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Determination of functional characteristics of a biogenous thermoplastic material

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At the Institute of Food Technology of the University of Agriculture in Vienna, a process was developed to produce thermoplastic materials out of food industry waste. The object of this study was to find methods to characterize the thermoplastic properties of these materials. In addition, we wanted to determine if rheological measurement data could provide information about injection-moulding suitability of the materials. Fourteen granulates of these materials differing in disintegration parameters and additives were analyzed. In order to determine the flow characteristics a capillar rheometer test was used to measure the energy needed to extrude the granulates through a nozzle. By this method, it was possible to determine the influence of the varied disintegration parameters and additives on the flow characteristics of the material. In order to determine the mechanical strength of injection-moulded samples of the granulates, uniaxial tensile tests were performed. Out of all the tested granulates, only those with an extrusion force less than 1·45 kN were suitable for injection-moulding. Therefore, the results of the capillar extrusion test can be used to predict the suitability of the granulate for injection-moulding.

INTRODUCTION

Owing to the fact that fossil-based raw material resources are limited and that the use of these resources creates waste-management problems, attempts to return to biogenous resources is becoming more and more important. There are three conditions for a successful substitution: first, the biogenous material should have similar or identical functional characteristics; second, the production of such materials should not require more energy than production with fossil materials; and finally, in order to ensure economic feasibility, the production costs should not significantly exceed those of the fossil materials replaced.

One promising possibility in this area is the substitution of biogenous polymers for synthetic ones, at least in part due to the increasing awareness that the two have principally similar characteristics. It is possible, for example, to transform the biogenous polymer 'starch' into a thermoplastic material that has qualities similar to those of materials produced from synthetic polymers. In order to transform starch into a thermoplastic material it is necessary to work the existing partially crystallized starch substance into a 'destructed' material (Fritz & Widman, 1993; Potente *et al.*, 1994). A disadvantage of starch as compared to synthetic polymers, and at the same time its greatest advantage, is its water solubility. This is the precondition for biological decomposition. This contradiction is inherent to the problem, as poor water solubility (unquestionably possible with biogenous polymers) automatically diminishes and/or slows down the process of biological decomposition.

In order to show thermoplastic characteristics, a polymer must fulfil certain molecular preconditions that are the same for synthetic and for biogenous polymers. The reaction to temperature determines the functional characteristics of a thermoplastic. According to Laeis (1972), the molecules of an amorphous synthetic polymer at low temperatures are in a so-called 'glass condition'. When the temperature is increased, the energy will eventually be enough to overcome the lateral valency which holds these molecular chains together. When the glass transition temperature (T_g) is reached and passed, the extensibility of the polymer increases. This thermoplastic condition allows various kinds of procedures to be performed on the material such as deep drawing. The next level of temperature increase is the flow temperature range, at first a highly viscous material, which with

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further temperature increase becomes ever thinner. Finally comes the decomposition temperature, where the kinetic energy of the molecules in the molecule chains is so high that the force of the principal valency is overcome by thermal energy, the linear chain molecules are irreversibly broken, and the macromolecules are destroyed.

Today the idea that the characteristics ascribed to synthetic polymers apply just as well to natural polymers is gaining acceptance (Slade *et al.*, 1993). Biogenous polymers can just as well be encountered in an amorphous, partially crystallized form or in a crystallized condition, whereby the amorphous polymers have a glass transition temperature (T_g) and the crystallized polymers, on the other hand, will melt down when brought to the fluxing temperature (T_m). A difference can be found, perhaps, in the fact that the biogenous polymers generally have a lower decomposition temperature. This may lead to a situation in which heating the material will cause disintegration before its thermoplastic characteristics can be exploited. For this reason, when working with biogenous polymers it is particularly important to use a plastification aid. These are sub-molecular substances which are used to 'thin' the material and enable the molecules of the polymer to move about more freely, thus reducing the temperature at which the material becomes malleable. The most common and effective plastification aid is water.

