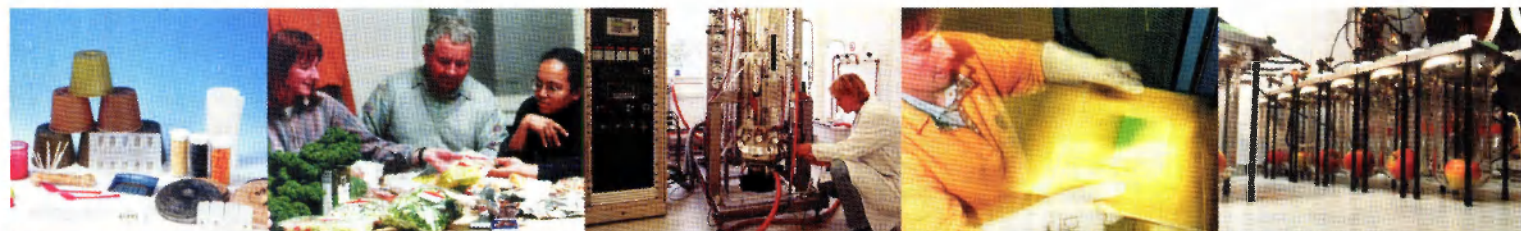


Report
Ref.nr. OPD 00/188b/190301

Development of laminates based on starch/PLA combinations

Confidential

G. Schennink
H. de Beukelaer
M. Wevers



Report
Ref.nr. OPD 00/188b/190301

Development of laminates based on starch/PLA combinations

Confidential

G. Schennink
H. de Beukelaer
M. Wevers

**Agrotechnological Research Institute
ATO**

Bornsesteeg 59
P.O. Box 17
6700 AA Wageningen
The Netherlands
Tel: +31.317.475000
Fax: +31.317.475347

2251518

Contents

page

1	Introduction.....	3
1.1	Starch based plastics: recent developments by AVEBE.....	3
1.2	Current commercially available starch/polyester combinations	5
1.3	Scope of the research	5
2	Materials and methods	7
2.1	Materials	7
2.2	Methods	7
2.2.1	Compression moulding.....	7
2.2.2	Filmblowing	7
2.2.3	Thermal properties using Differential Scanning Calorimetry (DSC)	7
2.2.4	Rheology	7
2.2.5	Thermal stability	7
2.2.6	Permeability	8
2.2.7	Mechanical properties	8
2.2.8	Moisture determination.....	8
2.2.9	Sealability testing.....	8
3	Results	9
3.1	Introduction	9
3.1.1	Development of multi-layered structures with PLA.....	9
3.1.2	Analysis of monomaterials	9
3.1.3	Choice of materials; definition of the layer sequence; adhesion aspects.....	9
3.1.4	Coextrusion and analysis of the produced films	10
3.2	Monomaterial PLA.....	10
3.2.1	Thermal properties (DSC)	10
3.2.2	Rheology	11
3.2.3	Thermal stability of PLA's.....	13
3.2.4	Water permeability and mechanical properties	13
3.2.5	Optical properties	14
3.3	Monomaterial starch	15
3.3.1	Reology	15
3.3.2	Water- and oxygen permeability and mechanical properties	15
3.4	Combinations of PLA on starch, or polyesters.....	15
3.4.1	Adhesion of compression moulded laminates.....	15
3.4.2	Sealability of PLA's on polyesters	16
3.4.3	Rheology	17
3.4.4	Coextrusion filmblowing.....	18
3.5	Analysis.....	18
3.5.1	Water vapour permeability	18
3.5.2	Mechanical properties	19
3.6	Summary of PLA materials	19
3.7	Application of the foils.....	20
3.8	Conclusions	20
3.9	Further research.....	21
4	Literature	22
5	Appendices	23

Summary

During the last five years AVEBE developed a thermoplastic material based on starch suitable for multilayered sheets/films. Applications of these films can be found in various areas. One of the most important and promising applications is as packaging material for food products. In this area a packaging material is needed that is transparent and that has specific gas and water barrier properties. Laminates out of suitable materials can fulfill these demands. The combination of starch based materials and poly-lactic-acid is very promising. The gas barrier properties of starch can be combined with the water barrier properties and clarity of poly-lactic-acid. Therefore during the summer of 2000 a project has been defined to "develop a clear, biodegradable food packaging out of renewable materials". One of the first tasks of this project was to perform a feasibility study. This study was performed in January-february 2001.

The most important issue of this study was to deliver a proof of principle concerning PLA/starch based plastics laminates. The results of this feasibility study are described in this report.

For PLA/Starch laminates it is shown that:

- Thin films (50 to 100 μm) of PLA/Starch can be coextruded in which the starch based plastic content can be varied from 25 to 70%
- Four types of PLA were tested: amorphous, (semi-crystalline) thermoform, (semi-crystalline) treated thermoform and rubbery material. For coextrusion processes treated thermoform grade PLA seems best suitable.
- PLA properties:
 - Water vapour permeability: for the tested materials this property varied from 0.1 to $0.15 \cdot 10^{-10}$ gram/m*s*Pa. These values are 3 to 10 times lower than values measured for other commercially available, biodegradable poly-ester materials and are in the range of values stated as goal for this project ($0.05 \cdot 10^{-10}$ gram/m*s*Pa).
 - Viscosities: viscosity behaviour of PLA is similar (same level, same trends) to that of Paragon.
 - Thermal stability: thermal stability of treated thermoform grade PLA is comparable with poly-caprolactone. Stability of this material is considered as sufficient. Thermal stability of other tested PLA-grades is much less.
 - Optical properties: optical properties of tested PLA grades was not sufficient. If possible the materials have to be more transparent.
- Direct adhesion between the PLA and Paragon is not sufficient. With help of a tie layer sufficient adhesion can be realized.
- Surface properties of PLA-film materials have to be modified. Blocking of the film material causes problems during handling on various machinery.

For future research the following (technical) subjects are important:

- Improvement of direct adhesion between PLA and starch based materials.
- Creating a PLA with better optical properties (transparency and haze) than materials used so far.
- Further improvement of water barrier properties.
- Improvement of processability of PLA on film blowing machinery e.g. addition of anti-block and slip agents.

Workplan of this research is summarized in the project proposal as submitted to the SNN

1 Introduction

In the past decade there has been a growing interest in protecting the environment. The abundant use (annually 25 million tons) of plastics in Western Europe in combination with its limited time of application (almost 40% shorter than 2 years) has stimulated the development of environmentally friendly, biodegradable alternatives. Several of such alternatives have successfully been introduced on the market, but a significant market share of, for instance, more than 5 % has not yet been realised.

There are several explanations for this limited success. First of all it should be mentioned that some materials have a limited field of application due to their properties. Materials based on carbohydrates (like ThermoPlastic Starch, TPS), while having in some cases a low price (< 4 DM/kg), are too water sensitive for a large number of applications. Other biodegradable materials, like polyesters, have very good properties, but are somewhat limited in their applications due to the high prices compared with bulk plastics like polyethylene or polypropylene (most of the times 300-1000 % higher in price). Another issue is the rather small scale commercial availability of these poly-esters.

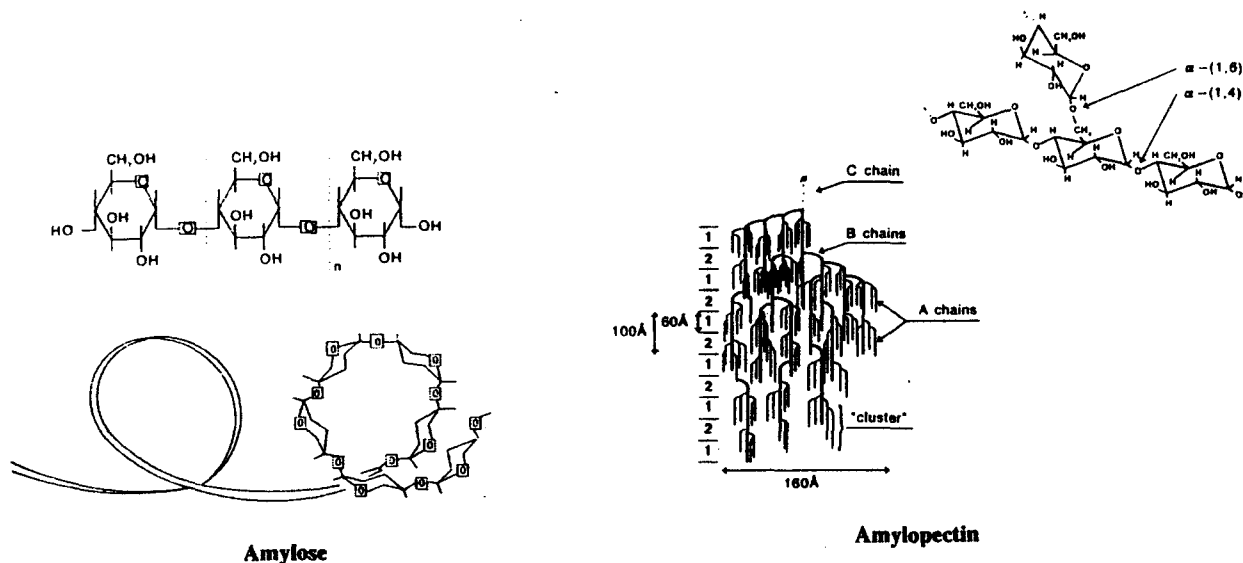
In this report it is described how thermoplastic materials/products can be developed that combine the properties of poly-lactic-acids from Hycail with that of renewables, especially starch. To this extent, several new concepts developed at AVEBE in cooperation with ATO BV, as well as in the field of polymer chemistry in general, are used.

