SOME ASPECTS CONCERNING THE RHEOLOGY OF BIODEGRADABLE STARCH BASED MATERIALS

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Lucrarea prezintă câteva aspecte privind reologia unor materiale pe bază de amidon. Aceste amestecuri au fost obținute prin modificarea fizică a amidonului cu alcool polivinilic (PVOH). A fost utilizată metoda indicilor de curgere deoarece aceasta este o metodă simplă, calitativă de obținere a informațiilor reologice. Selecția preliminară a compozițiilor şi a condițiilor s-a făcut pe baza aspectului extrudatelor şi a dependenței vâscozitate dinamică – viteză de forfecare. Studiul reologic a dat informații referitoare la posibilitățile de prelucrare a topiturilor pe bază de amidon.

This paper presents some studies regarding the rheology of starch based materials. These blends were obtained by physical modification of starch with polyvinyl alcohol (PVOH). It was used the flow indexers method because is a simple, qualitative method for obtaining rheological informations. The compositions and conditions were preliminary selected based on the extrudates aspect and the dependence dynamic viscosity – shear rate. The rheological study gave informations regarding the processing possibilities for starch melts.

Keywords: starch, rheology, extrudate aspect, dynamic viscosity, shear rate.

1. Introduction

Rheology generally deals with the study of deformation and flow of matter. Polymers are complex rheological materials in that they exhibit both viscous and elastic (viscoelastic) properties under varying conditions of stress, strain and temperature. The non-Newtonian, pseudoplastic behavior is in a simple way by the power law: $\eta = k\cdot\gamma^{n-1}$, where k is the consistency index and n is the power law index. The power law index is an indicator of a material's sensitivity to

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shear (rate) or the degree of non-Newtonian behavior. For Newtonian fluids n = 1, and for pseudoplastic fluids n < 1, with smaller values indicating greater shear sensitivity. At very high shear rates, the polymer chains are, in theory, fully aligned in the direction of flow. Thus, the viscosity cannot degrease further and is constant in the upper Newtonian plateau [1 - 6].

The processing techniques employed in converting plastics into finished products include injection molding, compression molding, blow molding, profile extrusion and sheet extrusion followed by stamping or thermoforming. In all these processes, the molten polymer is subjecting to shearing flow under a wide range of shear rates. The temperatures involved in the flow deformation also vary with the process.

There are known the ranges of shear rates and viscosity for all processing techniques [5, 7, 8].

Table 1

Shear rate and viscosity ranges for processing techniques

Process	Shear rate, s^{-1}	Viscosity, Pa·s
Pressing	1-10	8000-10000
Extrusion	10-1000	4000-8000
Injection molding	100-10000	300-700
Sinterization	0.01-0.1	3000-4000
Compression molding	0.1-1	1000-3000
Thermoforming	10-1000	100-3000
Tube extrusion	10-100	800-1300

Knowledge of the complete flow curve (rheogram) depicting the variation of the melt viscosity over industrially relevant range of shear rate and temperature is, therefore, essential in the design of polymer processing equipment, process optimization and trouble-shooting [7].

The most common device used for measuring the viscoelastic properties of melt polymers is a melt index, which is empirical method that provides a single point measurement of viscosity. The melt index actually is the amount of material which flows through a capillary under a standard set of conditions (temperature, pressure and time). It is most often used as a simple, quick way to grade the relative differences between polymers and plastics in a quality control environment. Its limitations are that it is not very sensitive to differences in molecular architecture and provides little useful information to simulate how a polymer or plastic will behave in a process [9].

The rheological study for polymers is important because their rheological properties affects the quality of finished product by aspects like: morphological structure obtained during processing, surface aspect (improper processing conditions could generate defects as distortions), material properties anisotropy and properties of the finished products.

The use of starch as a thermoplastic material is a recent development. Such developments were made especially for starch modification in order to reduce or eliminate its disadvantages like high hygroscopicity, poor physical and mechanical properties. Starch physical modification with polyvinyl alcohol (PVOH) is important because these materials degrade in the environment due to starch biodegradability and PVOH water solubility. This type of modification can be made through melt processing because this method takes place in a sequence of polymer transformations into finished products. A variety of such products can be obtained only by changing the nozzles and molds dimensions used for this purpose.

