University of Groningen

Material properties and glass transition temperatures of different thermoplastic starches after extrusion processing

Janssen, Léon P.B.M.; Karman, Andre P.; Graaf, Robbert A. de

Published in:
Starch-Starke

DOI:
[10.1002/star.200390020](https://doi.org/10.1002/star.200390020)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2003

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Janssen, L. P. B. M., Karman, A. P., & Graaf, R. A. D. (2003). Material properties and glass transition temperatures of different thermoplastic starches after extrusion processing. *Starch-Starke*, 55(2), 80 - 86. <https://doi.org/10.1002/star.200390020>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Robbert A. de Graaf^a,
Andre P. Karman^b,
Léon P. B. M. Janssen^b

Material Properties and Glass Transition Temperatures of Different Thermoplastic Starches After Extrusion Processing

^a Akzo Nobel, Safety Services, Deventer, The Netherlands

^b Rijksuniversiteit Groningen, Technische Scheikunde, Groningen, The Netherlands

Four different starch sources, namely waxy maize, wheat, potato and pea starch were extruded with the plasticizer glycerol, the latter in concentrations of 15, 20 and 25% (w/w). The glass transition temperatures of the resulting thermoplastic products were measured by Dynamic Mechanical Thermal Analysis (DMTA). Beside mechanical and structural properties also the transition temperatures of the materials were evaluated during tensile and impact tests. Above certain glycerol contents, dependent on the starch source, a lower glass transition temperature T_g resulted in decreased modulus and tensile strengths and increased elongations. Lowering the T_g at different glycerol contents did not influence the impact strength. When the amylose/amylopectin ratio increased a decrease in T_g was found. For pea, wheat, potato and waxy maize starch the T_g was 75 °C, 143 °C, 152 °C and 158 °C, respectively. Therefore products with higher percentages of amylose are more flexible. The shrinkage of the specimens made by injection molding was considerable compared to the specimens made by pressing.

Keywords: Potato starch; Wheat starch; Waxy maize starch; Pea starch; Glass transition temperatures; Extrusion; Plasticizing

1 Introduction

Environmental awareness of the consumers strongly stimulates the introduction of biodegradable materials based on renewable resources of natural origin. In recent years major research has been performed on a special group of natural materials, the starch based plastics [1, 2]. Using polymer technology designed for synthetic polymers, it should be possible to produce starch plastics that are a supplement to the existing synthetic products. Still starch plastics are not widely introduced as consumer goods due to some major drawbacks. One of the main problems of starchy material is its brittleness. This brittleness is caused by the relatively high glass transition temperature (T_g) and a lack of the so-called sub- T_g main-chain relaxation areas [3]. When stored, this brittleness even increases due to retrogradation and volume relaxation processes. During the retrogradation part of the starch recrystallizes. This process can be divided into two parts. The recrystallization of the amylose component is an irreversible and very fast process. However, the reversible crystallization of amylopectin is slower. So the retrogradation can be referred to as the long-term recrystallization of the amylopectin component [4]. This spontaneous recrystallization process is caused by the tendency of macromolecules to form hydrogen bonds under expul-

sion of water molecules or other solvents [5]. The retrogradation and volume relaxation also causes another problem, namely shrinkage. Dependent on the processing technology, these phenomena can last for a few weeks with a total shrinkage of more than 10%.

The T_g is an important and measurable parameter giving information about the retrogradation behavior. Besides that, the T_g is of great importance for the mechanical properties of the material. Beneath the glass-transition the material forms an amorphous, 'frozen' liquid structure with a stiff and brittle behavior. Below its T_g the intermolecular bonds are not broken due to the little room left for Brownian movement as is stated by Eyrings 'free volume theory' [6]. The specific volume increases relatively slowly with an increase in temperature. At the T_g the cohesive forces decrease drastically, the polymer expands and the free volume increases to such an extent that there is room for migration of segments, which contain about 20 to 40 monomer units. The polymer now starts to flow, its characteristics being determined by the temperature increase above T_g and the crystalline structure, if any. The free volume is equally distributed throughout the material and in rest the movements of the segments are random. However, when an external stress is applied, the segment migration will no longer be random but occur in that direction, which tends to relieve the applied stress and the polymer shows a rubbery behavior. A sub- T_g (glass transition temperature occurring at a lower temperature than expected) is in general of great importance to the impact