Until now, attempts to find a biogenous replacement for synthetic polymers have concentrated on starch. Although it is true that starch is a common material, the fact that it is derived from valuable vegetable raw materials means that at present it cannot pass the test of economical competitiveness against the synthetic polymers it would replace. There are many other kinds of biogenous polymer other than starch which may be economically competitive such as low-cost agricultural and food-industrial by-products and wastes. Such materials are, for example, the discard of presses from juice production, sugar-beet discard, vegetable waste products, potato pulp or spent grain. The structure of these food industrial by-products and wastes depends on the species of the raw materials and the preliminary treatment. These raw materials mainly contain saccharides, such as cellulose, lignin, hemicellulose, pectins, mono-, di- and oligosaccharides. There are also small contents of ash, protein and fat.

Voragen *et al.* (1983) proposed a method to subdivide cell-wall polysaccharides of fruit and vegetables into alcohol-soluble and alcohol-insoluble parts. Dürrschmid (unpublished) found in apple discard about 30% alcohol-soluble and 70% alcohol-insoluble substances. In sugar-beet discard he found a content of alcohol-insoluble substances of 94% and only 6% soluble substances. Further examinations of the insoluble fraction of apple discard showed a content of 14% pectins, 12% hemicellulose and 41% lignocellulose. With another method proposed by Asp *et al.* (1983) the dietary fibers are subdivided into water soluble (pectins and some hemicelluloses) and water-insoluble (cellulose, lignin and some hemicellulose) parts. In apple discard and sugar-beet discard have been found respectively 53% and 70% insoluble as well as 13% and 21% water-soluble dietary fibers (Mundigler, unpublished).

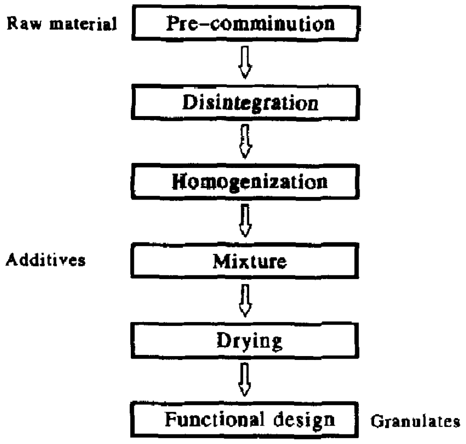

Fig. 1. Production of granules.

With the appropriate processing of these raw materials a granulate with thermoplastic characteristics can be produced which can be injection-moulded or deep-drawn (Berghofer *et al.*, 1993). Figure 1 shows a schematic of granulate production from these raw materials. This process is characterized by modifying the length of the linear chain molecules found in the polysaccharides of the cell membrane and by adding biogenous plastification aids, thus reducing the T_g to a point low enough to where thermoplastic malleability can be exploited before disintegration starts.

Our process fulfils the first two criteria mentioned before: (i) low-cost waste and by-products are economically competitive against raw materials for synthetic polymers; and (ii) the processing of the raw material is relatively simple and requires relatively little energy. The final criterion, however, is the most important: What are the functional characteristics of this material, and are they comparable to those of synthetic polymers? It seems logical to use the same methods for this material as are used for synthetic polymers. The question of whether these methods can be adopted without modification, or whether some modification is necessary, or if completely new methods must be developed to determine the characteristics of a biogenous thermoplastic material is the subject of this paper.

Methods for determining the characteristics of thermoplastic materials

In the technical usage of synthetic materials, one must distinguish between the characteristics of granulates on the one hand, and the characteristics of the resulting moulded parts on the other hand. The characteristics of a moulded part cannot be determined simply by the characteristics of the granulate out of which it is made. Also the standardized values recorded on a test specimen cannot describe the characteristics of the granulates, but rather those of the particular test specimen, in the condition in which it was tested (Bartnik *et al.*, 1977).

Tests of granulates

Thermoplastics with completely non-ordered molecular chains exist in a glass condition (are amorphous) in the temperature range in which they are used. They are as transparent as glass and usually brittle. Those with a partially crystallized structure are translucent, less brittle, and mechanically more resistant (Biederbick, 1974). Even after softening (after passing T_g and/or T_m), the physical forces between the molecules remain. It is not possible to shape a material without a certain orientation of the filamentary molecules. They act in the same direction and are to some degree also linear, and the shear forces which appear are frozen in when the material is cooled. These processes are usually characterized by rheological measurements.