Obtaining finished products based on starch materials is dependent on their rheology. This is an important fact because the selected processing conditions and equipment are correlated with the rheological properties. The understanding of the rheology of starch melts materials is needed in order to estimate the effects of processing on the finished products properties. The processing conditions are also important because the two polymers (starch and PVOH) degrade before they melt [10 – 12].

This paper discusses the processing possibilities for polyvinyl alcohol modified starch taking into account the aspect of extrudates and the dynamic viscosity dependence on the shear rate. Starch compositions which present rheological properties suitable for melt processing technique were selected.

2. Experimental part

For a preliminary selection, the extrudates surface aspect and the viscosity dependence of the shear rate were used. There has been studied also the shear stress, the flow index and the viscous flow activation energy (Ea). Ea was calculated based on the formula 1 taking into account the melt flow indexes measured at two different temperatures and the same shear stress:

$$E_a = R \cdot \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot \left| \ln\left(\frac{MFI(T_1, G)}{MFI(T_2, G)}\right) \right| \qquad (1)$$

2.1. Materials

There were obtained blends with different ratio of (0-100 %) starch / (100-0 %) polyvinyl alcohol / (10-80 %) additives using:

- Corn starch with melt temperatures at 278 ^{o}C and 296 ^{o}C, with 30 % crystallinity degree;
- Polyvinyl alcohol with melt temperature 185 ^{o}C and 84 % hydrolyze degree;
- Proper melt processing additives such as plasticizers, stabilizers and flow improving agents.

2.2. Characterization

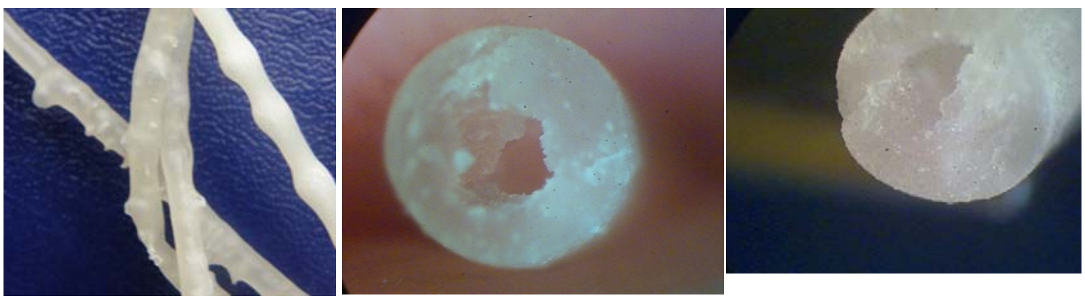
Rheological properties were determined using a melt indexer from Dynisco that can measure the melt flow index, melt density, dynamic viscosity, shear stress and shear rate. The measurements were made using different weights (2.16, 3.8, 5 and 10 kg). The methods used were A for melt flow index (MFI), A/B for melt density, B for dynamic viscosity and RATIO for flow ratio.

3. Results and discussion

3.1. Extrudates aspect

The first analyzed property was the aspect of extrudates obtained by melt flow index measurement. There were observed the following types of defects for all the studied blends, in some processing conditions:

D1. variable diameter leading to discontinuous extrudates with voids



a b1 b2

Fig. 1 D1 observed defects throughout the extrudates (a); cross-section from different angles (b1 and b2)