Correspondence: Robbert A. de Graaf, Akzo Nobel, Safety Services, Zutphenseweg 10, 7400 AA, Deventer, The Netherlands. e-mail: Robbert.deGraaf@akzonobel.com.

strength of the glassy polymer; it offers the possibility to dissipate energy in situations of shocks on a short time scale, so the polymer is less brittle. A sub- T_g can be caused by the release of limited motion possibilities in parts of the main chain or lateral groups or it is caused by the presence of a second, smaller polymer. Sub- T_g 's always occurs at lower temperatures than main T_g 's.

Addition of plasticizers such as water, glycols, sugars and amides will lower the T_g and make the starch more rubber-like. Plasticizers act by spacing out the molecules and reducing the interactions. Efficient plasticizers generally have low viscosities and low temperature coefficients of viscosity. This is expected from theories of T_g based on free volume concepts since free volume and viscosity are related. A plasticizer is often a polymer with a low molar mass and consequently a greater free volume. Because of this, polymer chains will have an increased mobility and thus the T_g shifts to lower temperatures, resulting in a less brittle polymer. An important requirement is that the plasticizer is perfectly mixed on a molecular scale, such that the plasticizer is homogeneously blended in the polymer, or the polymer in the plasticizer. The resulting T_g of such a homogeneous mixture is given by the following equation [7]:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (1)$$

where T_g is the glass-transition temperature of the blend, T_{g1} that of polymer 1 and T_{g2} that of polymer 2, respectively, W is the weight fraction. Plasticizers may also serve another purpose, they decrease the melt viscosity. The lower the melt viscosity, the easier the material may be processed or fabricated at lower temperatures. Furthermore the plasticizer should have a high boiling point to avoid its evaporation during further processing and storage of the final product [8]. Besides plasticizer features also starch properties, like the amylose/amylopectin ratio, have influence on the final material. As mentioned before, amylose and amylopectin recrystallize in a different way. Amylose will form the more crystalline- and amylopectin the amorphous part of the thermoplastic, the opposite behavior is found in the starch granule. The source of the starch determines the ratio and the molar mass distribution of amylose and amylopectin and consequently, the properties of the thermoplastics made out of it [7].

This paper describes and discusses the effects and relations between the plasticizer, the amylose/amylopectin ratio and the mechanical properties of four starches from different sources: potato, pea, wheat and waxy maize. Besides an overview of the properties, this finally has to lead to more insight in the behavior of starch materials during processing.

2 Experimental

2.1 Extrusion of thermoplastic starch

Thermoplastics are extruded from four starches together with different amounts of glycerol. The used potato starch (Avebe, Veendam, Netherlands) is food grade and has a moisture content of 13% (w/w). The pea starch originating from Parrheim foods (Manitoba, Canada) is also food grade and contains 9% (w/w) moisture. Cerestar Benelux BV (Sas van Gent, Netherlands) delivered the waxy maize starch with 9% (w/w) moisture. The wheat starch was supplied by Cerestar Germany (Krefeld) and contained 8% (w/w) moisture. The amylose/amylopectin ratios (information obtained by the starch suppliers) of the starches are represented in Tab. 1.

Starch was added to an intermeshing co-rotating twin-screw extruder (APV Baker MPF-50, Peterborough, UK), equipped with a double, round die opening of 3 mm. The APV has a length/width ratio of 25/1 and consists of 10 heating sections. The screws were constructed with transport, kneading (30°) and pressure elements in the following order: 9D transport - 1D kneading - 5D transport - 2D kneading - 3D transport - 5D pressure. Glycerol (0.3% w/w water and technical grade, Chemproha, Dordrecht, Netherlands) was added 10 cm downstream from the starch feed. The starch was gelatinized using a screw speed of 110 rpm and a linear increasing wall temperature varying from 45 – 150 °C from the feed zone to the die. The processed material was subsequently chopped to granulate, after which test specimens were produced by injection molding and pressing. To pea starch, an extra amount of water ($\pm 10\%$ with respect to the starch throughput) had to be added, to avoid degradation during extrusion. The obtained products were immediately packed in airtight bags and stored in a dark cool surrounding. The products were analyzed within two days.