1.1 Starch based plastics: recent developments by AVEBE

Starch is a cheap, naturally occurring polymeric material, and is isolated from cereals and tubers on a very large scale. It is the main energy storage supply in botanical sources. With cellulose, starch is one of the most abundant carbohydrates present in food and feed. As far as starch based plastics are concerned, it is the only industrial scale biopolymer which is cheaper than polyethylene.

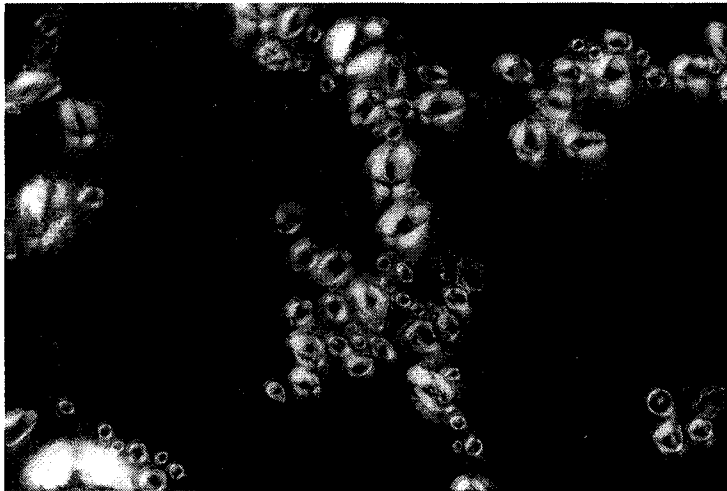
Starch consists of two distinct molecules: amylose and amylopectine, both containing α -D-glucose units. Amylose is a linear polymer, very easily shaped into a single or double helix, with a molecular weight of 10^5 - 10^6 g/mol. On the contrary, amylopectin has a highly branched structure with a molecular weight of 10^7 - 10^9 g/mol. In figure 1 the structure of amylose and amylopectine are schematically shown.

figure 1 The structure of amylose and amylopectine



In native starch, the amylose and amylopectine are locked up in granules (figure 2). The size of these granules are typically between 0.5 and 175 μm , depending on the source. The high molecular arrangement in these granules give rise to birefringence, visually seen as the Maltezer cross.

figure 2 granules in native starch



In order to be processed as a thermoplastic material, the starch in the granules must be converted into the molten and deformable state. This process is referred to as gelatinization. Dry starch will decompose at high temperatures (above 200 $^{\circ}\text{C}$) before the material will be processable. Therefore, water or other plasticizers are added to lower the transition temperature. The resulting material is a cheap, rapidly biodegradable material with a good gas barrier property. It turned out however that thermoplastic processing of starch is somewhat more expensive than the processing of for instance polyolefines. More important, however, appeared to be the water sensitivity of starch based materials. Water acts as a plasticizer, and with changing relative humidities of the air, the properties of such a material can range from rubberlike towards glassy. This is in most applications not tolerable. Only under very well described circumstances it is possible to have a number of niche products. However when the processing properties of these materials are combined with other properties as eatability, interesting markets (e.g. petfood) can be reached.

In order to make starch plastics less sensitive to water, there have been some efforts on the mixing (blending) with hydrophobic polymeric materials. In the first trials polyolefines like polyethylene were applied with a content of about 50-80%. These materials were not completely biodegradable and appeared to desintegrate in the environment. This desintegration lead to an uncontrolled and undesired spreading. These materials have been on the market only for a very limited time period.

After the bad experiences with the polyolefine based starch materials, there were some efforts to make starch blends with polymers like EVOH and PVOH. There was, however, no sufficient product improvement of these materials compared to the products that are fully starch based. Products like these are at the moment still commercially available. There is, however, the disadvantage that the biodegradability of these polymeric materials is not in all cases proven. Furthermore, the price is significantly higher than the synthetic bulk polymers, partially due to the intense marketing activities. It should be kept in mind that fully biodegradable plastics were in the beginning of the nineties a rather new phenomenon and a lot of effort was put in making these products known to companies and the public.

In case of thermoplastic starch, the combination AVEBE/ATO has experience in material research and product development for more than 10 years. The materials developed (free from materials like LDPE, EVOH or PVOH) are fully biodegradable, consist for more than 80 % out of starch (in most cases) and can be processed with several standard techniques e.g. injection moulding.

During the last five years AVEBE developed, in cooperation with ATO BV, a starch based material named Paragon™, especially suitable for coextrusion techniques together with other biodegradable polymers. Paragon consists of a starch-polyester blend, in which the polyester content is low in comparison to other commercially available starch/polyester combinations produced by for instance Novamont. Although the polyester content is low, the developed laminates show good water resistance.

1.2 Current commercially available starch/polyester combinations

Current starch based blends (e.g. marketed by Biotec or Novamont) on the market are mainly using polycaprolactone as a continuous phase. These materials are performing well, are fully biodegradable, but are rather high in price (about \$ 3-6/kg). This is partly caused by the high polycaprolactone content that is needed in order to get a reasonable performance during processing and as a product. Polycaprolactone has been considered to be a given material and it is not specially adapted for blending with starch. Therefore in commercially available products the polyester content is about 70%. The licenses that the companies in the market are paying to the inventors are contributing to the high prices.

1.3 Scope of the research

As mentioned during the last five years AVEBE developed a thermoplastic material based on starch suitable for multilayered sheets/films. Applications of these films can be found in various areas. One of the most important and promising applications, we think, is packaging material of food products. In this area a packaging material is needed that is clear and has to possess specific gas and water barrier properties. Laminates out of suitable materials can fulfill these demands. The combination of starch based materials and poly-lactic-acid is a very promising combination. The gas barrier properties of starch can be combined with the water barrier properties and clarity of poly-lactic-acid. Therefore during the summer of 2000 a project has been defined to “develop a clear, biodegradable food packaging out of renewable materials”. The duration of this project was estimated on 2 years and 8 months. The goal of this project has been translated in the following project deliverables:

1. Multilayer packaging film suitable for cheese
Demands for the laminate:
 - Barrier properties:
 - Oxygen permeability (70 % RH; 23 °C): max. 30 cm³/m² * day * bar * 100 µm.
 - CO₂-permeability (70 % RH; 23 °C): max. 120 cm³/m² * day * bar * 100 µm
 - Waterpermeability (60 → 100 % RH; 23 °C): max. 8.5 gram/m² * day * 100 µm
 - Mechanical properties:
 - Strain at break of the laminate has to be at least 25 %
 - E-modulus has to be in the range of 1000 to 2500 MPa.
 - Tensile strength has to be at least 25 MPa
 - Tear strength has to be enough: > 750 cN/mm (measured according ISO 6383/2 on film of 100 µm)
 - Puncture resistance has to be enough: > 5 J/mm (measured according ISO 7765 – 2 on film of 100 µm)
 - Processing properties:
-

- Processing has to be done on industrial available equipment
- Processing temperatures of all components have to be in a range of 150 – 200 °C; die-temperatures have to be under 150 °C.
- The thickness of the (film) laminates has to be in the range of 30 to 500 microns.
- Good sealability of the film has to be guaranteed
- Laminate consisting of 5 layers is maximum. Preferred is a 3-layer laminate
- Biodegradable/renewable

2. Additional deliverable

Optical properties of the laminate (50 microns): max. 5 % haze and min. 90 % transmittance

To realize such a packaging material the project has been divided in 5 phases:

- Project definition
- Feasibility study
- Material development
- Product development
- Market introduction

With the submission of the project proposal to the SNN in september 2000 the project definition phase was finished. In january 2001 the second phase, feasibility study, started. The most important issue here was to show a proof of principle concerning PLA/starch based plastics laminates.

The results of this feasibility study will be described in this report.

2 Materials and methods

2.1 Materials

ATO Paragon™ SE 1620 and sheets of ATO Paragon™ SE 1500 were supplied by ATO. Tie layer material was supplied by ATO and was dried prior to use at 80°C. PLA's were supplied by Hycail (The Netherlands) and dried prior to use. The types used are:

- PLA amorf (PLA AVEBE 6 dec)
- PLA thermoform (PLA AVEBE 29 nov)
- PLA treated thermoform (PLA AVEBE 23 jan)
- PLA rubber (PLA AVEBE 7 dec)

2.2 Methods

Material processing

2.2.1 Compression moulding

Compression moulding experiments of laminates for adhesion tests were performed on a PHI model 75U12095-2JCS-Y2-S5-7.

Compression moulding temperatures varied from 100-170°C.

For adhesion tests compression moulded PLA films (dried overnight before use in vacuum-oven at 40°C), polyester films and extruded Paragon films (conditioned at 60 or 90%RH) were used.

2.2.2 Filmblowing

Coextrusion experiments were carried out on a BFA coextrusion line with three extruders: A Battenfeld 45 mm extruder (type EX45) for the basic layer and two 30mm Battenfeld extruders for the coating and tie layer. All extruders have a Con-pro KTW-G3 automated feeding system. For processing conditions see appendix 5.

Analysis

2.2.3 Thermal properties using Differential Scanning Calorimetry (DSC)

DSC experiments were conducted on the Perkin Elmer series DSC 7. The temperature range used for the PLA's was -50°C up to 200°C.

2.2.4 Rheology

Rheological experiments were carried out on a Rosand Automated Capillary Rheometer RH7-2 with two 12 mm barrels. The die used was 16*1 mm. Temperatures varied from 100-175°C. Before measuring the material is heated in the barrel for 6 minutes.

2.2.5 Thermal stability

Thermal stability experiments were carried out on a Rosand Automated Capillary Rheometer RH7-2 with two 12 mm barrels. The die used was 16*0.5 mm. Temperatures varied from 165-175°C. Before measurement the material was heated in the barrel for 9 minutes to melt.