D2. quantitative variable flow

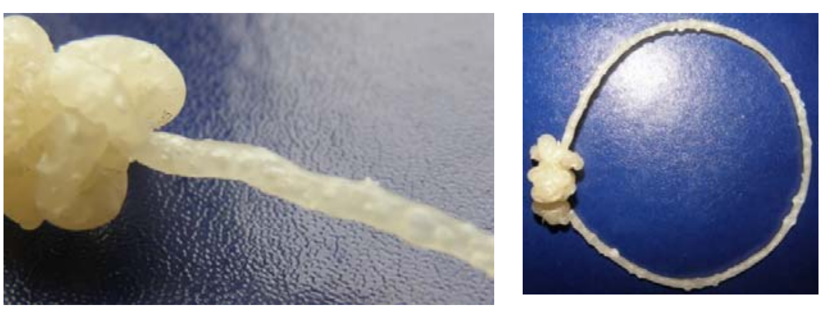


Fig. 2 D2 observed defects

D3. the materials didn’t flow and / or contains voids

Fig. 3 D3 observed defects

These defects appeared because the improper processing conditions when the starch based materials degrade. This process is dependent on the temperature and shear stress and shear rate. Analyzing the extrudates aspect dependence of these parameters is a good opportunity of selecting the proper composition and processing conditions in packaging obtaining.

Modifying the processing conditions involves the extrudates aspect modification from an improper one to a proper one, for all the compositions. For example, for a blend with 30 % starch, the improper aspect of the extrudates, with variable diameter and voids, obtained at a temperature of 135 ^oC and different shear stresses, is much improved by lowering the temperature with 15 ^oC. Thus, at 120 ^oC, the extrudate has a constant diameter, no voids and a good flow (Fig. 4).

A B C

Fig. 4 Extrudate aspect in different processing conditions (temperature and shear stress) proper (A) and improper (B, C)

3.2. Dynamic viscosity dependence on shear rate and blend composition

Based on the dynamic viscosity dependence on shear rate and depending of the processing conditions and the composition, the proper melt processing techniques of the starch blends can be selected. These criteria show that for the same composition, there are conditions in which the blend can be processed into a finished product and conditions in which the blends can not be processed through the mentioned techniques. For instance, it can be observed based on the dependence dynamic viscosity – shear rate, for a blend with 30 % starch, that the 125 °C temperature is not proper for the melt processing. At a temperature of 130 °C and low shear stresses assigned to a plastometers load of 2.16 kg, the blend can be processed through sinterization. At 145 °C and the same shear stress, the 30 % starch blend can be thermoformed (Fig. 5).

