Some Aspects Conditioning the Achieving of Filaments for 3D Printing from Physical Modified Corn Starch

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It was found that the obtaining of quality 3D printing filaments, without defects and natural color, from corn starch physical modified with PVOH, depends also on the melting behavior at compounding, both of starch and of PVOH, and on the controlling of the process sensitivity of the new compounds. A comparable melting behavior was possible by compounding the two polymers as powders with similar small sized particle. The controlling of the process sensitivity was achievable, mainly, by diminishing the melt resistance to flow, via formulation with a flow agent. The selected compounds which had controlled miscibility, few defects and natural color were shaped, with good results, as filaments with silky and smooth surface. These filaments were compatible with 3D printing because proved to have the ovality and the diameter tolerance in the accepted limits in the fields.

Keywords: Compounds, thermoplastic starch, 3D printing, miscibility, process sensitivity, melt degradation

After previous two industrial revolution from the past centuries, a mechanical one and energetic other, it is believed that, the next future revolution will be a digital one, possible the 3D printing, techniques which is gaining more and more ground, even in manufacturing items for heavy-duty areas [1]. The application of the 3D printing (additive/cumulative) procedure as compared with the substractive those, allows the achieving, in fast manufacturing processes, several, robust and compact items, sometimes even with layered structure, better adapted to the market requirements.

One of the used 3D printing techniques is the deposition of melted filaments (FDM) [2, 3]. These filaments are obtained from synthetic and/or renewable polymeric compounds [2-4] and must meet the characteristics required both by the 3D printing for doing printing in good conditions and by the desired application in order to make items with needed functional properties. A good 3D filament must have diameter of 1.75 mm or 2.85 mm (tolerance not greater than +/- 0.05 mm or even +/- 0.02 mm) and ovality (the difference between two perpendicular diameters) not exceeding 0.06 mm [3]. The polymeric filaments are discarded as inappropriate for 3D printing if they cause the clogging of the printer's nozzle (which has diameter not greater than 0.4 mm) or /and the deposited layers (with thickness between 0.07 mm - 0.3 mm) do not adhere well to each other because of the irregular flow of the melt during printing. The natural colored filaments are eliminated also when they are beige or even yellow-brown colored.

Starch has yet great potential to be used in polymer technology, as notable alternative of petrochemical plastics[5-8]. It is widely known as repeating glucose monomers, consisting of linear amylose and highly branched amylopectin. A new customized application for starch based-compounds is the 3D printing - FDM method. The obtaining of 3D printing filaments is not a simple task since even the achieving of thermoplastic compounds based on starch, via melt processing, is not an easy one.

For usage as thermoplastic compounds with functional properties suitable for various applications, starch was melt compounded with synthetic (both hydrophobic, non–degradable - polyolefin, polystyrene, polyvinyl chloride etc. or/and hydrophilic-, degradable - polyvinyl alcohol (PVOH), polyesters, etc.) or/and renewable polymers (cellulose, natural rubber, polylactic polymers, poly (hydroxybutirate) etc.) [9,10].

Several known studies regarding the starch - PVOH compounds [11-35] refer to issues as: acquiring methods [11, 12], plasticizer types [15-22], parameters influencing functional properties [10, 11, 13, 14], other polymeric modifiers [23, 24], nano-composites [25], compatibility [26, 28], cross-linking [26, 27], starch phase transition [29-34]. However, about the possibilities to control both the defects and the undesired color change of starch based materials at melt compounding, only general data, in the best case, are known [35]. Also, few knowledges can be found about the usage of starch based-compounds as 3D printing filaments, most of them only as commercial informations [36].

During compounding of white powder of starch with white powder of PVOH or during flowing of their compounds in an elongational extruder (indexer), nonconformities as changing of color from natural into shades of beige, yellow, brown or defects as cracks, fractures or voids, have been observed. Compounds with such nonconformities cannot be accepted in any circumstances, more in case of 3D printing.

Obviously, considering the already known high degradability of starch [7, 15] and of PVOH [36-40], the color change was linked with the degradation during melt compounding. Breaking or/and crosslinking of macromolecules with molecular weight diminishing and double bonds formation responsable for the coloring of the starch based–compounds, is the result of the first stage of mechano-thermo-oxidation during melt compounding [14, 15]. Protection against degradation, via stabilization

[41-45] at melt processing [41, 43-45] and/or for usage [42], as counter-methods, in technological practice is used. However, it was observed that, the formulation of the starch-PVOH compounds with melt processing antioxidants does not remove the undesirable coloring at compounding. The developed defects as voids, cracks and fracture, most likely, have other origins.

