as model is designed for.

Pursuing the research, we try to use the same model also for a lamellar filler as talc. In this case we use a plausible thickness of platelets as r_f value and the observed mean width (**Table 4**) for the L value. The resulting E_f talc value adopted is higher than literature data (80 GPa). This fact could cause the surface absorption of plasticizers by the talc with consequent strengthening of the matrix not taken into account in the model. Also in this case the λ coefficient is set to correct the model for the different temperatures and works greatly (**Figure 6**).

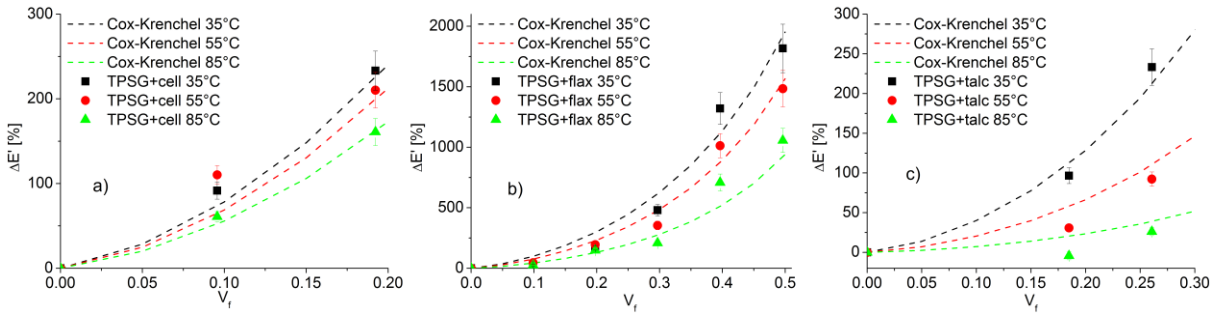


Figure 6. Storage modulus increase values of TPSG-cellulose (a), TPSG-flax (b), TPSG-talc (c) composites at 35, 55 and 85 °C and Cox-Krenchel modified fitting curves.

The Cox-Krenchel model is able to close fit the experimental modulus values for the three filler under study and with a simple modification is also able to follow the temperature dependence. It is interesting to note that with the three fillers under investigation, the λ factor

is different. From a physical point of view this means that interaction between natural fillers and TPSG decreases with temperature. Loss of properties is probably correlated to the decrease of strength in hydrogen bonding interaction between filler, glycerol and starch as well as a possible decrease of the neat fillers modulus (E_f) with temperature.

The evidence is that more high is the λ value, more is the loss of the properties with temperature. Under this viewpoint the cellulose (λ=0.008) is the filler that is able to maintain better the properties in temperature while talc (λ=0.035) is the worst.

Conclusions

Thermoplastic starch plasticized with glycerol was obtained by using a twin co-rotating screw extruder. Subsequently, in a second process step, the matrix was melt blended with cellulose, flax and talc with different loading (from 10 to 50 wt.-%) in a mini-extruder. Obtained composites revealed good TPS-fiber interfacial interactions. TPSG at room temperature and 50 % of R.H. has low mechanical performances. Natural fillers increases modulus of the thermoplastic starch: 20 wt.-% of cellulose or flax or 40 wt.-% of talc in TPSG matrix results in a storage modulus increase of about 200 % at room temperature. At 85 °C organic natural fillers used were more effective in reinforcing TPSG than talc.

The most interesting results were achieved with flax, where is possible to load the composite with a great amount of filler. Indeed, the high filler content of flax gave an increase of storage modulus of 18 times with respect the neat matrix.

Deeper analyses of the results was performed to correlate reinforcement with type, aspect ratio and concentration of the different fillers. Optical microscopy on extracted fillers was used to characterize the filler length and diameter after extrusion process. Some of these parameters were used in the Cox-Krenchel model to effectively fit the modulus experimental

data. The model can be considered useful mean for information to evaluate/customize the filler content on the basis of the application requirements. Furthermore, an additional parameter was employed in the model to follow the temperature dependence feature. This parameter is able to discriminate two phenomena: the loss of interaction between filler, glycerol and starch with temperature, probably correlated to the decrease of strength in hydrogen bonding interaction and the decrease of the modulus of the neat fillers. Under this viewpoint the cellulose is the filler that is able to maintain better the properties in temperature while talc is the worst.

Concluding, the high filler loading composites processed by melt blending evidenced a huge increase of composite storage moduli that is reflected in a reduction of the material to obtain the same performances or extending the possible matrix field of use.

Acknowledgements

The authors want to thank MANUNET ERA-Net Project called Bio-polymers for the funding.

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Table 1. Composition of melt-blended TPS biocomposites.

Sample	TPS [wt.-%]	Cellulose [wt.-%]	Flax [wt.-%]	Talc [wt.-%]
TPSGcell10	90.0	10.0	-	-
TPSGcell20	80.0	20.0	-	-
TPSGflax10	90.0	-	10.0	-
TPSGflax20	80.0	-	20.0	-
TPSGflax30	70.0	-	30.0	-
TPSGflax40	60.0	-	40.0	-
TPSGflax50	50.0	-	50.0	-
TPSGtalc30	70.0	-	-	30.0
TPSGtalc40	60.0	-	-	40.0

Table 2. Density of components and thermoplastic starches

Filler	starch	glycerol	TPSG	cellulose	flax	talc
Density [g/cm^3]	1.5	1.26	1.43	1.5	1.45	2.7

Table 3. Storage Modulus E', per cent increase ΔE' and volume fraction (V_f) of melt-blended samples after 15 days of conditioning at 23 °C and 50 %RH.

Sample	E'$^{1)}$ at 35 °C [MPa]	E'$^{1)}$ at 55 °C [MPa]	E'$^{1)}$ at 85 °C [MPa]	ΔE'$^{2)}$ at 35 °C %	ΔE'$^{2)}$ at 55 °C %	ΔE'$^{2)}$ at 85 °C %	V_f
TPSG	60	39	23	-	-	-	0
TPSGcell10	115	82	37	92	110	61	0.095

TPSGcell20	200	121	60	233	210	161	0.192
TPSGflax10	75	57	29	25	46	26	0.099
TPSGflax20	160	115	57	167	195	148	0.197
TPSGflax30	348	177	71	480	354	209	0.297
TPSGflax40	852	434	186	1320	1013	709	0,396
TPSGflax50	1150	618	266	1817	1485	1057	0.496
TPSGtalc30	118	51	22	97	31	-4	0.185
TPSGtalc40	200	75	29	233	92	26	0.261

1) E' error of ±5 % 2) ΔE' = (E' composite -E' matrix)/E'matrix

Table 4. Fiber analysis obtained throw ImageJ.

Sample	TPSGcell		TPSGflax		TPSGtalc
	L	d	L	d	L
Min	14	2.6	13	0.6	2.8
Max	592	27.1	733	26.3	15.6
Mean	97	10.8	84	5.3	7.9
SD	95	8.1	93	6.6	3.0

Table 5. Cox-Krenchel parameters for fitting curves.

Sample	E_f [GPa]	r_f [μm]	L [μm]	λ
TPSGcell	50	4	90	0.008
TPSGflax	40	3	80	0.02
TPSGtalc	80	0.45	7.9	0.035