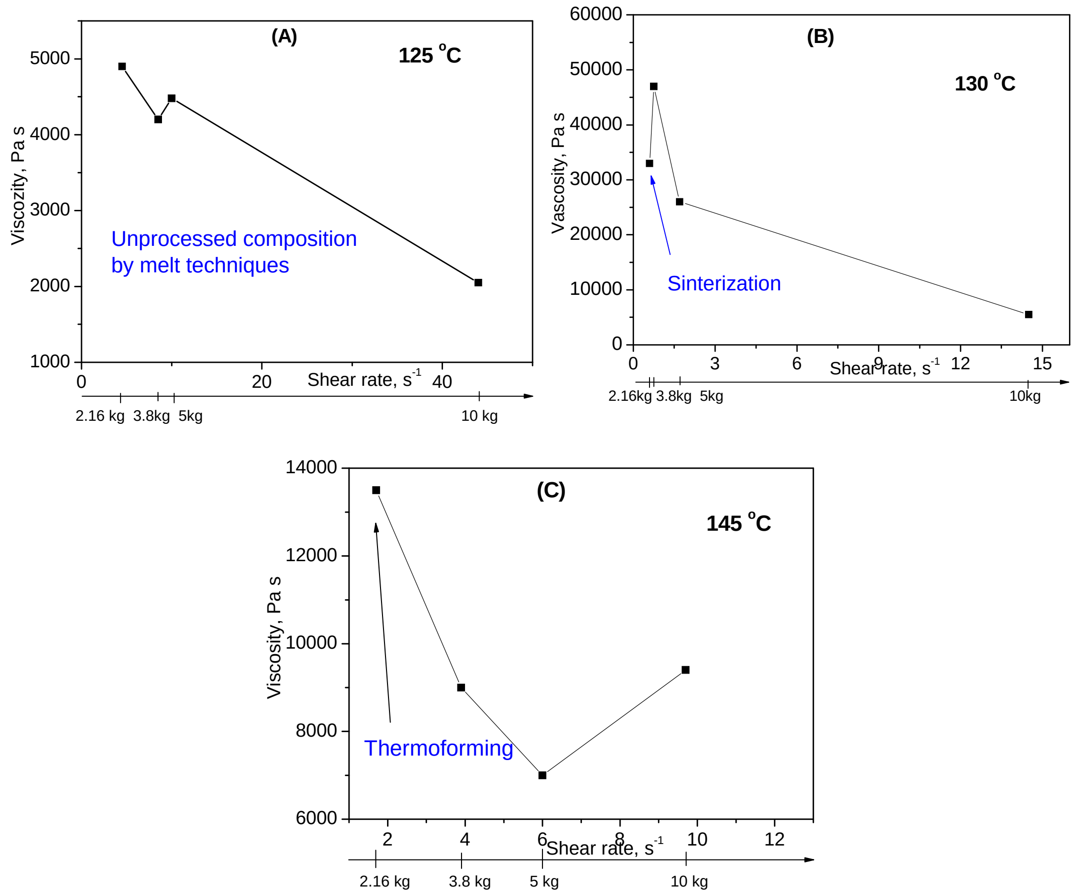


Fig. 5 Melt processing possibilities of a 30 % starch blend at different temperatures: 125 °C (A), 130 °C (B) and 145 °C (C)

The blend with 10 % starch can't be processed by melt techniques at a temperature of 135 °C. At a smaller temperature (120 °C) and small shear stresses assigned to a plastometers load of maximum 5 kg, the compound can be processed through thermoforming. The viscosities in these cases are between 5500 and 8000 Pa s (Fig. 6).

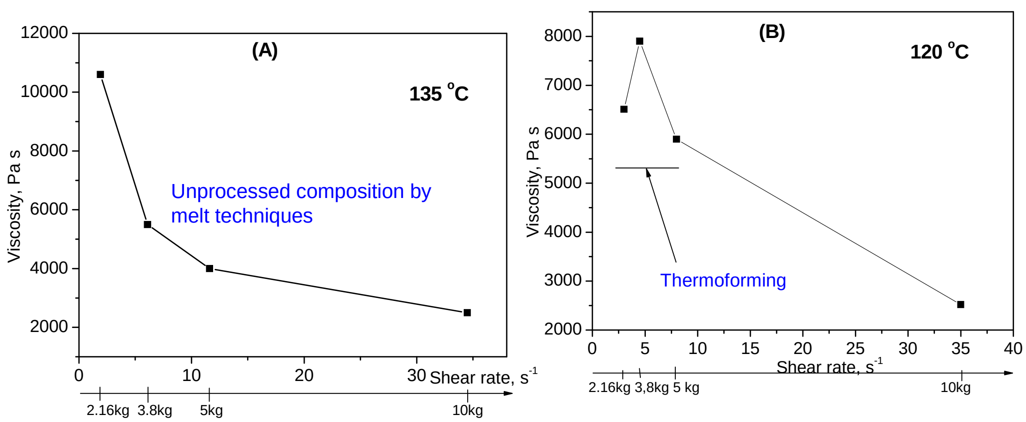


Fig. 6 Melt processing possibilities of a 10 % starch blend at 135 °C (A) and 120 °C (B)

By determining the flow index, it can be seen that the temperature affects the materials fluidity. For example, in case of a 10 % starch blend (Table 2), increasing the temperature will increase the melt fluidity only if the mechanical stress is small (for plastometer load between 2.16 and 5 kg). If the stress in higher, than the fluidity isn't affected of the temperature, the values of the flow indexes aren't different.

Table 2

Values of the flow index at different temperatures and shear stresses

Temperature	Plastometer load, kg			
	2.16	3.8	5	10
120 °C	1.984	2.099	7.670	34.570
135 °C	3.380	6.160	11.290	34.950

The composition with 50 % starch can be processed through injection molding and coatings, depending of the processing conditions (Fig.7). This blend requires high shear stresses for its processing into finished products. At the temperature of 140 °C, the viscosity for coatings is of about 1300 Pa s, and at 155 °C for injection molding it is of about 100 Pa s (Fig. 7).