The paper presents the possibility to engineer the turning of corn starch through modification with PVOH into thermoplastic compounds with few defects and natural color, which can be shaped as quality filaments with silky and smooth surface, compatible with 3D printing.

Experimental part
Methods and materials

For avoiding the development of defects (cracks, voids, fractures, etc.) and the coloring of the starch-PVOH compounds at their achieving, later at shaping as filaments and at 3D printing, a method based on monitoring both the melting behavior of the two polymers and the controlling the process sensitivity of each compound, has been conceived. In this context the following experimental paths were investigated:

-The melting behavior of starch and PVOH powder;

-Controlling the process sensitivity of each compounds via:

-The influence of the stabilization -plasticization level;

- Finding the windows of melt compounding conditions;

- Diminishing the melt internal friction.

To achieve *soft compounds compatible with 3 D printing for various, multifunctional, applications,* the formulations have been so designed to control the glass transition values. Starch–PVOH compounds with 0/100–100/0 blending ratio and following additives related to 100 parts blend of starch with PVOH: (5-60 parts) plasticizers, (0-5 parts) stabilizers, (0-2 parts) flow agent were made. For each composition, the two polymers and additives were first pre-blended in solid state, according to the *dry-blending* technique. The compounding was made in a Brabender plastograph, in composition-dependent conditions (110-170°C temperature, 5-10 min compounding time, 75 rpm-100 rot/min rotors speed). After melt compounding, each blend was rolled into sheets, on a laboratory roller, under chosen conditions (125-160°C temperature and 24 rpm/28 rpm-rolls speed). Selected formulations were compounded - granulated on a double screw extruder (150 - 175°C, 25 rpm) and then, were shaped on a Gottfert rheometer (95°C-125°C) as bands to measure the surface roughness. The second selection was made according to the roughness of the extruded bands. The compounds which had an optimal roughness were shaped than as 3D filaments with 1.75 mm diameter, on a Gottfert rheometer (95-125°C, 35 rpm) equipped with a laboratory line for calibration, cooling, pulling, rolling of the resulted filaments. The samples for mechanical characterization have been obtained through injection (Ray-Ran injection device) in selected conditions (90-170°C, 5min.-10min.-10min., 200 barr). Because the starch-PVOH compounds with less then 50 % starch are more susceptible at temperature changes [14], only the influence of the injection temperature on the mechanical properties was studied. The 3D printing has been done on a 3D printer–model UP Plus 2.

In order to identify *the influence of the two polymers particles size* on the melting behavior and on the compounds defects, both unsieved polymers as well as, sieved fractions separated from the two polymers (P1 - starch and P2 - PVOH) were 1/1 compounded, in the same formulation and conditions.

The new compounds were characterized with the following methods and equipment:

a. Particle size analyses of polymer powder - shaking sieve HAVER- Test Sieve Shaker EML 200, working at amplitude of 1.0 mm, 15 min and 60 s.

b. Compounds morphology:

-X-Ray diffraction (XRD) - diffractometer Panalytical XPERT MPD type with Bragg- Brentano geometry.

- *Scanning electron microscopy (SEM)* - scanning electron microscope Quanta INSPECT F equipped with electron field emission gun - EFG with a resolution of 1.2 nm was used. Lyophilisation was performed in a CHRIST ALPHA 1-2 LD plus freezer in the following conditions: main drying at - 42.9 and 0.091 mbar and finally drying at - 43.2°C and 0.012 mbar.

c. Rheological properties of the melts - the melt flow index method [46, 47]. The measurements were performed on a 4000 DYNISCO indexer - LMI type, which had provided the following properties: shear rate (Sh R), melt flow index (MFI), dynamic viscosity (DV), and melt density. The activation energy of viscous flow (E_a) was calculated according to [46, 47]. Working conditions: nozzle of 2.09 ratio between height and diameter (h/D), in the temperature range from 145 to 175°C, at three loading levels: low (2.16 kg and 3.8 kg), medium (5 kg) and high (10 kg) and cutting time of 30 s.

d. Degradation by color change: Yellow index was measured with leucometer, Carl Zeiss 2781135/1 Jena.

e. *Mechanical tests* - Universal Testing Machine Instron 3382 with 100 kN load-cell at room temperature, with previous temperature and humidity conditioning for 48 h. The specimens 5A type according to ISO 527, were tested for each sample and analyzed using the Bluehill Software with a rate of 5 mm/min until fragmentation occurred. The experiments were performed on parallel specimens to ensure consistency. Measurements were done 5 times for each sample and the average value was reported.

f. Dynamic mechanical analysis (DMA) - TRITEC 2000 B (Triton Technologies) in a single cantilever mode, from -60 to 100°C with 1Hz frequency and 5°C/min. heating rate.

g. *Roughness of* the extruded bands -Portable digital roughness TR 200 type - Phynix

h. *The filament diameter tolerance*: measurement of the diameter at every 0.5 m for 300 m filament length.

i. Ovality of the filaments -SEM micrographs.