Tab. 1. Extrapolated glass transition temperature and related amylose/amylopectin ratios of the used starches, according to *de Graaf* [15] and *Whistler* et al. [16].

Source of origin	T_g extrapolated from Fig.2 [°C]	Amylose/ amylopectin*
Pea	75	2 : 1
Potato	152	1 : 4
Wheat	143	1 : 4
Waxy maize	158	1 : 99

* Information from starch suppliers.

2.2 Analyses

2.2.1 Mechanical testing

Specimens, with a shape according to ASTM- D 638, were prepared using an injection molding machine from Arburg BV (Nieuw-Vennep, Netherlands) (Allrounder type 221-55-250). The injection molding temperatures were 150 °C. The obtained products were immediately packed in airtight bags and stored in a dark cool surrounding. The water content of all test specimens used varied a little around 9–10 % w/w moisture. In case of pea and potato starch a higher moisture content was found (around 12–13 %, w/w).

An Instron Corporation model 4301 (Canton, Massachusetts) with clamps of 5.0 kN, operating at a grip distance of 23.0 mm and a crosshead speed of 10.0 mm/min was used for tensile tests. At least five specimens of each type of material were tested.

Impact tests were done with specimens, according to ASTM- D 256-56 unnotched, which were made on a press at ± 150 °C under 30×10^3 N/m². The unnotched type was used because of the brittleness of some materials, which made notching impossible. A Cantilever Beam (Izod type) impact machine from Zwick Materialprüfung with hammers exerting an impact from 0.5–4.0 J was used for the impact tests. Unnotched specimens of some synthetic polymers (PS, PP, LDPE and HDPE) were also tested for comparison. At least ten specimens of each material type were tested

2.2.2 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic Mechanical Thermal Analysis tests were used to measure the glass transition temperatures of the batches. With this technique the modulus of a polymer can be monitored against the frequency of an oscillating deformation of a sample bar at different constant temperatures. For a viscoelastic polymer two moduli can be distinguished, a storage modulus E' , which is related to recoverable elastic energy, stored in the sample and a loss modulus E'' , related to deformation energy dissipated as heat of friction. Both moduli will show a decrease around the glass transition temperature and the dissipation factor (damping), $\tan \delta = E''/E'$, will give a peak around phase transitions. The temperature at which this occurs is referred to as the glass transition temperature [9] Actually, the conventional T_g is 5 to 15 °C higher than the temperature of maximum damping [10]. The used analyzer was from Rheometric (Piscataway, NJ, type: Solids analyzer RSA II). The specimens were made by pressing and had a width of 6 mm and a thickness of 1.5 mm. During

Fig. 1. Plots of the DMTA tests for potato (◆), wheat (■), waxy maize (▲) and pea starch (×) with a glycerol content of 15%.

testing, the temperature of the sample was raised with 2 °C/min and the angular frequency was 6.28 rad/s.

3 Results

3.1 Glass transition temperature

The influence of the amylose/amylopectin ratio and the amount of glycerol on the glass transition temperature T_g was determined by comparing the results of thermoplastic starches made from various sources with three different percentages of glycerol (15, 20 and 25%, w/w).

Fig. 1 shows broad $\tan \delta$ peaks for starches with 15% glycerol. The products with 20 and 25% glycerol, that are not illustrated, show comparable characteristics. A broadened transition region diminishes the temperature sensitivity of the mechanical material properties. This broadening is caused by heterogeneity [10] in the tested material. Increasing the glycerol content decreases this broadening. The broadening increases when the amylose/amylopectin ratio increases (Fig. 1). This means that a certain extent of heterogeneity exists between amylose and amylopectin, thus glycerol not only acts as a plasticizer but also as a solvent in which both amylose and amylopectin dissolve, forming a more homogeneous mixture. The measurement is not smooth any more after passing the T_g . High amylose starch (pea) will break down less quickly than high amylopectin starch (waxy maize) indicating increased temperature processibility of the former. Thus the temperature region between the T_g and the flow point will increase for materials containing higher percentages of amylose. This difference in heat resistance can be con-

Fig. 2. Glass-transition temperature of potato (♦), wheat (■), waxy maize (▲) and pea (X) starch as a function of the glycerol content. The drawn lines are trend lines.

tributed to the irreversible retrogradation of amylose in contrast to the reversible retrogradation of amylopectin. The initial rate of development in stiffness of starch gels after gelatinization is dependent on the botanical source and the amount of amylose solubilizing during gelatinization. This initial crystallization is not reversed on heating to 100 °C. However, there is also a long-term increase in gel stiffness, which is thermally reversible below 100 °C and which can be attributed to amylopectin crystallization [11]. This is the reason why waxy maize can be processed at lower temperatures compared to pea starch, because it already flows at lower temperatures.