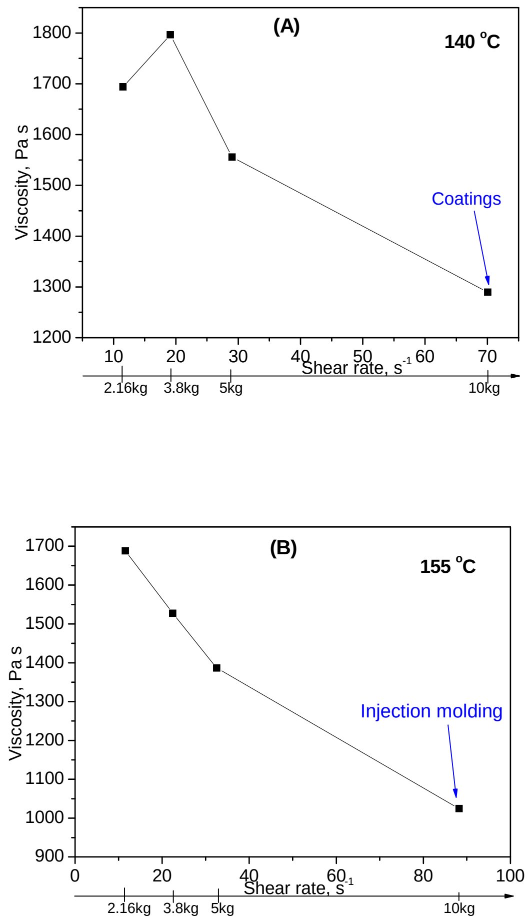


Fig. 7 Melt processing possibilities of a 50 % starch blend at 140 ^{o}C (A) and 155 ^{o}C (B)

The increasing of the starch content in the studied blends improves the processability. For example, the compound with 70 % starch (Fig. 8) can be processed mainly for coatings, at temperatures between 125 and 155 ^{o}C. At low temperature, the shear stress must be higher, obtaining viscosities of 1000-2000 Pa s for plastometer loading of 5 and 10 kg. At higher temperature, the shear stress is smaller. The viscosity decreases with increasing the temperature from values of 1000-2000 Pa s at values of 800-1600 Pa s. This blend can be also processed by injection molding la temperatures of 145 and 155 ^{o}C and high stress assigned to a plastometer load of 10 kg. The viscosity is of about 700 Pa s, according to the literature values (Fig. 8). Viscous flow activation energy for this blend has small values, not exceeding 100 kJ/mol.