The following materials, thermo-stable in the compounding–shaping as filaments-3D printing sequence, were used:

-Corn starch (Pilot synthesized) with 70% amylopectin, glass transition at 80°C and melting at 180°C. Up to 210°C it loses 10.63% weight, and between 200 and 400°C it loses 73.35%;

-Polyvinyl alcohol (Pilot synthesized, filme degree) with 84% degree of hydrolysis (HD), T_g of 60°C and melting at 150°C. Mass loss up to 120°C approx. 3.01 and 81.43% between 170 a and 400°C;

-Plasticizers: Glycerine (ReAgent Chemical Services Ltd., GLYC-2593-06), urea (SABIC, also as micro-organism nitrogen source, technical grade);

-Stabilizers: 3/1 sterically hindered phenol and sterically hindered phosphite (Innua Petrochem, Irganox B 215);

-Flow agent: metalic stearates (calcium stearate-technical grade, Parchem CAS1592-23-0).

Results and discussions
The melting behaviour of starch and PVOH powder

The particles of each of the two pilot obtained polymers, respectively the corn starch and PVOH particles, had own size distribution and shape. The corn starch has rectangular

particles, smaller than 100 µm in proportion of 94% (100 - 80 µm/22%, 80-63 µm/18%; 63-40 µm/28%; 40 -20 µm/ 5%). The PVOH has spherical particles [48] with larger diameter than 100 µm, in proportion of 90% (100 -80 µm/ 32%; 200 -100 µm/27%; 300 -200 µm/30%) .

Since the particles of the two polymers were compounded as such, without sieving, all the acquired compounds had defects as cracks, voids, fractures etc. and were, more or less colored, in beige or even brown. The XRD diffractograms of the 1:1 starch-PVOH compounds achieved using the same formulation and identical compounding conditions but different sieved fractions have almost comparable shape, totally different from those of starch and PVOH [49] (fig. 1).
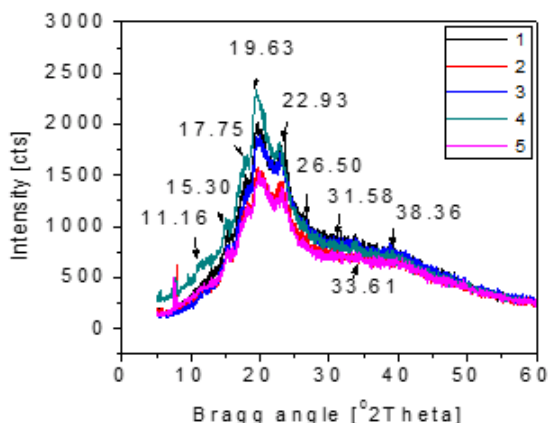

Fig. 1. Relationship between the XRD diffractograms shape and the particles size of sieved fractions used in achieving of each compounds: 1 -Φ P1 (80-100 µm)/ Φ P2 (80-100 µm); 2 -Φ P1 (80-100 µm)/ φ P2 (100-200µm); 3 -Φ P1 (80-100 µm)/ Φ P2 (200-300 µm); 4 -Φ P1 (63-80µm)/ Φ P2 (80-100µm); 5 - P₁ (40-63µm)/ P₂ (80-100 µm)

All the obtained diffractograms have the same wide diffraction angle, between $5^0 2\theta$ and $50^0 2\theta$, with maximum at almost the same diffraction angle of about $19^0 2\theta$ as the main diffraction peak of PVOH [49]. This large diffraction angle presents small shoulders, at diffraction angles easily translated as those found either in starch or in PVOH ($23.57^0 2\theta$ / $22.93^0 2\theta$ /$15.16^0 2\theta$ from starch and $40.72^0 2\theta$ /$11.85^0 2\theta$ from PVOH [49]).

These diffractograms have proved the advanced miscibility between starch and PVOH as it has been demonstrated already [14]. The novelty is related to the dependency of the compound miscibility on the particles size of the fractions compounded in each situation. The most convenient miscibility was obtained for the compound achieved from starch fraction with small particles particles of 63 - 80 µm and those of PVOH sized as 80 µm - 100 µm (fig. 1).

The SEM micrographs emphasized that the compounds achieved with sieved fractions containing large particles, enclosed many defects, sometimes visible to the naked eye (figs. 2-4). The greater the particles size of the compounded fractions was, the bigger the imperfections as voids, cracks and fractures of the resulted compounds were.