Fig. 2 shows the glass transition temperatures in dependence on the glycerol content. It is clear that the T_g decreases in the order waxy maize > wheat > potato > pea

starch and with regard to the glycerol content in the order 15% > 20% > 25%.

Products containing a higher amount of amylopectin (waxy maize) have higher T_g 's than materials with less amylopectin (pea). The lower molar mass of amylose and its lack of branches results in a greater free volume of pea starch so that (parts of) the chains can move more easily. This explains the lower T_g of amylose compared to the branched amylopectin, so materials with a higher amylose weight fraction will give a lower T_g .

It can be expected from Equation 1 that glycerol lowers the transition temperature. Characteristically, the T_g of an undiluted polymer is much higher than that of a typical low molar mass, glass-forming diluent. As the diluent concentration of a solution is increased, the T_g decreases monotonically, because the average molar mass of the homogeneous polymer-plasticizer mixture decreases, and its free volume increases [11]. The small plasticizer molecules make chain movements easier. The greatest effect of glycerol is shown for waxy maize, so glycerol has a greater impact on materials containing more amylopectin. This effect can be explained by the fact that the T_g 's of amylopectin and glycerol are more different from each other than those of amylose and glycerol. Extrapolation of the glycerol content in the starch mixtures to zero result in an approximation to the T_g of the pure starch. These T_g 's are listed in Tab. 1.

3.2 Tensile tests

Fig. 3 shows different stress-strain behaviors, depending on the percentage of glycerol and the starch source. For a low content of glycerol (15%) the sample breaks brittle for potato, wheat and waxy maize; for the latter material

Fig. 3. Stress-strain diagrams of potato, waxy maize, pea and wheat starch.

the sample even fractures while the stress is still increasing. This occurred despite the fact that glycerol lowered the T_g of these materials compared to the pure starches, obviously this decrease was not sufficient to make them flexible. With higher percentages of glycerol and for pea starch in all cases, a stress maximum is observed together with a clearly higher elongation. High glycerol amounts decrease the stress. The stress maximum is less dominant or not observed at all. At a temperature of 20 °C and a low glycerol content the materials with a higher amylopectin percentage are far below their T_g . Therefore, the chain mobility is very low and the samples show a brittle stress-strain behavior. Pea starch, which has a much lower percentage of amylopectin and therefore a lower T_g , is more flexible.

At higher glycerol/starch ratios the starch chain mobility increases as the glycerol molecules weaken the inter-chain hydrogen bonding. The T_g is lowered, approaching the usage temperature. The starch chains can adapt to the applied stress and the possible elongation increases, because the chain mobility is increased. If the T_g is lowered below 20 °C, no stress maximum is observed at all because the movements of chain are facilitated again to lead to lower stress and larger elongation [6].

Fig. 4 shows the mean tensile strength and elongation as a function of glycerol content for the four different sources of starch at 20 °C and a humidity of 50%. The course of the modulus against glycerol content is not illustrated, as this is comparable to the tensile strength. The modulus varies from 900 MPa for waxy maize with 15% glycerol to 7.3 MPa for pea starch with 25% glycerol.

It is obvious that pea starch has a low tensile strength and modulus, which steadily decreases with increasing percentage glycerol. Besides that, the pea starch product shows a large elongation at break as already observed in the plots. The relatively large content of linear amylose molecules makes that the entanglement between the chains is not very strong, so they will slide easily along each other with low stress and large elongation. The maximum tensile strength and modulus, obtained with 15% glycerol, can be compared with that of LDPE (10 MPa), the elongation at break with polypropylene (250%).