2.2.6 Permeability

Water Vapour Transmission Rates (WVTR) were measured according to ASTM E96-80. A thin film was clamped on a water reservoir (16.62 cm² surface). By measuring the film thickness and the water loss through the film, the WVP (in g/m².day) could be calculated (20°C). The RH inside the reservoir was 100% and outside 60% RH. Demineralised water was used. WVTR were measured using single PLA films.

2.2.7 Mechanical properties

Mechanical properties were measured according to ISO 6239. Prior to measuring all samples were conditioned at 60%RH, 90%RH and put into water for one week.

2.2.8 Moisture determination

The moisture content of granules was measured by a Sartorius MA-40 infrared dryer. Prior to measuring the granules were powdered in liquid nitrogen and sieved by a 212-micron sieve. The measurements were done at 95°C.

2.2.9 Sealability testing

Sealability testing was performed on compression moulded plates of PLA and foils of various polyesters. The tests were conducted on a pressure driven seal apparatus (pressure=4.7bar). Seal (heating characteristics when sealing) and cool parameters (cooling characteristics during sealing process) were changed between the experiments.

3 Results

3.1 Introduction

3.1.1 *Development of multi-layered structures with PLA*

The use of a multi-layered laminate which consists out of a combination of PLA and a starch based material is one of the possibilities to make optimal use of the advantages of these materials. The starch layer can act as the gas barrier, whereas PLA makes the laminate water barrier. After the demands of the laminate has been defined (as listed in paragraph 1.3) the development can start.

During such a development, several stages of research can be identified:

- Step 1: Determination and making an overview of most important properties of PLA and Paragon possibly used
- Step 2: Choice of the exact materials to be used; definition of the layer sequence; adhesion aspects.
- Step 3: Coextrusion and analysis of the produced films. In this case we tested a several applications of the created films too.

3.1.2 *Analysis of monomaterials*

In this project 4 PLA's were delivered by Hycail to use during the filmblowing experiments. Several analysis were performed to determine the most important properties of these materials.

- Thermal properties (Differential Scanning Calorimetry (DSC))
- Rheology
- Thermal stability
- Water permeability
- Mechanical properties
- Optical properties

3.1.3 *Choice of materials; definition of the layer sequence; adhesion aspects*

In general 3 types of layers can be defined:

- basic layers.
This is the layer that determines the mechanical properties. In this case starch was chosen as the basic layer. At the same time this layer is the oxygen barrier
 - coating layers
layers, developed for special purposes. In this case PLA will be the coating layer and functions as a water barrier.
 - tie layers
in most cases the adhesion between the basic material and the barrier material is very poor. A special polymerblend with good adhesion properties has been developed to join the different layers.
-

Adhesion aspects are very important in multilayered laminates. In general different polymers don't adhere to each other. Therefore much effort is put in determination of the adhesion properties between Paragon and PLA. These tests are performed with compression moulding and seal equipment.

3.1.4 Coextrusion and analysis of the produced films

The coextrusion experiments are the most important part of this feasibility study. As described in the experimental part these experiments has been performed with a five layer BFA film blowing coextrusion line. To estimate the value of these films for practice several properties of these films are determined such as mechanical properties and water vapour permeability.

3.2 Monomaterial PLA

In this report the PLA materials were renamed from their original codes as follows:

- PLA (7 dec) : PLA rubber
- PLA amorf (6 dec) : PLA amorf
- PLA thermoform (29 nov) : PLA thermoform
- PLA treated thermoform (23 jan) : PLA treated thermoform

3.2.1 Thermal properties (DSC)

Appendices 1a-1d show the thermal properties of the PLA's as measured by ATO using the DSC method. Table 1 shows the values of the different thermal properties of the PLA's. Tg is the glass transition temperature of the material, Tm is the melt temperature and Trecrys. is the recrystallization temperature.

table 1 thermal properties of PLA materials

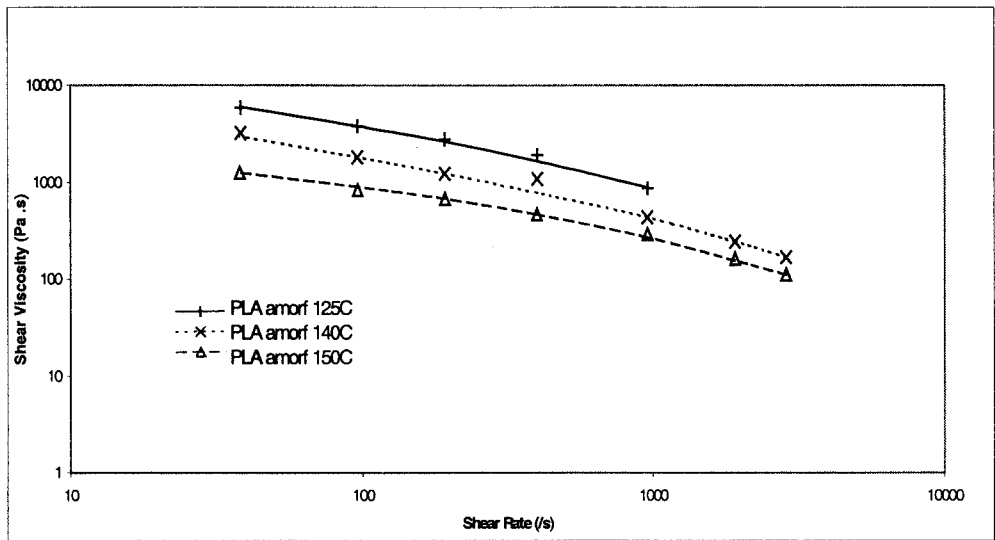
Material	Tg (°C)	Tm (°C)	Trecrys. (°C)
PLA amorf	54	-	-
PLA thermoform	51	160	116
PLA treated thermoform	46	160	104
PLA rubber	21	-	-

As can be seen, the thermal properties of the PLA thermoform and PLA treated thermoform show high melting temperatures and must be processed above this temperature. The Tg of the PLA rubber is around room temperature and must therefore be cooled when processed because of melting of the material and therefore blocking the machinery.

3.2.2 Rheology

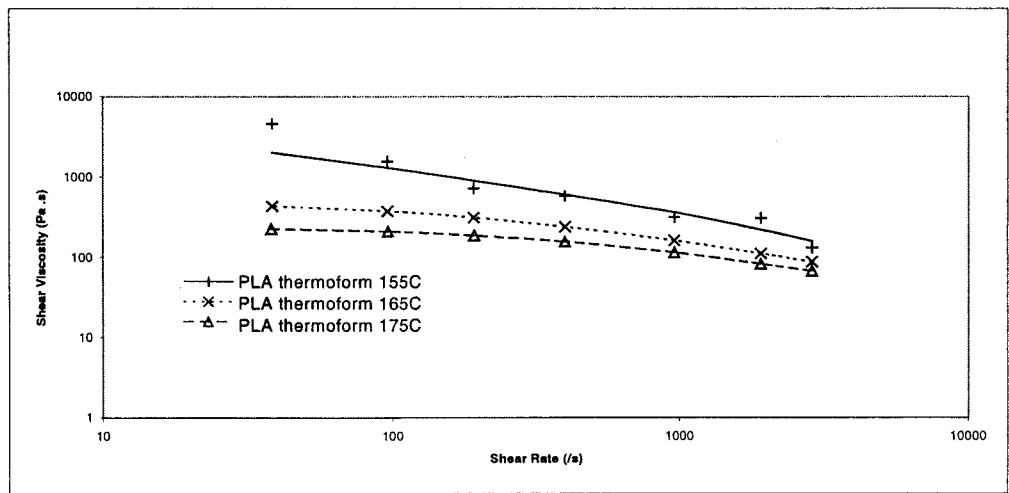
In figure 3a the rheological properties of PLA amorf as measured by ATO are shown.

figure 3a viscosity profiles of PLA amorf at different temperatures



As can be seen, the viscosity of the PLA amorf changes a lot between 125°C and 150°C (between 125°C and 150°C there is an approximately 5-fold decrease in viscosity). This means great dependence of the material behaviour on the temperature. In figure 3b the rheological properties of PLA thermoform as measured by ATO are shown.

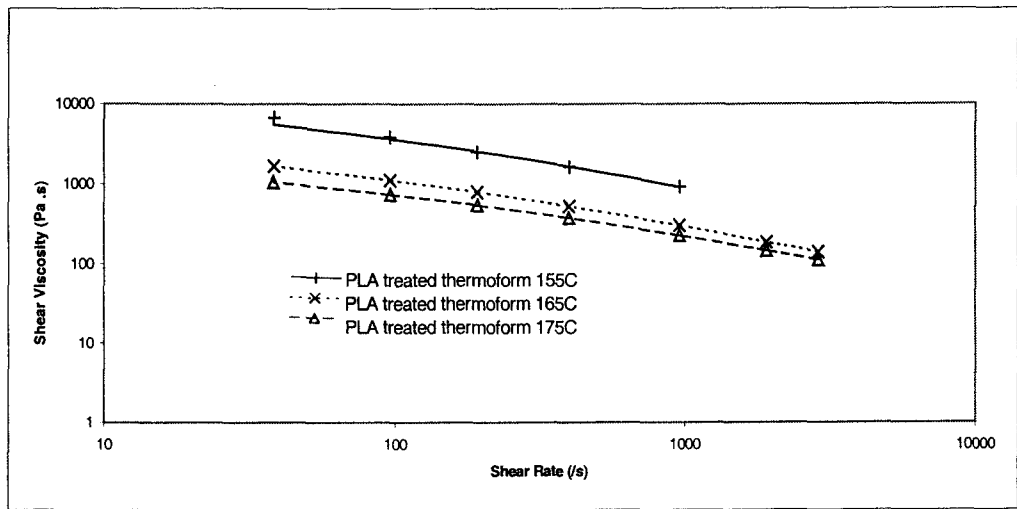
figure 3b viscosity profiles of PLA thermoform at different temperatures



As can be seen, the viscosity of PLA thermoform between 165°C and 175°C is relatively low and shows no large difference at both temperature and shear rate. At 155°C there is an approximately 5 to 10-fold increase at lower shear rates but at greater shear rates there is an approximately 3-fold increase. An explanation for the difference might be that the temperature of 155°C is too low to melt the PLA completely.