The number and the magnitude of the appeared defects were related with the dependency of the melting behavior on the particles size. At the same temperature, in the same time, some particles will melt, the smaller ones will degrade and will change the new compounds color and the larger ones will remain as unmelted insertions into the

polymeric matrix, around which the defects (cracks, voids, fractures etc.) will appear. The new compounds always will contain, near unmelted particles because of their size, rests from the starch grains, represented by the clustered amylopectin macromolecules which cannot be intimately compounded with linear macromolecules of PVOH or amylose[28]. Otherwise these rests are very well visible on the SEM micrographs (figs. 2-4).
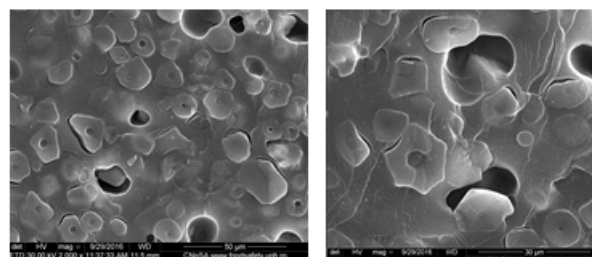

Fig. 2. Morphological defects of the compound obtained using starch with particles of 80-100 µm and PVOH with particles of 100-200 µm (1/1 blending ratio)
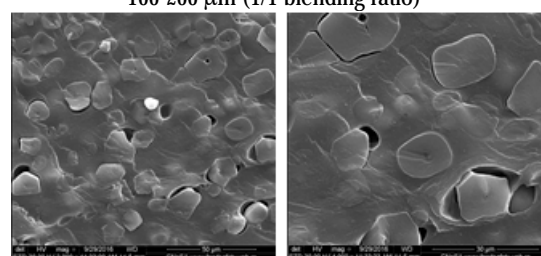

Fig. 3. Morphological defects of compound obtained from 80-100 µm sized starch with PVOH having particles of 200 -300µm (1/1 blending ratio)
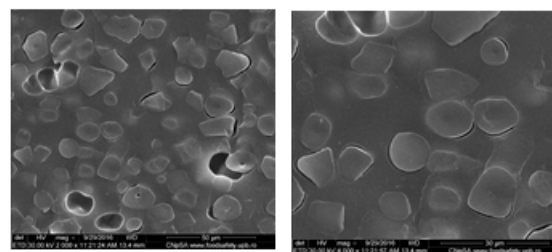

Fig. 4. Morphological defects of the compound achieved from starch with 40-63 µm sized particles and PVOH with particles of 80 - 100 µm (1/1 blending ratio)

Since the sieving was not very narrow and each fraction still contains particles with differences in size of 20µm, the coloring of the compounds was very much diminished, but not entirely eliminated.

The viscoelastic properties of the new compounds depend as well on the two polymers particles size (fig. 5). The studied compounds exhibited elastic behavior in a large temperature range, from -80°C to -60°C, when, controlled by the particles size, the storage module (E') had values from 2.3 *103 MPa to 6.4 *103 MPa (fig. 5 a). The smaller was the particles size of the two polymers which were compounded, the higher was the elastic deformation which was generated through compounding (e.g. blend obtained from starch of 80µm - 63 µm; curve 5, fig. 5 a).

In the same temperature limits from -80 to -60°C, regulated by the particles size, the energy loss due to the material morphological defects (viscous deformation), expressed by the loss modulus (E''), varied between 2.1*102 MPa and 1.2*103 MPa (fig. 5b). The highest energy

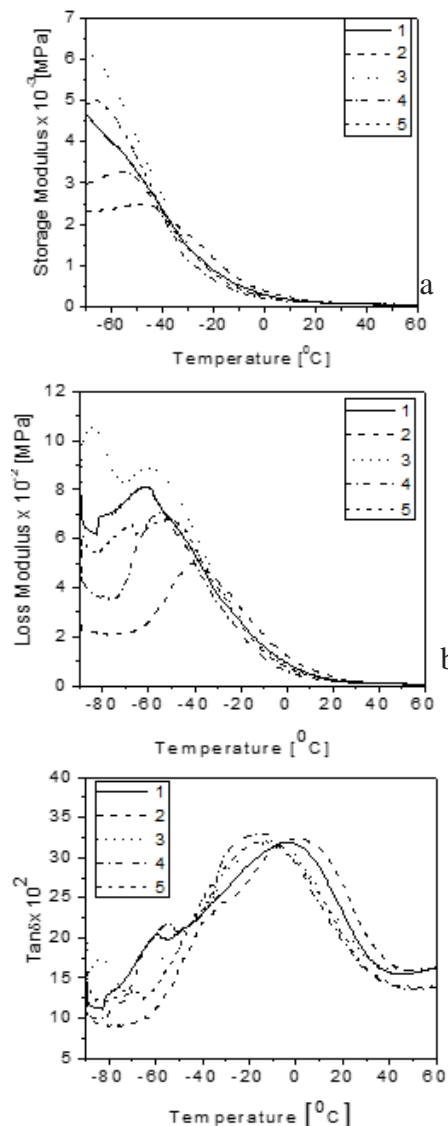loss was recorded for the compound achieved using big PVOH particles of 300 -200 μm and starch sized as 80 μm -100 mm.