The starches of potato, wheat and waxy maize became very brittle at low levels of glycerol (15%). This results in a modulus between 700 and 900 MPa, comparable to HDPE, and a tensile strength around 35 MPa, which is equal to the value for polystyrene. The higher content of amylopectin makes that the chains, because of the branched structure, are less ordered and therefore have a greater degree of entanglement, causing a brittle fracture with a higher stress. Glycerol gives the chains more mo-

Fig. 4. Tensile strength and elongation of potato (X), wheat (■), waxy maize (▲) and pea (◆) starch after 1 day as a function of glycerol content.

bility and because of this the interactions between the chains are lowered. This is the reason why the tensile strength and modulus decreases and the elongation increases with increasing glycerol content. Looking at the tensile strength, a smaller effect of glycerol is observed for pea, the high amylose starch, compared to the other starches with a relatively lower amylose content.

The difference in tensile strength between potato and wheat starch, where the amylose/amylopectin ratios are nearly the same, can be explained by the difference in moisture content. The higher moisture level in potato (13%) compared to wheat (9%) will lower the T_g and consequently the tensile strength [12]. However, it is not directly explainable why the tensile strength of wheat is higher than that of waxy maize starch in spite of the considerably lower amylopectin content. More research should be performed to confirm this conclusion.

The aging of starch is illustrated in Fig. 5 on the basis of waxy maize and pea starch. As can be seen, modulus and tensile strength increase, whereas the elongation decreases with time. The assumption is that the starch retrogrades further during storage. Recrystallized amylopectin acts as physical cross-links and increases the strength and decreases the elongation [13].

3.3 Impact strength

As depicted in Fig. 6, the impact strengths of all samples are very low and around the impact strength of PS. Again, the effect of the glycerol is quite obvious; the impact

Fig. 5. Aging of waxy maize (▲) and pea (X) starch reflected by the tensile strength and elongation after 1 day (—) and after 21 days (---) as a function of the glycerol content.

Fig. 6. Impact strength of potato (◆), wheat (■), waxy maize (▲) and pea (X) starch as a function of glycerol content.

strength increases with glycerol contents. The T_g is lowered by glycerol, as could be expected from Equation 1, and this is of great importance for the impact strength. The T_g indicates the temperature from where the polymer can react on deformations; below the T_g it is a stiff and often brittle material. In our case the T_g decreases which means that the polymer toughness and impact strength should increase.

There is a large difference in behavior on slow deformations as in the tensile tests with a movement of 10 mm per minute, and deformations on a short time scale, like the impact tests. For instance potato starch with 20% glycerol and a T_g of 57 °C is very flexible, also illustrated by the elongation of 40% during the tensile tests, and nevertheless has a very low impact strength. The same phenomenon occurs for potato, wheat and waxy maize with 25% glycerol and pea with 15, 20 and 25% glycerol. The assumption is that the broad peaks of $\tan \delta$, generated by the DMTA tests, are the basis of this phenomenon. With a peak around 57 °C, the T_g of potato starch with 20% glycerol is far above the temperature of testing, which is 20 to 25 °C. However, $\tan \delta$ already increased before the test temperature. On the acclivity of $\tan \delta$ there is a matter of limited mobility of the chains. This is apparently enough to distort the material during slow deformations, like bending and the tensile tests, but deformations on a short-time scale, as impact tests are, will cause a brittle fracture at this point.

3.4 Shrinkage

The sample bars made by injection molding change in size during storage. In the injection direction there is an obvious shrinkage and in the direction perpendicular to it, an increase in size is detectable. In Fig. 7 the results of the shrinkage of the sample bars after 1 week are shown. No further shrinkage was measured after this period.

At lower glycerol contents (15%) there is hardly any shrinkage of starch with a higher percentage of amylopectin. So it can be concluded that the chains need a

Fig. 7. Shrinkage in the injection direction of the injection-molded specimens after 1 week for potato (◆), wheat (■), waxy maize (▲) and pea (X) starch as a function of the glycerol content.

certain amount of plasticizer, which enables the relaxation process. When the starch contains more amylose, a lower amount of glycerol is necessary due to the more mobile linear amylose chain.