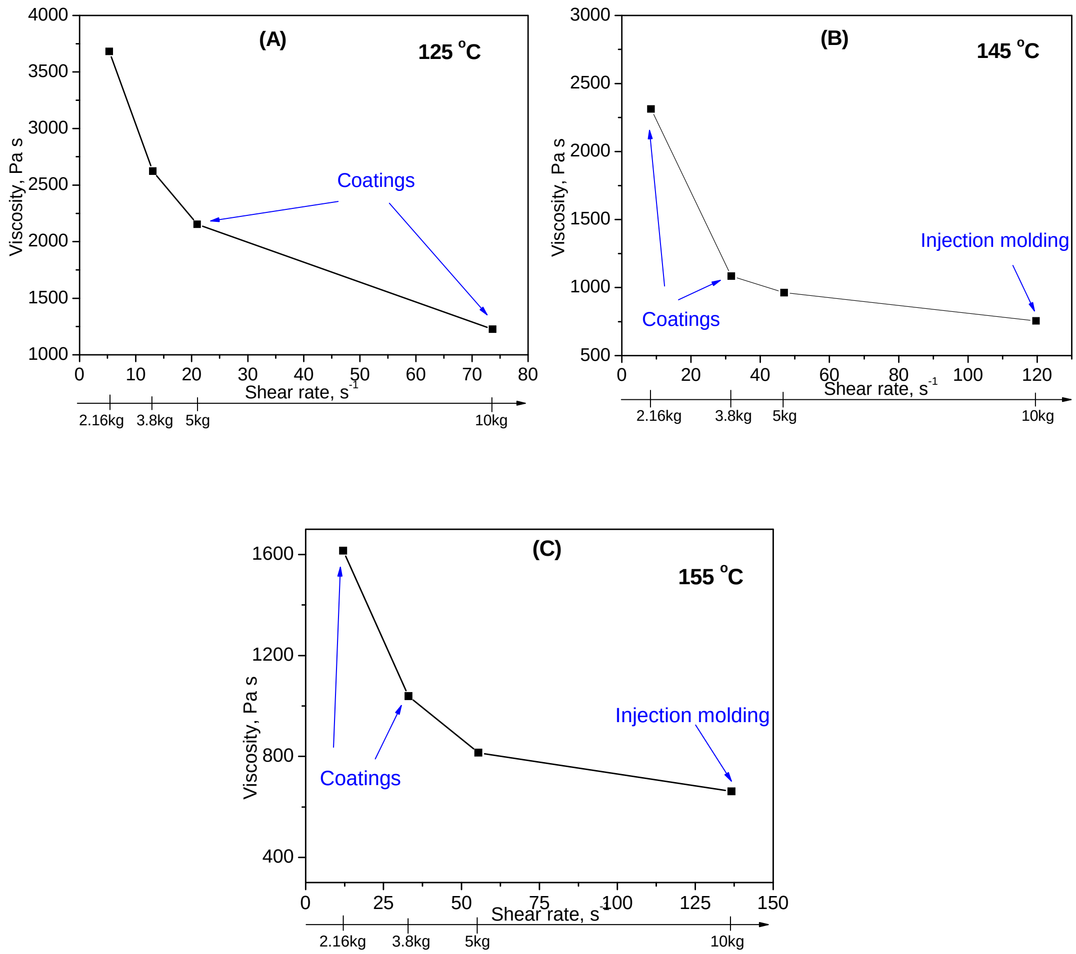


Fig. 8 The melt processing possibilities for a 70 % starch blend at 125 °C (A), 145 °C (B) and 155 °C (C)

For improving the processability and for diversification of melt processing possibilities, a method of addition of extra additives was tried and the results were examined. For example, the 70 % starch blend which could be processed for coatings and by injection molding it can be processed also by extrusion with extra additives.

For instance, at the temperature of 130 °C, the material can be processed by extrusion into tube or other extruded profiles on all the shear stress and shear rate range. The viscosity in these cases is between 2000 and 7000 Pa s (Fig. 9A).

At 145 °C, at high shear stress assigned to the plastometer load of 10 kg, the blend can be processed through blowing molding and injection molding (Fig. 9B). At 155 °C, the blend can be processed by extrusion, and injection molding at high stresses, and for coatings at small and high shear stress (Fig. 9C).