The most common techniques for synthetics use the flow behavior of the heated material in liquid form as an important parameter. This applies both to the continuous finishing processes of calendering and extrusion, as well as to the intermittent finishing of moulded parts out of thermoplastics and duroplastics through injection-moulding. Measuring the viscosity is also a way of measuring the size of the molecules, thus determining how thick the material will be at a particular temperature, thus making it an important characteristic of a material's processability.

In polymer manufacturing the capillar rheometer is most commonly used to investigate the flow characteristics of granulates, which are extruded through a capillary at controlled temperature.

In the 'Spiral Test' an injection-moulding form with an inlaid spiral of either square, circular or crescent shape is used. The better a material flows, the longer the spiral. Since the spiral length depends greatly on machine and processing parameters, this test is valuable only as a method of comparing materials under identical test conditions.

Tests of moulded samples

Mechanical tests of synthetics are performed on test samples which are produced specifically for the experiment which is to be performed. The test parameters like the environmental conditions or test speed must be determined in order to measure particular characteristics appropriate to the applied load in usage. For a tensile test, specific norms can be applied, depending on the material used. For example, the force-deformation behavior under uniaxial tension is tested according to DIN 53455. A test specimen is fixed with clamps in a tension-testing machine and uniaxially deformed at constant speed until failure. The resulting force and the deformation of the test sample are recorded. The tensile test provides insight into the force-deformation behavior under uniaxial tension. The results are most useful as a means of controlling quality, as well as initial comparison of characteristics.

EXPERIMENTS

To test the influence of disintegration parameters and additives on the characteristics of granulates as well as on the characteristics of injection-moulded samples different samples of granulates were produced. The granulates were conditioned and characterized by capillar extrusion tests. From the conditioned granulates also test specimens were produced by injection moulding and characterized by tensile tests.

Production of granulates

Fourteen different granulates were produced in a pilot plant from apple discard as shown in Fig. 1 according to experimental designs (Table 1). Granulation was achieved with the use of a conical twin screw extruder (Cincinnati Milacron CM 45).

In design No. 1, disintegration conditions have been investigated with focus on the acid concentration. Here, the two most important factors (acid concentration and temperature) were tested at two levels. Other processing parameters as well as the additives were held constant.

In design Nos 2 and 3, the influence of additives on the properties of the granules and injection-moulded samples have been investigated. The additives (filler 1, filler 2 and plasticizer) were biogenous and decomposable, and were added after disintegration and homogenization. The parameters of disintegration (acid concentration and temperature) were held constant at a high level. Fillers 1 and 2 were tested with the plasticizer at two levels. Because the amount of plasticizer could not be controlled exactly at the two levels, the concentration of the plasticizer in the granulate was analyzed after granulation.

Conditioning of granulates

As the characteristics of many materials depend to a great extent on the temperature, humidity, and other environmental factors, it is of importance to take these factors into consideration. For synthetics, the environment is prescribed in DIN 50 014. The granulates were conditioned before each individual experiment by storing them over concentrated saline solution in a desicca-

Table 1. Processing parameters and results of tested samples

Design No.	Sample No.	Disintegration parameters		Additives			Water content of granulate	Capillar extrusion of granulate	Tensile test of injection-moulded samples	
		Acid conc.	Temperature	Plasticizer	Filler 1	Filler 2	W (%)	F210 (kN)	σ_B (kN/mm^2)	ε_B (%)
1	1	0	−1	0·8		1	10·99	1·70		
	2	0	1	0·5		1	11·02	1·45	6·4	6·1
	3	−1	1	0·8		1	11·17	2·20		
	4	1	−1	0·2		1	11·05	1·90		
	5	−1	−1	0·0		1	10·37	2·48		
	6	1	1	−0·4		1	11·73	1·18	4·9	6·9
2	7	1	1	−1·8	−1		10·26	4·15		
	8	1	1	0·9	−1		10·90	1·35		
	9	1	1	−1·0	1		10·29	3·28		
	10	1	1	0·6	1		11·53	1·35	5·6	6·8
3	11	1	1	−0·8		−1	10·53	2·23		
	12	1	1	1·0		−1	12·11	0·90	4·8	8·8
	13	1	1	−0·8		1	11·30	1·65		
	14	1	1	0·8		1	11·37	1·05	7·0	13·3
Reference	PE-LD								10·6	93·0
Replications							2	4	5	5
Standard dev.							0·011	0·03	0·14	0·31