The injection of the polymer in the mould induces an elongation flow [14] and consequently, the chains of the polymers are orientated in the injection direction. Therefore the chains are in a stretched conformation and lie parallel to each other. When the injection is stopped, reorientation starts and the chains realign in a helix configuration. This explains the shrinkage in the injection direction and the swelling in the width. Besides that, retrogradation will also cause shrinkage by the forming of hydrogen bonds between the chains with repulsion of water molecules.

As expected, the shrinkage is faster at increasing glycerol fraction. This is due to the decreased local viscosity and concomitant increased mobility of the chains, which makes a faster relaxation possible.

The shrinkage of waxy maize takes much more time than that of the other starches. The large amount of amylopectin makes that the chains are more entangled, which causes a lot of interactions and consequently a limited freedom to move compared to starch with a higher amylose content. Finally it can be stated that the specimens made by pressing do not shrink to the degree as the injection molded specimens. During pressing there's no elongation flow present, resulting in less relaxation of the chains.

4 Conclusion

Glycerol tends to decrease the glass transition temperature of extruded starches and narrow the transition region. However, with glycerol contents up to 25%, the T_g is not lowered below 20 °C for the used starches. The lower T_g 's cause an increase in impact strength but with glycerol contents of 15 to 25% this increase remains quite low (up to 15 kJ/m²). The modulus and tensile strength decrease while the elongation increases with glycerol content. The same effect is noticeable in case of the amylose/amylopectin ratio of the starches; an increase of the ratio lowers the modulus and tensile strength and increases the elongation.

The shrinkage of thermoplastic starch products made by injection molding is considerable for the ones with glycerol contents above 20%. This shrinkage is caused by the elongation flows during injection.

References

- [1] R. A. de Graaf, L. P. B. M. Janssen: The production of a new partially biodegradable starch plastic by reactive extrusion. *Pol. Eng. Sci.* **2000**, 34, 2-10.
- [2] R. A. de Graaf, L. P. B. M. Janssen: Properties and manufacturing of a new starch plastic. *Pol. Eng. Sci.* **2001**, 41, 3-12.
- [3] J. W. Donovan: Phase transition of the starch-water system. *Biopolymers* **1979**, 18, 263-275.
- [4] J. J. G. van Soest: Ph. D. Thesis University of Utrecht, The Netherlands, 1996.
- [5] I. I. Rubin: *Injection Moulding: Theory and Practice*, John Wiley & Sons, New York, **1972**.
- [6] H. G. Bader, D. Göritz: Investigations on high amylose corn starch films, part 3: stress strain behavior. *Starch/Stärke* **1994**, 46, 435-439.
- [7] O. B. Wurzburg: *Modified Starches: Properties and Uses* (Ed. O.B. Wurzburg), CRC Press, Boca Raton, FL, **1986**.
- [8] L. Slade, H. Levine: Thermoplastic Starches. *Carbohydr. Polym.* **1993**, 12, 105-109.
- [9] G. Challa: *Polymer Chemistry: an Introduction*, Ellis Horwood, Chichester, **1993**.
- [10] L.E. Nielsen: *Mechanical Properties of Polymers*, Chapman & Hall, London, **1963**.
- [11] M. Gudmundsson, A. C. Eliasson: Retrogradation of amylopectin and the effects of amylose and added surfactants/emulsifiers. *Carbohydr. Polym.* **1990**, 13, 295-315.
- [12] R. L. Shogren, G. F. Fanta, W. M. Doane: Development of starch based plastics, A reexamination of selected polymer systems in historical perspective. *Starch/Stärke* **1993**, 45, 276-280.
- [13] R. L. Shogren, C. L. Swanson, A. R. Thompson: Extrudates of corn starch with urea and glycols; structure/mechanical property relations. *Starch/Stärke* **1992**, 44, 335-338.
- [14] M. Walker: *Injection Moulding of Plastics*, Iliffe Books Ltd., Oxford, **1966**.
- [15] R. A. de Graaf: Ph. D. Thesis RU Groningen, The Netherlands, 1996.
- [16] R. L. Whistler, E. F. Paschall: *Chemistry and Technology II Industrial Aspects*, Academic Press, New York, **1967**.

(Received: February 12, 2001)

(1st Revision received: March 30, 2002)

(2nd Revision received: December 1, 2002)