Fig. 5. The dependence of the storage modulus (a), loss modulus (b) and tan δ (c) of new compounds on the temperature and the particle size of fractions used in obtaining of each of them (1 - P_1 (80-100 μm)/P_2 (80-100 μm); 2 - P_1 (80-100 μm)/P_2 (100-200 μm); 3 - P_1 (80-100 μm)/P_2 (200-300 μm); 4 - P_1(63-80μm)/P_2 (80-100 μm); 5 - P_1(63-80μm)/P_2 (80-100 μm))

The dependence of tan δ on the temperature indicated, as it was expected that, because of the high plasticizing degree, these compounds exhibit a wide glass transition, mainly in the negative temperature range. Depending on the particles size compounded in each situations, this transition has the onset temperature from -70 to -55°C, the maximum temperature between -20 and 7°C and end temperature from 30 to 45°C (fig. 5 c). Controlled by the particles size, the glass transition presents, greater or

smaller shoulders which indicate enhanced or reduced miscibility. The diffractograms of the compounds achieved from fractions with large particles had some shoulders between 45 and -75°C which means lower miscibility. The compound obtained from starch with particles of 40 μm-63 μm and PVOH containing particles ranged as 100-80μm had a glass transition without shoulders meaning miscibility at thermodynamical level, even the starch content was 50 %. Taking into account that miscibility at this level is a guaranty of compound stability unlimited period of time, it can be concluded that the polymeric particles, through their size, control even the life time of the resulted compound.

The DMA and SEM results are in good agreement. They reveal that the starch -PVOH compounds obtained from small sized particles are almost total miscible, presenting a single glass transition without shoulders, entirely different as those of individual components and almost a continuous phase with few defects as voids etc. If the two polymers would had as result of the obtaining procedure particles of comparable size than the obtaining of less defects and compact morphology starch-based compounds would be much easier.

Controlling the process sensitivity
Stabilization–plasticization

The polymer degradation at melt processing can be controlled by scavenging the newly appeared radicals [50]. The plasticizers are used in polymers formulation to make them more flexible as result of decreasing the physical attractions between the macromolecules making, in this way the macromolecules less susceptible at compounding degradation [50, 51]. In this respects, starch–PVOH compounds, with different blending ratios and selected plasticizing and stabilization content have been analyzed (table 1, 2).

Table 1
THE COLOR OF THE 60 / 40 (STARCH /PVOH) COMPOUND, THE SAME STABILIZATION[a] AND DIFFERENT PLASTICIZING LEVEL

Plasticizer, %[b]	Stabilizer, %[b]	Visual color	Yellow index
20	0.5	light brown	40
30	0.5	brown	39
60	0.5	yellow	40

[a]0.5 % antioxidant Irganox B215; [b]reported at 100% blend of starch with PVOH (60/40 blending ratio)

However, regardless the antioxidants and plasticizers content, the results were not what was expected, mainly because all the compounds were, more or less, still colored. The color of the unstabilized compounds or of those with small amount of antioxidant (0.1%) was almost the same (tables 1, 2).

Furthermore, the additional stabilization did not eliminate the coloring (table 2). It seems that, for the starch -PVOH compounds, the appearance of radicals because of degradation cannot be stopped via stabilization-plasticization.

Starch-PVOH blending ratio Plasticizer, %	Stabilizer [a], [b], %	Visual color	Yellow index
70/30 / 60	5	white	19
70/30 / 40	5	white	20
70/30 / 40	5	white	22
70/30 / 40	2.5	white- yellowish	21
70/30 / 50	0.5	yellow	33
60/40 / 40	-	light brown	32
60/40 / 40	0.5	dark brown	38

[a] reported at 100% blend of starch with PVOH; [b] 0.5 % Irganox B215

Table 2
THE COLOR OF SOME COMPOUNDS OF STARCH WITH PVOH (88% HD) AND VARIED PLASTICIZING AND STABILIZATION LEVEL

Table 3

Table 3

THE DEPENDENCE OF TENSILE PROPERTIES AND COLOR OF STARCH - PVOH COMPOUNDS ON THE STARCH CONTENT AND COMPOUNDING TEMPERATURE