tor at a constant temperature. The absorption of water in the case of the present material is much higher than, for example, in the case of synthetics. Thus the influence of humidity in the air is more important, and the influence of preconditioning is magnified. Pretests using a capillar rheometer indicated that storage in an environment of 50% relative humidity is more appropriate than either 30% or 70%. Thus, a saturated solution of sodium bichromate was chosen for the preconditioning, which gives a relative humidity of 54% in the surrounding air at 25°C. The conditioning time was 6 weeks.

Determination of water content

The water contents of the granulates were determined by storing 5 g (± 1 mg) of each sample in 200 ml water-free methanol at 25°C. The strong hygroscopicity of the methanol caused the water in the material to move into the methanol. By determining the water content of the methanol before and after 3 weeks of storage using Karl-Fischer titration (KF titrator, Mettler DL 18) it was possible to calculate the water content of the granulates.

Capillar extrusion tests of granulates

A capillar rheometer (Zwick 7901) was used in connection with a universal testing machine (Zwick 1362: capillary: length = 235 mm, diameter = 10 mm; nozzle: length = 5 mm, diameter = 2 mm). 10 g (± 10 mg) of conditioned granulate was placed in the heated capillary at 135°C. After 10 min the test plunger was lowered at a rate of 12 mm/min. The resulting force was recorded during extrusion. First the force increased until the sample started to flow and then the force decreased as the sample was extruded out of the nozzle. From the force–time graph (Fig. 2), only the forces at 210 s (F210) were evaluated, because forces before 90 and after 330 s varied owing to uncontrollable actuating factors.

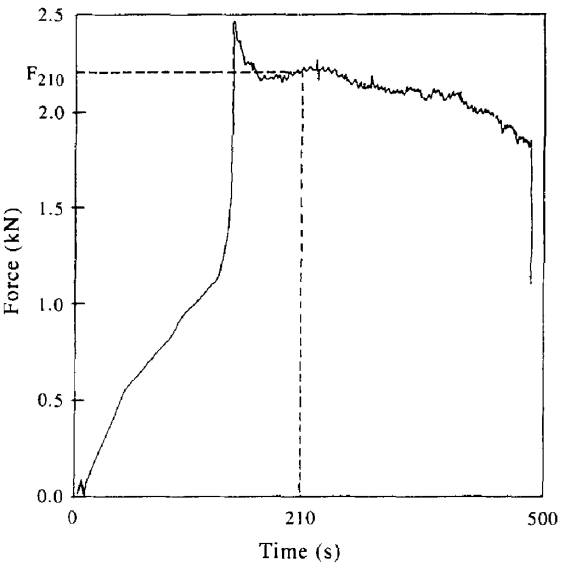

Fig. 2. Typical force–time graph of a capillar extrusion test of a granulate.

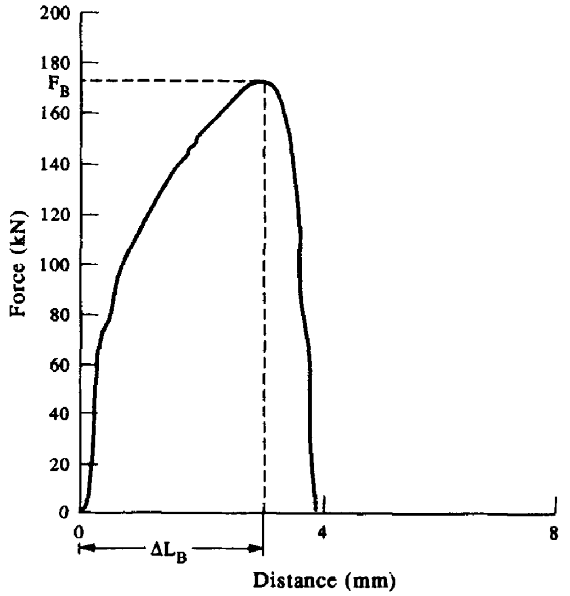

Fig. 3. Typical force–distance graph of a tensile test of an injection-moulded sample. F_B, tensile force at failure; ΔL_B, difference in gauge length at failure.