In figure 3c the rheological properties of PLA treated thermoform as measured by ATO are shown.

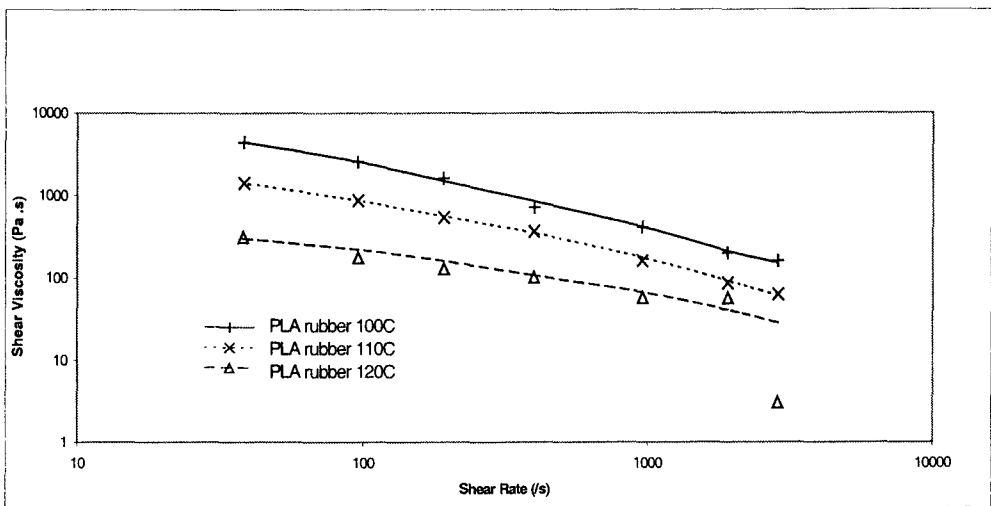
figure 3c viscosity profiles of PLA treated thermoform at different temperatures



As can be seen, the viscosity difference of PLA treated thermoform at temperature ranges between 165°C and 175°C is low and shows no large differences although shear rate dependency looks somewhat more evident. At 155°C there is an approximately 5-fold increase in viscosity. If we compare the results of the rheology experiments of the PLA thermoform and PLA treated thermoform we can see that there is an approximately 4 fold increase in shear viscosity (at the same shear rate and temperature) between PLA thermoform and PLA treated thermoform at low shear rates. At higher shear rates there is an approximately 2-fold increase in shear viscosity between PLA thermoform and PLA treated thermoform.

In figure 3d the rheological properties of PLA rubber as measured by ATO are shown.

figure 3d viscosity profiles of PLA rubber at different temperatures

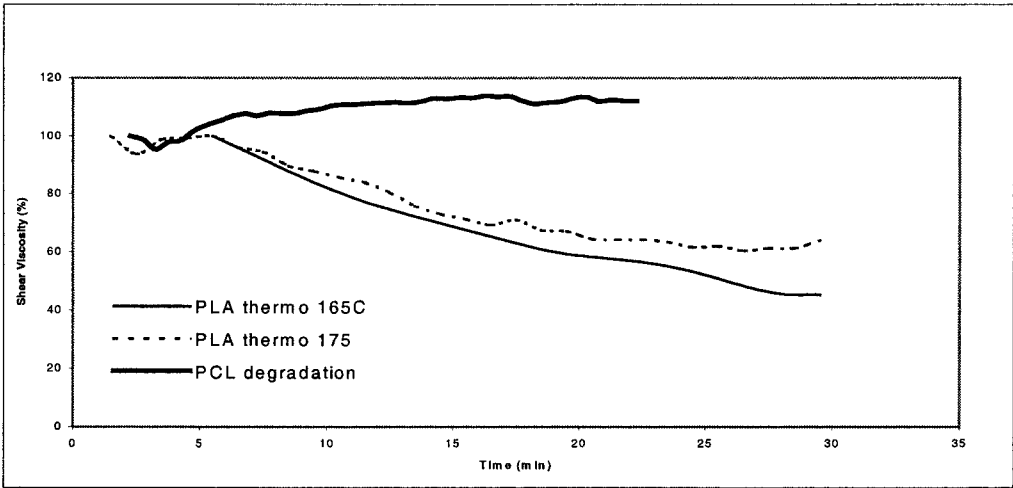


As can be seen, the viscosity of the rubber PLA at temperature ranges between 100 and 120°C is large (between 100°C and 120°C there is an approximately 10-fold decrease in viscosity). This means great dependence of the material behaviour on the temperature.

3.2.3 Thermal stability of PLA's

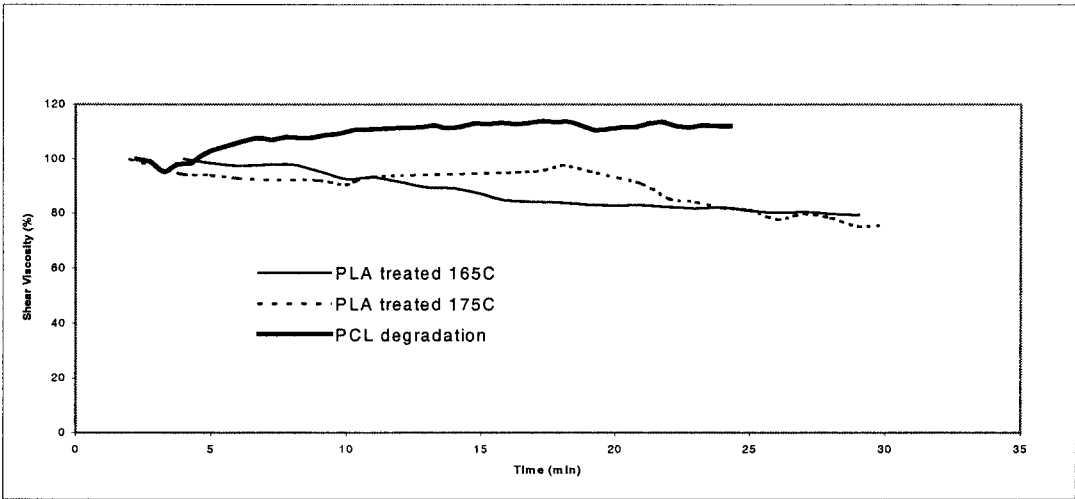
In figure 4a and 4b the thermal stability of various types of PLA's are shown as measured by ATO. Also the degradation of PCL is included to compare the thermal stability.

figure 4a degradation profile of PLA thermoform and PCL



As can be seen, the viscosity plot shows that thermoform PLA is sensible for thermal degradation at 165°C or 175°C (especially when compared with polycaprolactone). There does not seem to be much difference between the degradation at 165°C or at 175°C. The viscosity of the thermoform PLA decreases approximately 40% in 30 minutes

figure 4b degradation profile of PLA treated thermoform and PCL



On the contrary the viscosity plot of the treated thermoform PLA shows us a rather stable material when kept at 165°C or 175°C for at least 20 minutes. No big differences can be detected between stability at 165 or at 175°C. Even compared with PCL, the stability of PLA is not much different. The viscosity of the treated thermoform PLA decreases approximately 20% in 30 minutes

The thermal stability of the amorphous PLA was also tested. However due to instabilities during measurement reliable data could not be gathered.

3.2.4 Water permeability and mechanical properties

The water vapour transmission rate was measured for the amorf, thermoform and the treated thermoform material. Table 2 lists the results from these measurements.

table 2 WVTR values of the different PLA's

Material	WVTR (10^{10} g/m.s.Pa) at 60%RH	WVTR (g/m ² .dag.100μm) At 60%RH
PLA amorf	0.10	8.1
PLA thermoform	0.10	7.9
PLA treated thermoform	0.15	11.9

The WVTR properties of the materials look very promising. In the project proposal which has been sent to the SNN a goal of $0.05 \cdot 10^{-10}$ g/m.s.Pa has been mentioned.

The mechanical properties on injection moulded samples as measured by ATO at different circumstances are listed in table 3.

table 3 Mechanical properties of PLA grades

Material		E Modulus (MPa)	Strength (MPa)	Elongation at break (%)
PLA rubber	60%RH	299 [33]	10.4 [0.4]	9.8 [0.1]
PLA amorf	60%RH	3253 [138]	45.5 [3.2]	4.4 [1.2]
	90%RH	3168 [142]	44.4 [6.7]	4.6 [2.1]
	Water	3176 [58]	33.4 [1.6]	8.5 [2.8]
PLA thermoform	60%RH	3134 [232]	47.6 [7.7]	4.6 [2.2]
	90%RH	3207 [41]	46.9 [5.3]	3.2 [0.7]
	Water	3044 [66]	35.6 [2.3]	7.0 [1.1]
PLA treated Thermoform	60%RH	2959 [196]	40.5 [2.6]	6.6 [2.7]
	90%RH	2985 [110]	28.5 [6.1]	10.2 [3.5]
	Water	2688 [113]	36.0 [0.9]	6.2 [1.4]

As can be seen, the mechanical properties are only slightly influenced by the relative humidity. A full overview of the measurements can be found in appendix 2.