Starch, %	T Brebender, °C	T roller, °C	Tensile strength at break, MPa	Elongation at break, %	Visual color	Yellow index
10	140	140	6-7	350-400	yellow	29
	170	140	7-8	350	brown	38
20	140	140	5.8-7	350-400	yellow	27
	170	140	6-7	320-348	yellow-brown	35
30	140	140	5.5-7	300-400	yellow-cream	26
	170	140	4.5-6	265-325	brown	36
40	140	140	5	300-350	cream	24
	170	140	4.5-5	50-380	yellow	28

Finding the windows of melt processing conditions

Some compounds with less than 50% starch were injected at two different temperatures, respectively at 140 and 170°C. At 140°C, the tensile properties and color depend on the starch content od each compound. The smaller the starch content were, the greater the tensile properties and the smaller the color changing were (table 3).

On the other side, at 170°C, the increasing of the tensile strength, the decreasing of elongation at break and the coloring of all compounds can be explained only through PVOH crosslinking because its thermo-oxidative degradation. The degradation was stronger as the starch content of the compound was smaller (table 3).

If, at 145°C, the specimens achieved from compound with 50 % starch were incomplete, yellow and contained voids, at smaller temperature of 90°C they enclosed un-melted material. The specimens obtained from the blend with 70% starch incorporated also, between 90°C and 120°C, unmelted material. The specimens were yellow - brown and had discontinuous surfaces when the injection temperatures was between 150 and 170°C. The melt was very sticky and the specimens were hardly removed from the mold if the injection temperature was 170°C. If the injection was made at 180°C, the melt had smallest viscosity and flowed together with a lot of degradation gases which did impossible the filling of the molds and the obtaining of complete specimens. It has been observed that the temperature range in which fewer defects and smaller color change depend on the content of each starch compound and was of 110°C - 120°C for the compound with 10- 50% starch and by 125°C-135°C for those with 60 -90 % starch.

Consequently, the process sensitive materials like compounds based on starch and PVOH require the finding of the windows of the obtaining conditions for two main compositional groups, one with starch as minor and the other as major component. The slightly yellow shades of the specimens injected even under selected conditions showed that the problem of the color change at melt compounding is not solved yet, probably because the formulation still needs to be improved.

Diminishing the melt internal friction

If the compounds did not contained flow agent, then, regardless the starch content and the extrusion conditions, the SR (is defined as ratio between the melt flow rate through a capillary and its gap [52-54] and controls the degree of homogenization) had low values ranged as 1.2 s^{-1} - 25 s^{-1}, (fig. 6 a). In case of formulation with flow agent (fig. 6 b), the SR reached values as 25 s^1 -70 s^{-1}, mainly at 5 kg -10 kg indexer load.

At high indexer load, the dependence of the SR on the starch content was much obvious.

In the absence of the flow agent, the fluidity of the compounds, expressed by the MFI values, was dependent on the indexers load and was ranged from 1 to 15 g/10
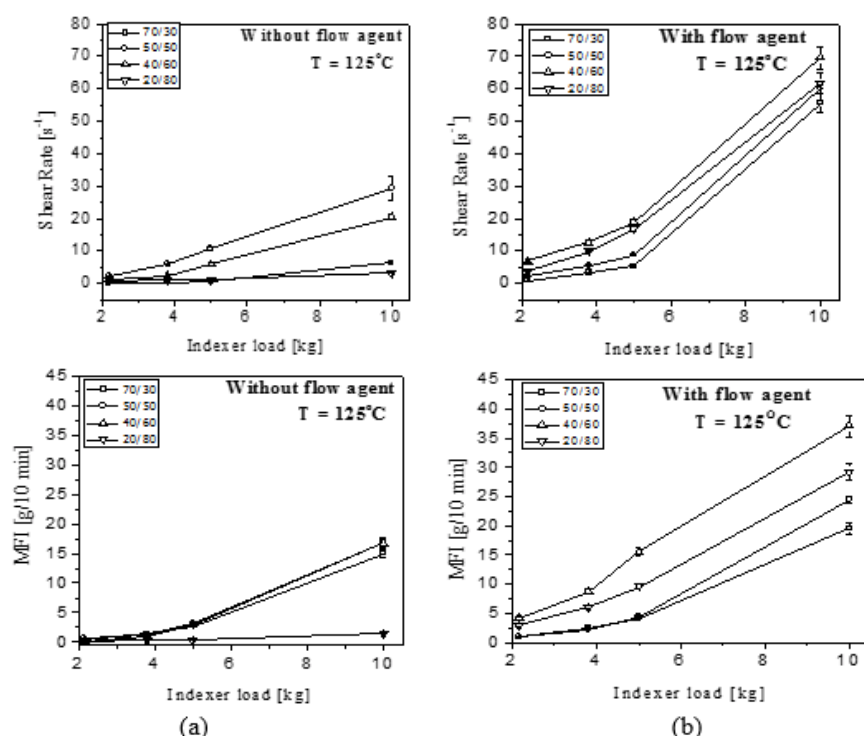