Tensile tests of injection-moulded samples

From each granulate test specimens have been produced according to DIN 16700 and DIN 53455 using an injection-moulding machine (Engel Austria ES 330/80 HL). The test specimen (rod No. 3) was stored as well as the granulates for 6 weeks in desiccators over a saturated sodium bichromate solution. Then tensile tests were carried out according to DIN 53455 with a universal testing machine (Zwick 1484) at constant speed of 50 mm/min. From the recorded force–distance graph (Fig. 3) the tensile strength ($\sigma_B = F_B/A_o$) and the strain at failure ($\varepsilon_B = 100 * \Delta L_B/L_o$) were calculated, where F_B is the force at failure, A_o the initial cross-sectional area, ΔL_B the difference in gauge length at failure and L_o is the original gauge length of the test sample.

RESULTS AND DISCUSSION

Table 1 shows the average values of the test results. Because the plasticizer, which was present in all samples, could not be adjusted to the exact concentration required by the experimental design, the results have been evaluated by regression analysis in order to calculate the influences of the disintegration parameters and additives.

Capillar extrusion tests of granulates

Influence of disintegration parameters

Figure 4 shows the effects of the acid concentration and disintegration temperature on the extrusion force F210 at the high level of plasticizer. Increasing acid concentrations and increasing disintegration temperature clearly improved the flow. From the contour plot of the regression model (Fig. 5) the possible combinations of acid concentrations and disintegration temperature can be seen, which will yield granulates that can be injection-moulded (F210 less than 1·45 kN).

Influence of additives

Figure 6 shows the effects of plasticizer and filler 1 on the extrusion force F210. Whereas filler 1 shows little effect, increasing the amount of plasticizer improved the flow. From the contour plot of the regression model (Fig. 7) the possible combinations of plasticizer and filler 1 can be seen, which will yield granulates that can be injection-moulded (F210 less than 1·45 kN).

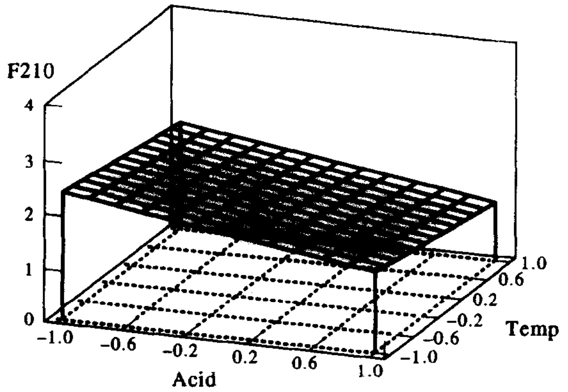

Fig. 4. Influence of the acid concentration and disintegration temperature on the extrusion force (F210) at plasticizer concentration level = 1.

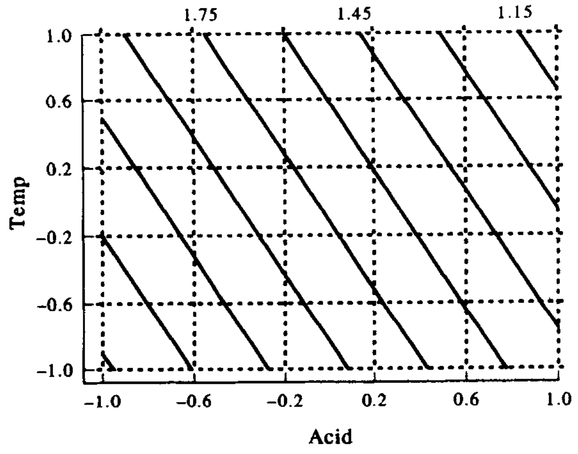

Fig. 5. Contour plot of the model: F210 = 1·86–0·43 (acid) −0·21 (temp) −0·14 (acid × temp) at plasticizer concentration level = 1.