3.2.5 Optical properties

The optical properties were derived manually from injection moulded plates of the PLA's. Table 4 shows the results of the tests.

table 4 optical properties of PLA's

Material	Remarks
PLA amorf	Good transparency, a lot of contamination in the material, lightly brown colouring
PLA thermoform	Good transparency, some contamination in the material, brown colouring
PLA treated thermoform	Good transparency, some contamination in the material, lightly brown colouring
PLA rubber	Not transparent, brown colouring

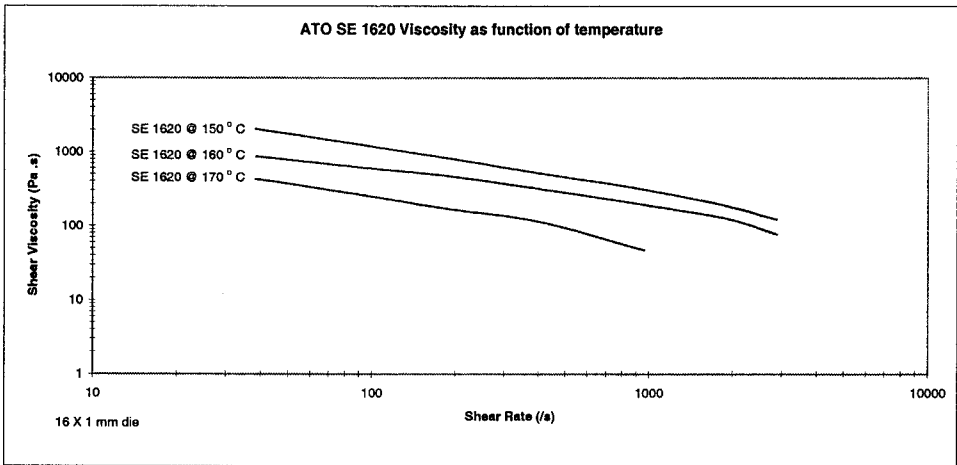
As can be seen, most PLA materials are transparent but because of the contamination and the brownish colouring the optical properties are not so good.

3.3 Monomaterial starch

3.3.1 Reology

Figure 5 shows the viscosity of ATO Paragon SE 1620 at different temperatures.

figure 5 viscosity profile of ATO SE1620 as a function of temperature



As can be seen, the viscosity of the starch material changes with increasing temperature. At 150°C there is an approximate 7-fold increase in viscosity compared to 170°C.

3.3.2 Water- and oxygen permeability and mechanical properties

In table 5 the mechanical properties of Paragon™ materials are shown.

table 5 Mechanical properties of Paragon-SE 1620 materials

Material	E-modulus (MPa)	Strength (MPa)	Elongation at break (%)
ATO Paragon SE 1620	1250-1500	20-25	> 30

WVTR of Paragon™ materials are typically in the range of 1000 - 3000 g/ m².day at 60% RH and 100µm thickness.

Oxygen permeabilities of Paragon™ materials are in the range of 1.5-60 ml/m².day at room temperature and 50% and 70% RH resp. and 100 µm. In appendix 3, a plot of the oxygen permeability against RH is in comparison to synthetic oxygen barriers is shown.

3.4 Combinations of PLA on starch, or polyesters

3.4.1 Adhesion of compression moulded laminates

As a basic layer an existing commercially available starch grade was used, under the trade name Paragon. Next to that, some polyesters were examined that could possibly used as a tie layer.

In table 6 the qualitative results of compression moulded PLA/starch and PLA/polyester sheets are shown.

table 6 adhesion testing of PLA/starch and PLA/polyester compression moulded samples

Materials	PLA rubber	PLA amorf	PLA thermoform	PLA treated Thermoform
SE 1500 (60%RH)	+/-	+/-	-	-
SE 1500 (90%RH)	+/-	-	-	-
BAK foil	--	--	--	-
Ecoflex foil	-	++	++	++
Tie layer foil	+/-	+/-	++	+

As can be seen, that the adhesion of the PLA's on the SE 1500 samples is not good. The adhesion of most PLA's on the Ecoflex and tie layer foils is very good. The adhesion of the PLA's on BAK is bad. It seems to be the best idea to use a tie layer consisting of tie layer to insure good adhesion on both layers.

3.4.2 Sealability of PLA's on polyesters

Table 7 shows the adhesion energy of seals made from PLA amorf and polyester materials. Table 8 shows the adhesion energy of seals made from PLA treated thermoform and polyester materials. It also shows the conditions used for the seals. The term seal stand for the time the apparatus is heating while sealing. The term cool stands for the time the apparatus does not heat anymore but stays closed.

Table 7 adhesion testing of PLA amorf/polyester seals

Seal Condition	Adhesion force (N/mm) on		
	BAK	Ecoflex	Tie layer
Seal=1, Cool=1	0.023	1.053	0.312
Seal=1, Cool=3	0.015	1.002	0.391
Seal=1, Cool=5	0.048	0.998	0.473
Seal=2, Cool=1	0.057	0.510	0.677
Seal=3, Cool=1	0.087	0.843	0.917

table 8 adhesion testing of PLA treated thermoform/polyester seals

Seal Condition	Adhesion force (N/mm) on		
	BAK	Ecoflex	Tie layer
Seal=1, Cool=1	Broke before measurement	0.790	0.661
Seal=1, Cool=3	0.176	0.650	0.695
Seal=1, Cool=5	0.061	0.881	0.434
Seal=2, Cool=1	0.063	0.820	0.728
Seal=3, Cool=1	0.089	0.961	0.938

When measuring the adhesion, all samples, except for the PLA/Ecoflex samples, broke at the seal. Of the PLA/Ecoflex samples some broke on the seal as well as on the foil. For a detailed description of these experiments see Appendix 4.

As can be seen from the measurements the seal adhesion of the BAK samples is very bad. The tie layer and Ecoflex samples show high adhesion energies and look very promising. In general an adhesion > 0.8 N/mm can be considered as good.

3.4.3 Rheology

In fig 6a-d resp. the viscosity profiles of the basic layer SE 1620 compared to different PLA's are shown resp.

figure 6a viscosity profiles of the basic layer ATO SE 1620 compared to PLA amorf

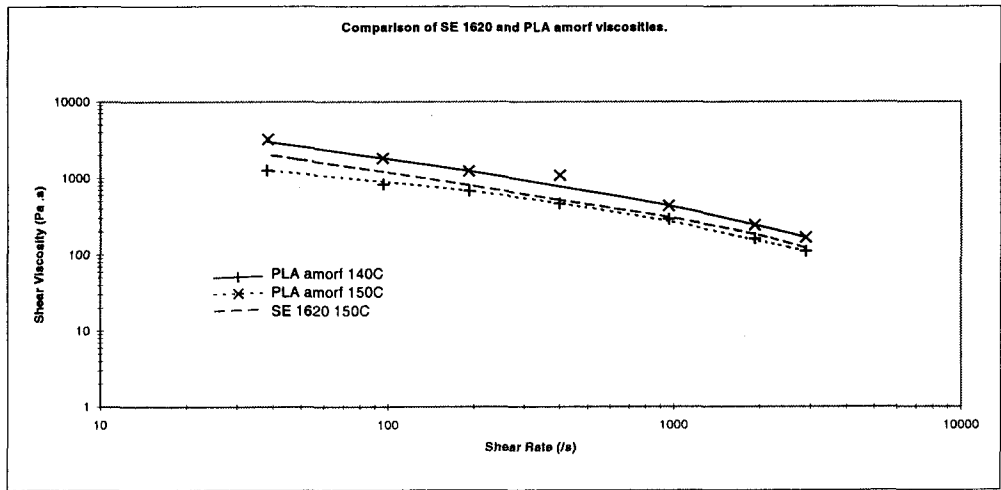


figure 6b viscosity profiles of the basic layer ATO SE 1620 compared to PLA thermoform

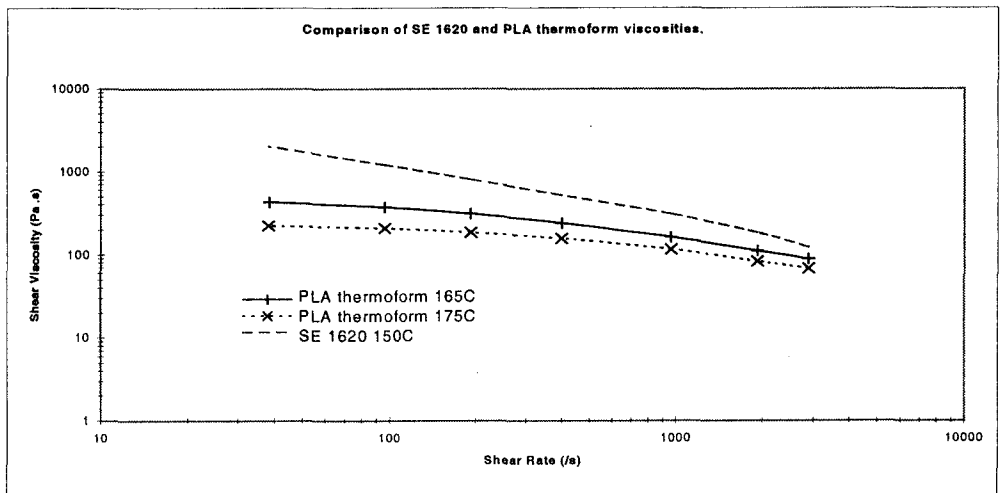


figure 6c viscosity profiles of the basic layer ATO SE 1620 compared to PLA treated thermoform