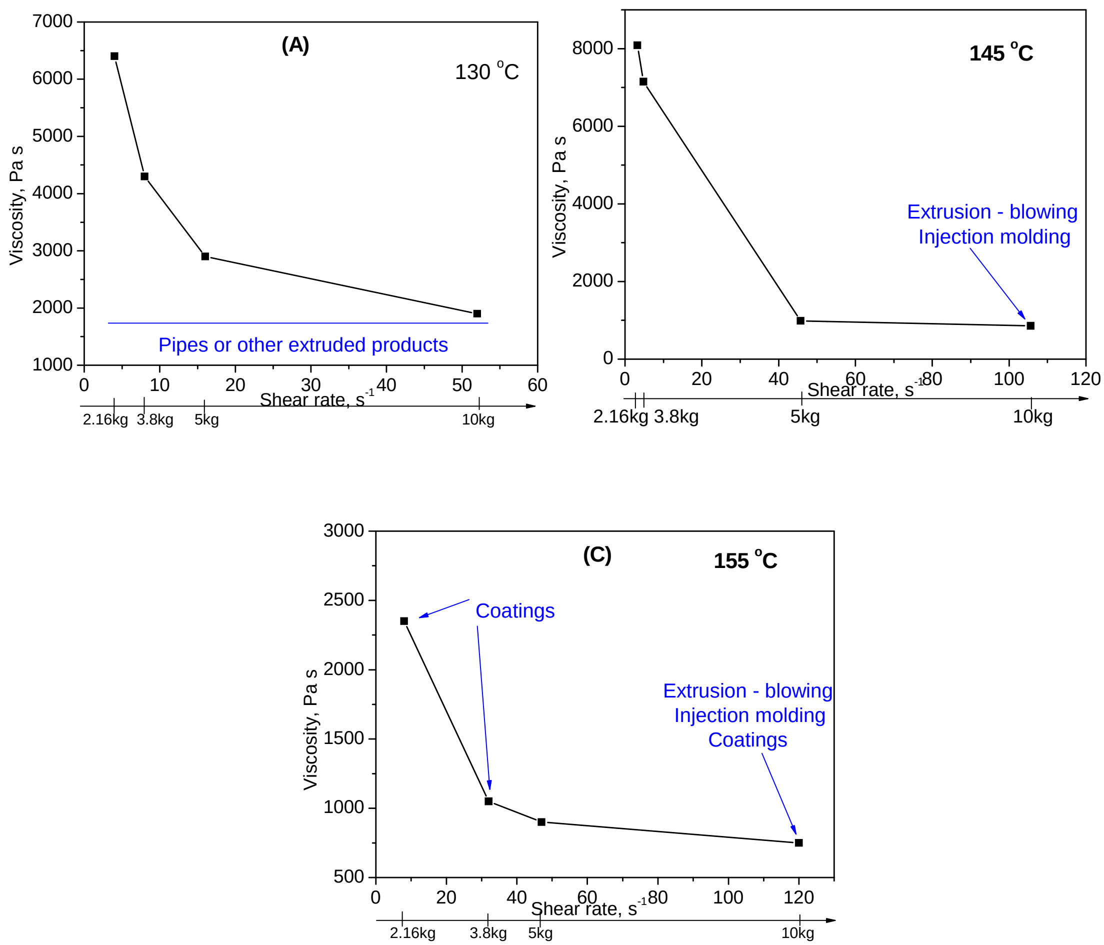


Fig. 9 The melt processing possibilities for a 70 % starch blend with extra additives at different temperatures: 130 °C (A), 145 °C (B) and 155 °C (C)

It was observed that the blends whose extrudates had a proper aspect, without defects, can be melt processed through the techniques selected by the viscosity dependence on the shear rate. From the blends with variable composition, with up to 90 % starch, only few of them can be processed by the proper techniques selected on this dependence.

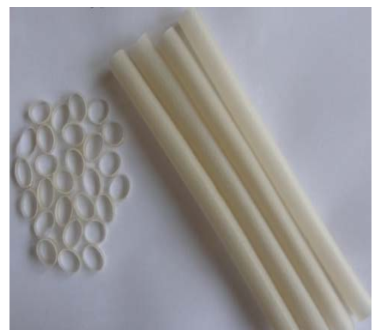
The range of the further processing techniques into a finished product can be enlarged through addition of extra additives to the selected recipes.

Based on the rheological study, the proper compositions and their processing conditions were selected. Compositions with up to 90 % starch could be processed, obtaining extrudates with proper aspect, which had been subsequently granulated. There were identified the melt flow and the extrudate aspect improving techniques, considering also the solid homogenization procedure. It was set that the work sequence must consist of: solid mixing, extrusion on a single screw extruder and granulation.

The blends could be processed also by injection molding, blowing molding and extrusion in bands leading to extrudates (A), injected specimens (B), tubes (C) and bands (D).

A

B



C

D

Fig. 10 Finished products obtained from the selected starch blend: extrudates (A),), injected specimens (B), tubes (C) and bands (D)

6. Conclusions

The extrudate aspect is a qualitative parameter useful in identifying the proper compositions and qualitative estimation of the melt processing conditions for starch based materials. The developed shear rate values are generally qualitative indicators for identifying the most suitable melt processing techniques for starch based materials. The blends whose extrudates had a proper aspect can be processed by melt techniques dependent of the shear rate. Based on these results the composition selection and the qualitative estimation of the possible melt processing techniques were possible. There were obtained granules from 10-90 % starch blends, by the working sequence: solid mixing/ extrusion / granulation. The checking of the melt rheology results was achieved by the processing of the selected compositions in different finished products.

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