Fig. 6. Dependency of the shear rate of the starch -PVOH compounds on the starch content, the melt flow conditions and the formulation without (a) or with (b) flow agent

Fig. 7. Dependency of the fluidity of the starch - PVOH compounds on the starch content, the melt flow conditions and the formulation without (a) or with (b) flow agent

(a)   (b)

min. (fig. 7 a). In case of the compound with 20 % starch without flow agent, no variation of the fluidity with indexer loading has been observed, probably because it needs to flow well a higher temperature than 125⁰C. If the formulation was made with flow agent, then the fluidity increased according to the indexer load and the starch content (fig. 7 b). At 10 kg, the fluidity is almost twice greater as for the compound without flow agent.

The flow agent decreased to half the dynamic viscosity of the studied compounds melt (η) (internal friction resulted in a melt when a fluid layer moves in relation to another, namely the melt's resistance to flow -Newton's friction law [46, 52, 55, 56]) (fig. 8).

The melt resistance to flow of the compounds with flow agent and more than 50% starch, was mainly at low load (of 2.19 kg and 3.18 kg), 2-3 times greater than those of the compounds with less than 50% starch. The explanation is related to the high content of clustered branched amylopectin in case of the compounds with more than 50 % starch. Amylopectin flows more heavily than the linear macromolecules of amylose or PVOH. The flow temperature of 125°C is optimal for all the studied compounds with the exception of those with 20 % starch, which probably, because of high content of PVOH, flow well at higher temperature.

Obviously, small values of melt resistance to flow are helpful firstly, to ensure good flow during compounding and 3D printing. Secondly, low melt resistance to flow is equivalent with low mechanical stress acting on the melted macromolecules and thus a small probability of new radicals appearances at melt processing.

The formulation with flow agent diminished by almost 6 times the activation energy (E_a) of the melt viscous flow for all the studied compositions (table 4).

A smaller Ea is equivalent with low energy needed at melt compounding, latter at shaping as filament of the obtained compounds and then during 3D printing. The melt density is higher for all the compounds with flow agent (table 5) because by increasing the macromolecules capacity to move by flow, the resulted packaging degree will be higher as in its absence. For this reason the melt density will be higher and the new products will contain smaller defects as voids or cavities.

The diminishing of the melt density for the compounds with less than 50% starch formulated with flow agent and their good flowability under high load of 5 kg and 10 kg when need the smallest activation energy to flow (table 5), is understandable. It is more easier to pack a melted linear polymer such amylose or/and PVOH than a branched one like amylopectin which represents almost 70% from the used corn starch.

It can be concluded that the flow agent acts as a good improver of the flowability for the melt of all the studied starch - PVOH compositions because control properties as fluidity, resistence to flow, activation energy of the viscous flow and the melt density.
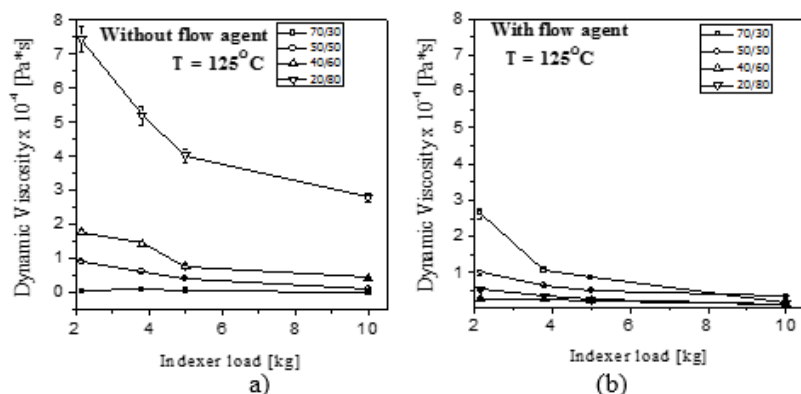

Fig. 8. Dependency of the melt flow resistance of the starch - PVOH compounds on the starch content, the melt flow conditions and the formulation without (a) or with (b) flow agent