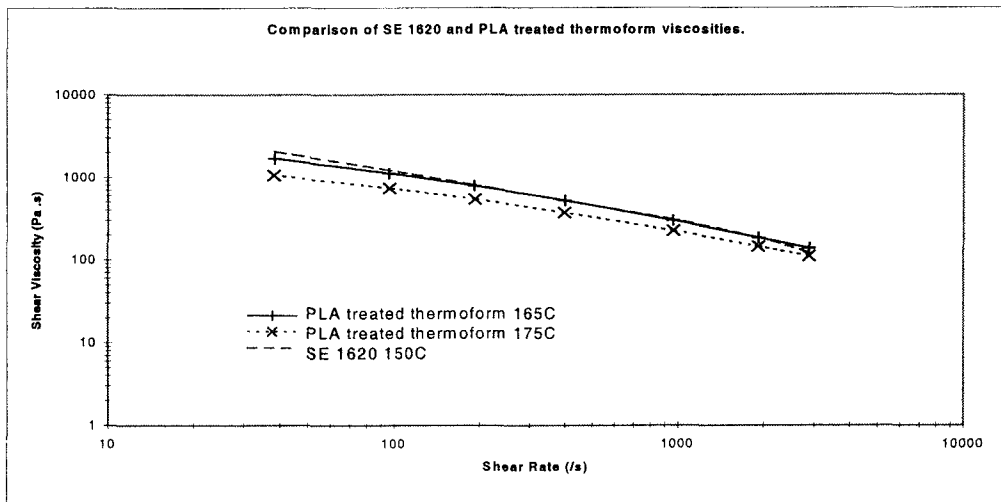
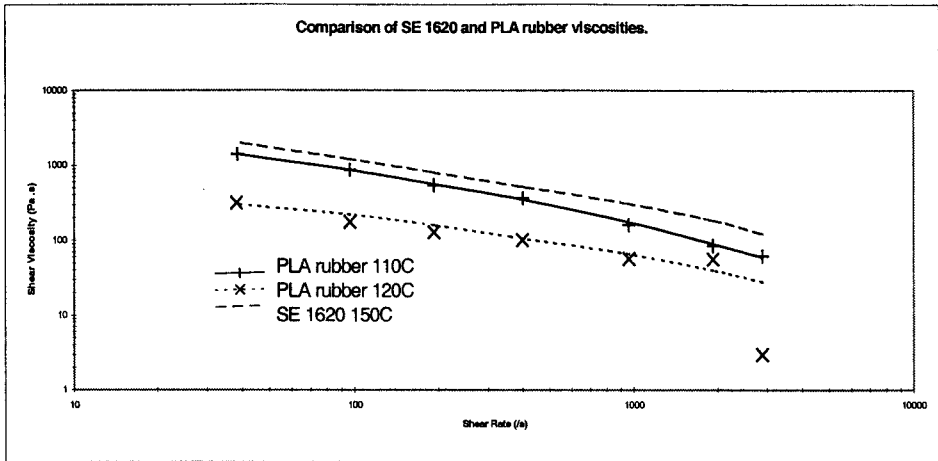


figure 6d viscosity profiles of the basic layer ATO SE 1620 compared to PLA rubber



3.4.4 **Coextrusion filmblowing**

With Paragon SE 1620, film blowing experiments were carried out in which the ratio of thickness distribution between starch material, tie layer and PLA was varied. Three types of PLA were used. The codes and layer profile are given in table 9.

table 9 layer profile of starch/PLA laminates

Sample code	Layer profile (base:tie layer:PLA)
682	50 : 15 : 35 (PLA amorf)
683	50 : 15 : 35 (PLA treated thermoform)
684	25 : 15 : 60 (PLA treated thermoform)
685	70 : 15 : 15 (PLA treated thermoform)
686	70 : 30 (PLA treated thermoform no tie layer)

A complete list of process parameters is given in appendix 2

During extrusion it was found that the amorphous PLA was not equally distributed on the Paragon material. After some problems with this material it was decided to continue with PLA treated thermoform. These tests were very promising and should be considered for further testing. The thermoform material was not tested in the coextrusion facilities it will perform roughly the same as the treated thermoform material. Samples 682 till 685 are five layered structures. It was chosen to start with t

At the end some problems were seen when the PLA rubber material was extruded. This material started to get viscous at the inlet of the extruder. Further experiments with this possibly tie layer material could not be continued.

One general remark about the produced films is the difficulty to open the films after productions. In future anti-block/slip agents have to be added to PLA to facilitate the processability of the film in for example packaging machinery.

3.5 **Analysis**

3.5.1 **Water vapour permeability**

The WVTR of the laminates was measured for one sample (film 683). Table 10 shows the value of the WVTR of the film.

table 10 WVTR value of PLA/polyester/starch foil

Foil nr	WVTR (10 ¹⁰ g/m.s.Pa) at 60%RH	WVTR (g/m ² .dag.100μm) at 60%RH
683	0.37 [0.02]	28.3 [0.8]

8,5 (desired)
cheese packaging

3.5.2 Mechanical properties

Table 11 shows the mechanical properties of the various PLA/starch laminates. For processing and material properties see appendix 5. For a full report of the mechanical properties see appendix 6.

table 11 Mechanical properties of PLA/starch laminates

Foil		E-Modulus (MPa)	Strength (MPa)	Elongation at break (%)
682	60% RH	1459 [258]	22.9 [2.8]	7.0 [3.3]
	90% RH	956 [61]	16.4 [1.2]	22.1 [12.9]
683	60% RH	2096 [62]	37.6 [0.9]	11.1 [3.0]
	90% RH	1294 [61]	22.8 [1.0]	36.2 [13.3]
684	60% RH	2249 [177]	41.1 [3.6]	9.7 [2.7]
	90% RH	1898 [54]	34.9 [2.]	14.0 [2.7]
685	60% RH	1729 [188]	32.1 [2.2]	11.5 [5.9]
	90% RH	639 [37]	13.2 [0.6]	46.8 [11.8]
686	60% RH	2360 [79]	39.2 [1.1]	7.4 [3.1]
	90% RH	1171 [89]	19.8 [1.3]	23.8 [6.6]

As can be seen, the mechanical properties of the foils at different humidity conditions differ a lot. The E-modulus and maximum strength decrease and the elongation increases with increasing RH. The materials are very depending on the environmental conditions and when usage will be discussed these influences must be taken in the discussion.

3.6 Summary of PLA materials

Table 12 shows a summary off the positive and negative results from experiments carried out on the various types PLA.

table 12 summary of positive and negative results of experiments with PLA

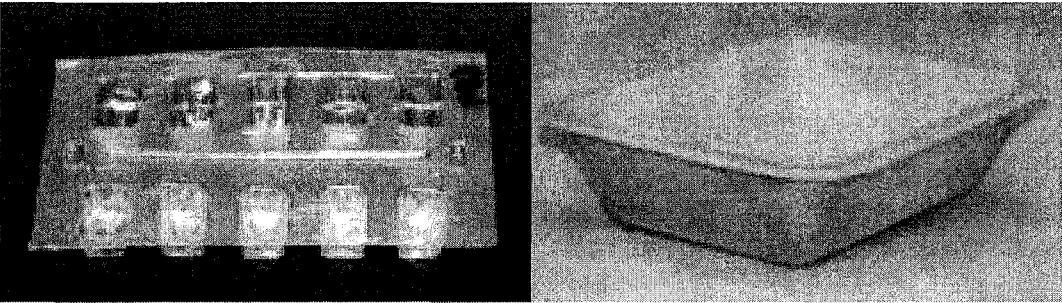
Type		Negative	Positive
Process temperature		PLA rubber (PLA amorf)	(PLA amorf) PLA thermoform PLA treated thermoform
Thermal stability		(PLA thermoform)	(PLA thermoform) PLA treated thermoform
WVTR			PLA amorf PLA thermoform PLA treated thermoform
Optical		PLA thermoform PLA rubber	PLA amorf PLA treated thermoform
Adhesion	Starch	All PLA's	
	BAK	All PLA's	
	Ecoflex	PLA rubber	PLA amorf PLA thermoform PLA treated thermoform

	Tie layer	PLA rubber PLA amorf	PLA thermoform PLA treated thermoform
Sealability	BAK	PLA amorf PLA treated thermoform	
	Ecoflex		PLA amorf PLA treated thermoform
	Tie layer		PLA amorf PLA treated thermoform

As can be seen, the best results from the experiments are given for the treated thermoform material. This material was also tested in filmblowing and produced a good foil. This material looks the most promising of the 4 PLA types. PLA thermoform and amorf also show some interesting possibilities. The PLA rubber doesn't seem to be a much promising material also because of the difficulties at processing.

3.7 Application of the foils

One application for which the foils might be interesting is packaging. To test this application a foil has been sealed onto a starch tray, which has been covered with a starch/Ecoflex foil created by ATO BV. Figure 7 shows the starch/Ecoflex foil which has been vacuum-formed at ATO BV. Figure 8 shows a starch tray that has been coated by vacuum-forming with a starch/ecoflex soil. Figure 9 shows the tray sealed with the Starch/PLA film and containing a piece of meat.



picture 7

picture 8



picture 9

3.8 Conclusions

- For PLA/Starch laminates it is shown that:
- Thin films (50 to 100 μm) of PLA/Starch can be coextruded in which the starch based plastic content can be varied from 25 to 70%

- Four types of PLA were tested: amorphous, (semi-crystalline) thermoform, (semi-crystalline) treated thermoform and rubbery material. For coextrusion processes treated thermoform grade PLA seems best suitable.
- PLA properties:
 - Water vapour permeability: for the tested materials this property varied from 0.1 to $0.15 \cdot 10^{-10}$ gram/m*s*Pa. These values are lower than values measured for other commercially available, biodegradable poly-ester materials and are in the range of values stated as goal for this project ($0.05 \cdot 10^{-10}$ gram/m*s*Pa).
 - Viscosities: viscosity behaviour of PLA is similar (same level, same trends) to that of Paragon.
 - Thermal stability: thermal stability of treated thermoform grade PLA is comparable with poly-caprolactone. Stability of this material is considered as sufficient. Thermal stability of other tested PLA-grades is much less.
 - Optical properties: optical properties of tested PLA grades was not sufficient.
- Direct adhesion between the PLA and Paragon is not sufficient. With help of a tie layer sufficient adhesion can be realized.
- Surface properties of PLA-film materials have to be modified. Blocking of the film material causes problems during handling on various machinery.