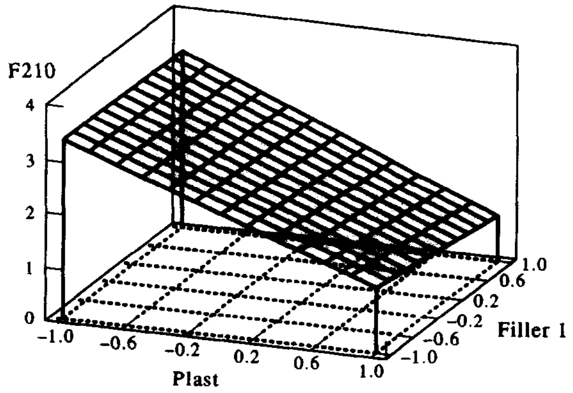

Fig. 6. Influence of the concentrations of plasticizer (Plast) and filler 1 on the extrusion force.

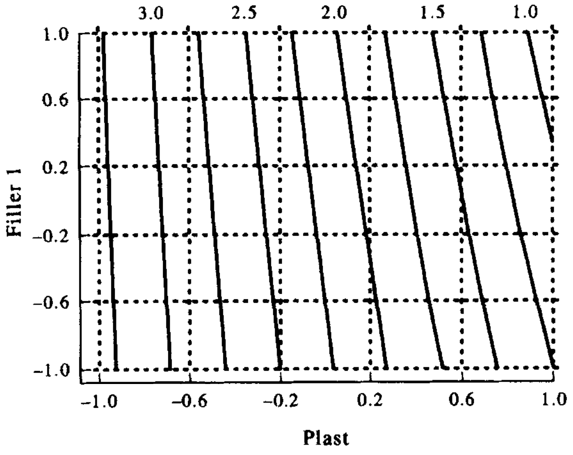

Fig. 7. Contour plot of the model: F210 = 2·18–0·10 (filler 1) −1·12 (Plast) −0·08 (filler 1 × Plast).

Figure 8 shows the influence of plasticizer and filler 2 on the extrusion force F210. Whereas filler 2 shows little effect (similar to filler 1), increasing the amount of plasticizer improved the flow. From the contour plot of the regression model (Fig. 9) the possible combinations of plasticizer and filler 2 can be seen, which will yield granulates that can be injection-moulded (F210 less than 1·45 kN).

Further it can be seen, comparing Figs 6 and 8, that filler 2 gives granulates with a better flowability than filler 1 at low levels of plasticizer.

Injection-moulding tests of granulates

Nine of the 14 analyzed granulates could not be injection-moulded due to poor flow. These samples (with the exception of sample 8) also had high extrusion forces in the capillar extrusion tests. Sample 8, which should have been injection-mouldable according to the values of the extrusion force, could not be fed into the injection-moulding machine. Unfortunately the test could not be repeated as there was no more sample left for testing. Out of these results, however, in the case of this

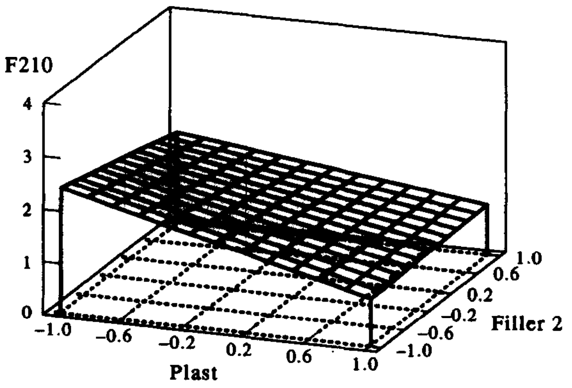

Fig. 8. Influence of the concentrations of plasticizer (Plast) and filler 2 on the extrusion force (F210).

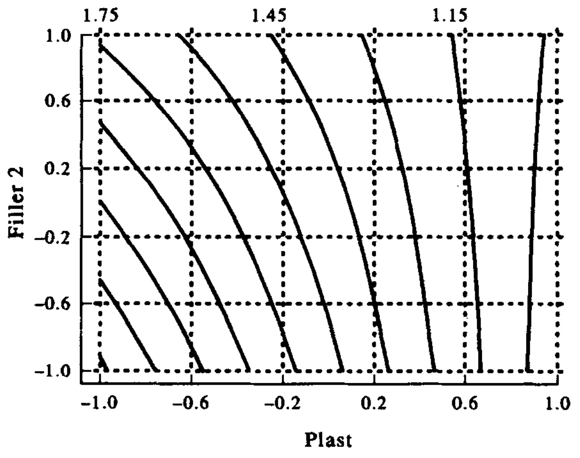

Fig. 9. Contour plot of the model: $F210 = 1{\cdot}49 - 0{\cdot}14$ (filler 2) $- 0{\cdot}56$ (Plast) $+ 0{\cdot}18$ (filler 2 × Plast).

biogenous material we can undeniably draw conclusions about injection-mouldability from the values of the extrusion forces of the capillar extrusion tests.