Table 4

DEPENDENCY OF THE ACTIVATION ENERGY OF THE VISCOUS FLOW OF THE STUDIED COMPOUNDS ON THE STARCH CONTENT, FLOW CONDITIONS AND THE FORMULATION WITHOUT OR WITH FLOW AGENT

Starch content of the blend, %	E_a, kJ/mol							
	Without flow agent				With flowing agent			
	Indexer load, kg				Indexer load, kg			
	2.16	3.8	5	10	2.16	3.8	5	10
70	97.31	111.61	92.02	96.01	18.64	30.52	34.17	28.57
50	249.26	278.14	235.17	208.85	170.29	215.07	190.17	185.43
40	243.75	201.09	127.23	123.81	67.06	106.58	56.37	114.30
20	272.47	299.04	336.54	381.26	154.57	155.69	135.87	134.46

Table 5

DEPENDENCY OF THE MELT DENSITY OF THE STARCH – PVOH COMPOUNDS ON THE STARCH CONTENT AND THE FORMULATION WITHOUT OR WITH FLOW AGENT

Starch content of the blend, %	Melt density, g/cm³							
	Without flow agent				With flow agent			
	Indexer load, kg				Indexer load, kg			
	2.16	3.8	5	10	2.16	3.8	5	10
70	0.097	0.166	0.213	0.616	0.244	0.641	0.786	1.132
50	0.082	0.173	0.279	1.071	0.559	0.986	1.228	1.338
40	0.101	0.133	0.164	0.528	1.296	1.281	1.205	1.155
20	0.096	0.139	0.176	0.634	1.198	1.180	1.133	1.115

Fig. 9. The filaments obtained from compound with 70 % starch using un-sieved starch and PVOH without controlling the process sensitivity (a) or sieved starch and PVOH and controlled process sensitivity (b, c, d) (a - M*any defects* as voids; b, c, d - W*ithout defects* and natural colour)

The main effect of the improving of the melt flowability of the starch-PVOH compounds with the help of the flow agent was the achieving, white, undegraded compounds. The double bonds responsible for the coloring of the starch-based compounds [14] had no conditions to develop, as the radicals no longer appear.

As it was demonstrated [57-59], during extrusion of starch, significant shear degradation happened in amylopectin component of starch, while high amylose starch could resist to the chain scission. Amylopectin with high branching density and short branch length is of higher susceptibility to shear degradation due to its inflexible structure [58, 59]. Considering also the high content of amylopectin of the used starch (70 %) it can be appreciated that the observed degradation during melt compounding, were generated, both by the degradation of the amylopectin from starch and of the PVOH .

As compared with the known solution of scavenge of the radicals from the melted polymeric compounds through stabilization, which can be ineffective for process sensitiv starch-based compounds, the prevention of the radicals formation through diminishing the melt resistance to flow is much safer. Otherwise, as it has been shown, this is the only solution to make non-stained, white starch based-compounds.

Shaping of selected compounds into 3D printing filaments
*To test the e*xtrudability and to analyze the surface roughness of the new filaments, selected compounds with various starch contents (20 - 90%) were first shaped as bands with 1 mm thickness and 10 mm width. It was observed that if the roughness of these bands was of +/- 0.04 mm, the corresponding filaments had silky and smooth surface, suitable diameter tolerance (+/- 0.047 mm) and ovality and have proven good behavior at 3D printing (fig. 9).

Conclusions

It was found, that the turning of corn starch via melt modification with PVOH, into thermoplastic compounds for high quality 3D printing filaments can be engineered by providing similar melting behavior of the starch and PVOH powder and by controlling the process sensitivity of the new compounds.

Defects like voids, cracks, etc. appear around both the un-melted polymer particles due to their too much large size and/or in proximate of the residues of the amylopectin from the starch grains which, because of its clustered structure, cannot be intimately compounded with the linear macromolecules of amylose and/or those of PVOH. The more the unmelted polymeric particles because of their size and/or the amylopectin content are, the greater the overall defects of the final compounds will be. By compounding the two polymers as powder, with similar small sized particles it was controlled even the miscibility of the two polymers and so, by using starch with 70 % amylopectin, a miscible compound having a single glass transition have been obtained.

The controlling of the process sensitivity of the starch based-compounds proved to be a better solution to obtain natural colour filaments and was mainly achieved by diminishing the melt resistance to flow via formulation with a flow agent.

The filaments obtained from the selected starch based-compounds obtained using starch and PVOH with similar sized particles and controlling the process sensitivity at melt compounding had silky, smooth surface, diameter tolerance of +/- 0.04 mm, ovality of (0.005 mm -0.06 mm) and had a good behavior at 3D printing.

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