Tensile tests of injection-moulded samples

Although tensile strength and tensile strain at failure are not affected very much by the used processing parameters even some samples were significantly different at a confidence level of 95% in tensile strength at failure (samples: $2 > 6 = 12$, $6 < 14$, $12 < 10 < 14$) and in tensile strain at failure (samples: $2 < 12 < 14$, $6 < 14$, $10 < 14$). Because of the few samples which could be injection-moulded and because the processing parameters of these few samples are not directly comparable, only few comparisons can be made: at high levels of disintegration parameters the amount of filler 2 (comparing samples 12 and 14), the amount of plasticizer (comparing samples 6 and 14) and filler 2 compared with filler 1 (samples 10 and 14) seemed to increase tensile strength and tensile strain at failure.

Further the tensile strength at failure of the tested biogenous materials is about half the value of low density polyethylene (PE-LD). Compared with other synthetics, however, the values of PE-LD are very low. The tensile strain at failure of the biogenous materials is much less compared with PE-LD.

CONCLUSION

The object of this project was to determine appropriate methods for testing the characteristics of a biogenous thermoplastic material, and thus to gain insight into the influence of process parameters on the characteristics of this material.

In order to test the process parameters, two important factors were chosen. The acid concentration was set at three different levels and the disintegration temperature was set at two levels. In order to test the additives used in the production of the granulates, two types of filler (fillers 1 and 2) were tested in combination with a plasticizer at two levels and constant processing parameters. The used additives were biogenous, degradable materials and were added after disintegration and homogenization.

In order to ensure repeatable conditions, the granulates were conditioned at constant water activity levels (sodium bichromate: 54% relative humidity at 25°C) for 6 weeks. The water absorption of this biogenous material was much higher than that of synthetics. Thus the influence of relative environmental humidity is much greater, and the importance of preconditioning increases. In pretests using the capillar rheometer, it was determined that samples stored at 54% relative humidity had flow curves that could be easily evaluated.

After extensive pretesting, a valuable method for testing the flow of the granulates could be found by using the capillar rheometer. The variable measured was the resulting force during extrusion of the material through a nozzle.

Both increasing acid concentration and increasing disintegration temperature improved flowability. The acid concentration affects the extrusion force more than the disintegration temperature (Fig. 4).

Whereas increasing concentrations of the plasticizer improved the flow the concentrations of the fillers had little effect. However, it is important to note that the type of filler can effect flow at low levels of plasticizer (Figs 6 and 8). This would seem to indicate that the plasticizer and filler 2 are at least to some degree substitutable, which would be important for future determination of content requirements for production.

Nine of the 14 granulates could not be injection-moulded due to their poor flow characteristics. Interestingly, these granulates showed high forces during extrusion in the capillar rheometer. This result is a clear indication that the extrusion force can be used to draw conclusions about the injection mouldability of a biogenous material.

Tensile tests are able to give insight into the force–deformation behavior of the injection-moulded samples under uniaxial load. The measured parameters are not affected very much, but in some cases are significantly by the processing parameters used. Therefore, this test would be able to determine characteristics of injection-moulded samples.

In conclusion, it is evident that a biogenous raw material such as apple discard can be transformed into a thermoplastic material and injection-moulded. Further, it is possible to use standard methods for synthetics testing in order to determine the functional characteristics of this biogenous material. Injection-moulded products from food industry waste could make a small contribution to current efforts to replace synthetic polymers with biogenous polymers. This would be a small step in the right direction, for in the future biogenous raw materials will have to be used. Even now, rare and valuable fossil-based raw materials should be used only for purposes for which biogenous raw materials cannot be used.

ACKNOWLEDGEMENTS

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