3.9 Further research

Further research should be done on the following subjects:

- Improvement of direct adhesion between PLA and starch based materials.
- Creating a PLA with better optical properties (transparency and haze) than materials used.
- Further improvement of water barrier properties.
- Improvement of processability of PLA on film blowing machinery e.g. addition of anti-block and slip agents.

Workplan of this research is summarized in the project proposal as submitted to the SNN

4 Literature

J.J.G. van Soest; Starch Plastics: structure property relationships. PhD thesis 1996.

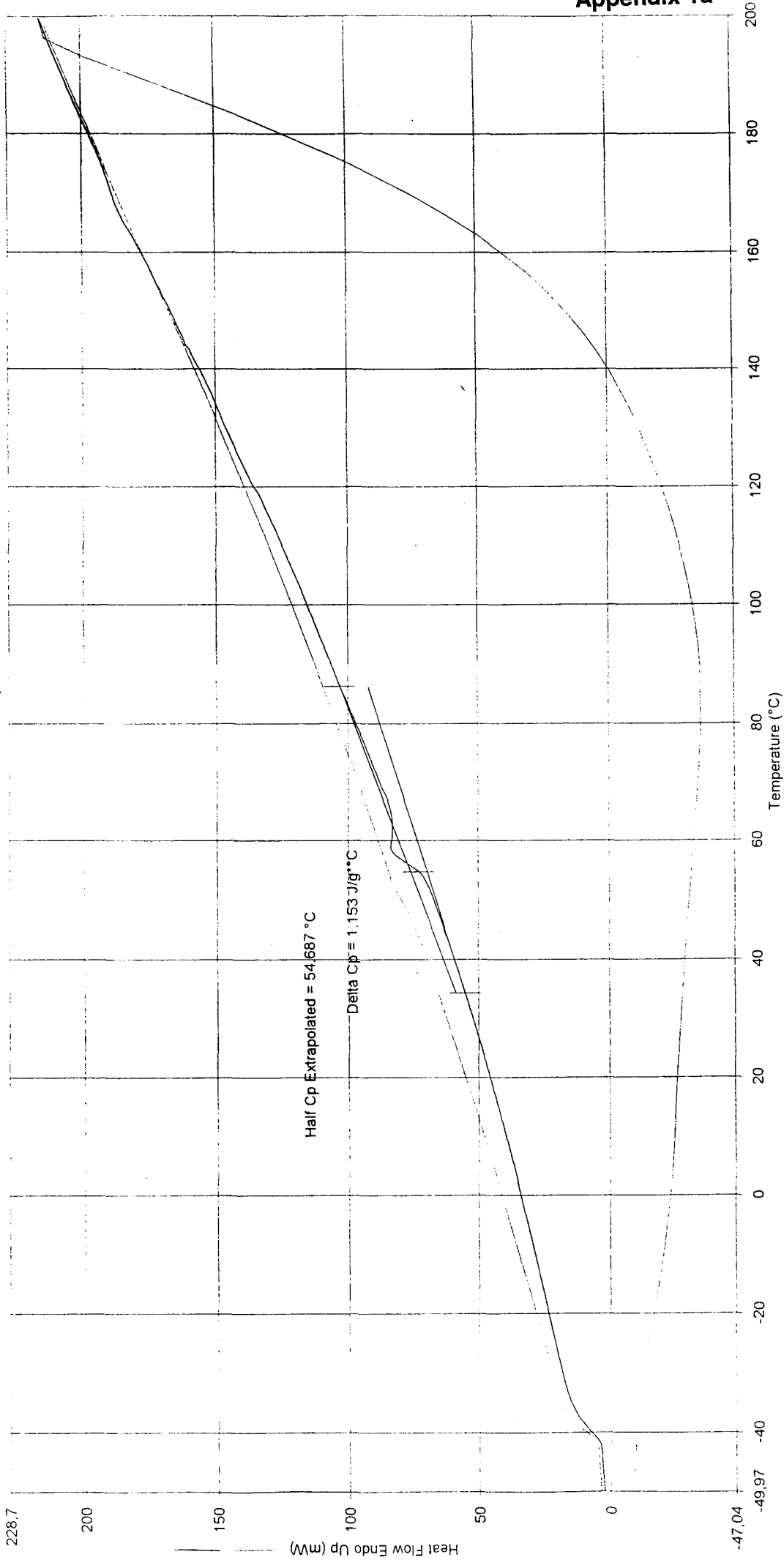
5 Appendices

- 1a Thermal properties of PLA amorf
 - 1b Thermal properties of PLA thermoform
 - 1c Thermal properties of PLA treated thermoform
 - 1d Thermal properties of PLA rubber
 - 2 Mechanical properties of monomaterial PLA
 - 3 Oxygen permeabilities
 - 4 Sealability of PLA's on polyesters
 - 5 Coextrusion matrix
 - 6 Mechanical properties of PLA/starch foils
-

Filename: C:\PE\Pyris\Data\Aldo Kran... \pla1.dsd
Operator ID:
Sample ID: PLA amorf (6 dec)
Sample Weight: 33.000 mg

PLA amorf (6 dec): pla1.dsd
Heat Flow Endo Up (mW) : Step: 2
PLA amorf (6 dec): pla1.dsd
Heat Flow Endo Up (mW) : Step: 3
PLA amorf (6 dec): pla1.dsd
Heat Flow Endo Up (mW) : Step: 5

Perkin-Elmer Thermal Analysis



- 1) Hold for 5.0 min at -50.00°C
- 2) Heat from -50.00°C to 200.00°C at 10.00°C/min
- 3) Cool from 200.00°C to -50.00°C at 100.00°C/min
- 4) Hold for 5.0 min at -50.00°C
- 5) Heat from -50.00°C to 200.00°C at 10.00°C/min

File name: C:\PE\Pyris\Data\Aldo Kra...pla 3.dsd

Operator ID: PLA thermoform (29 nov)

Sample ID: 31.000 mg

Sample Weight:

PLA thermoform (29 nov): pla 3.dsd

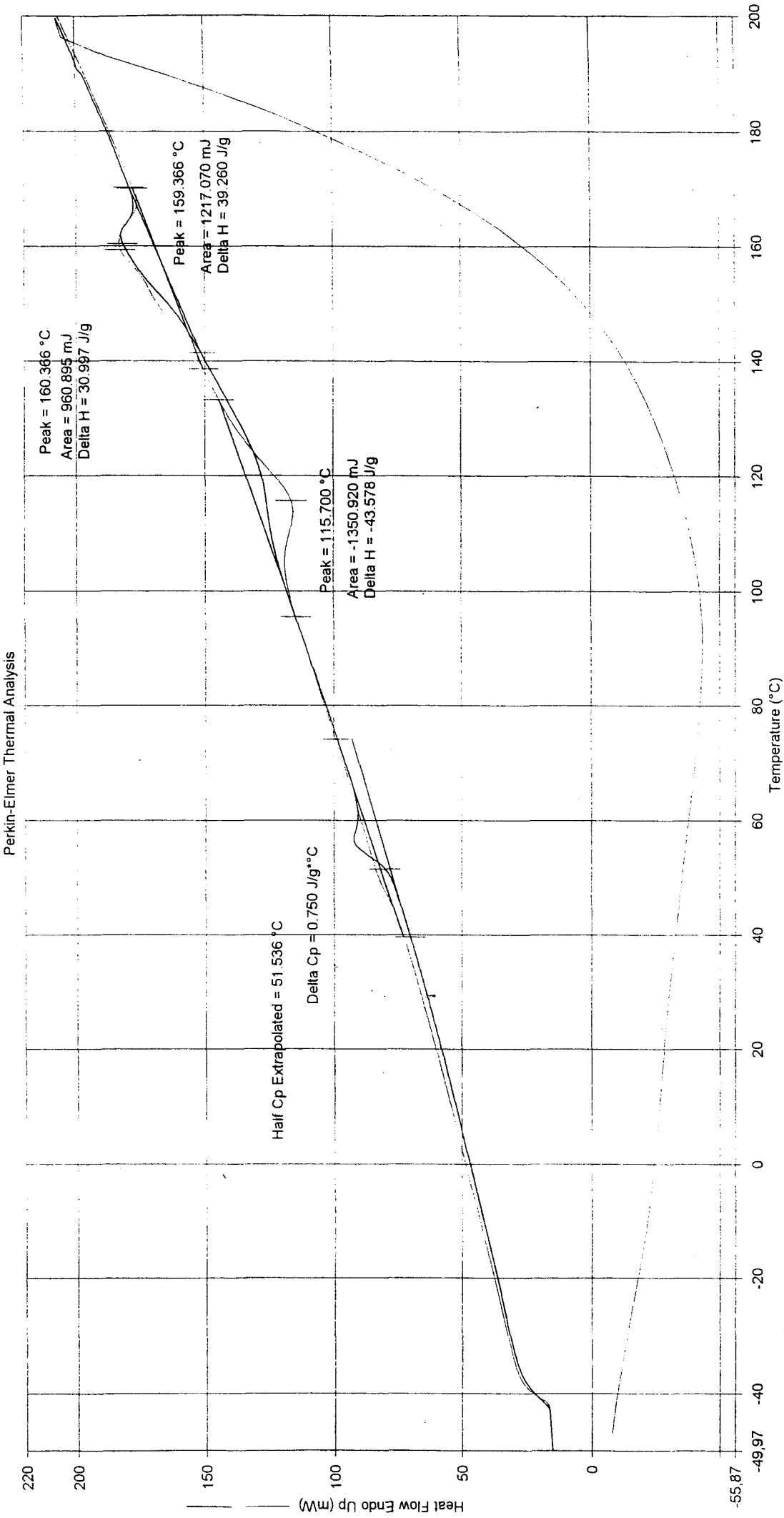
Heat Flow Endo Up (mW) : Step: 2

PLA thermoform (29 nov): pla 3.dsd

Heat Flow Endo Up (mW) : Step: 3

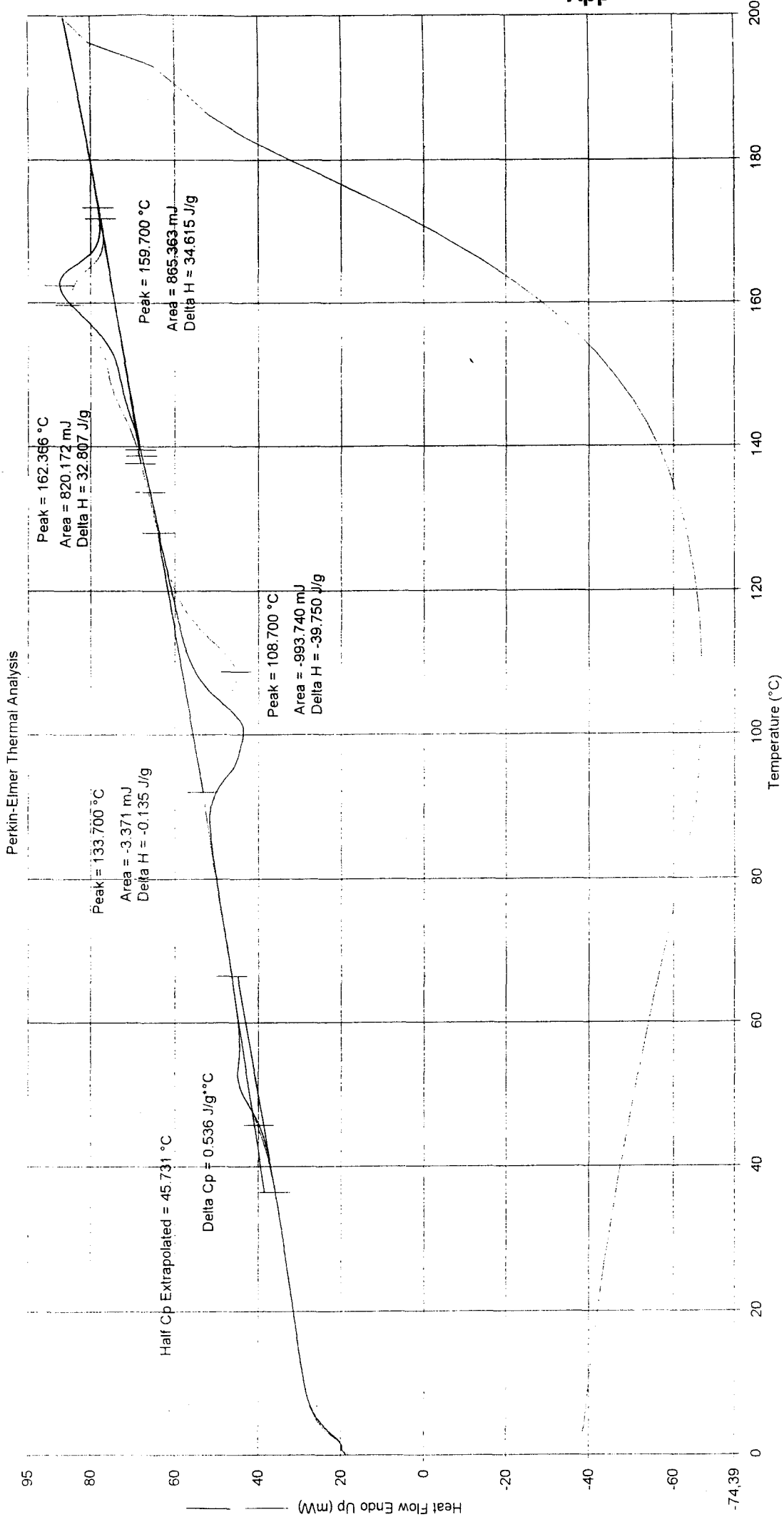
PLA thermoform (29 nov): pla 3.dsd

Heat Flow Endo Up (mW) : Step: 5



Filename C:\PE\pyris\Data\H...pla treated2 dsd
Operator ID
Sample ID: PLA treated thermoform (23 jan)
Sample Weight: 25 000 mg

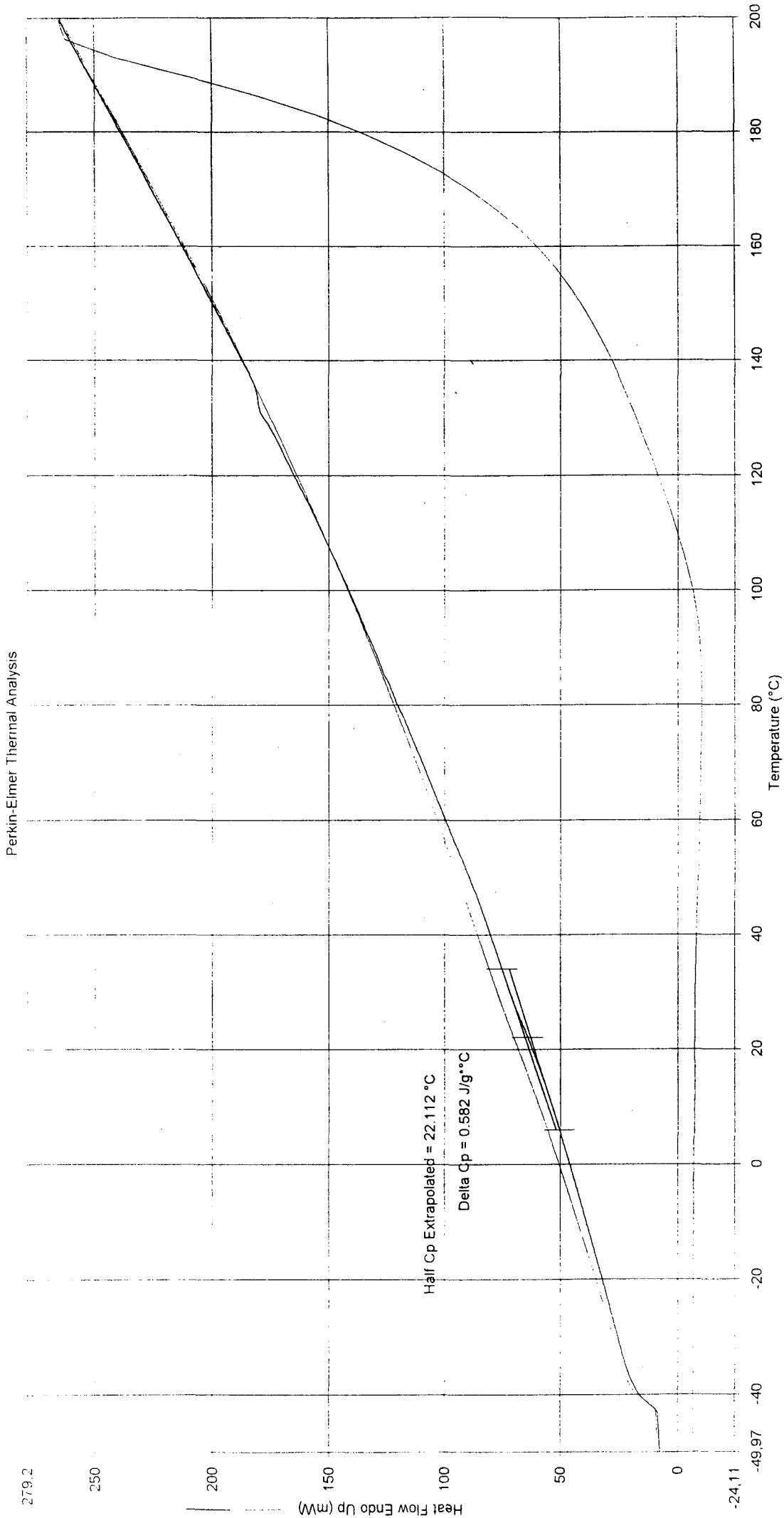
PLA treated thermoform (23 jan): pla treated2 dsd
Heat Flow Endo Up (mW) : Step: 2
PLA treated thermoform (23 jan): pla treated2 dsd
Heat Flow Endo Up (mW) : Step: 3
PLA treated thermoform (23 jan): pla treated2 dsd
Heat Flow Endo Up (mW) : Step: 5



- 1) Hold for 5.0 min at 0.00°C
- 2) Heat from 0.00°C to 200.00°C at 10.00°C/min
- 3) Cool from 200.00°C to 0.00°C at 100.00°C/min
- 4) Hold for 5.0 min at 0.00°C
- 5) Heat from 0.00°C to 200.00°C at 10.00°C/min

PLA rubber (7 dec) : pla4.dsd
Heat Flow Endo Up (mW) : Step. 2
PLA rubber (7 dec) : pla4.dsd
Heat Flow Endo Up (mW) : Step. 3
PLA rubber (7 dec) : pla4.dsd
Heat Flow Endo Up (mW) : Step. 5

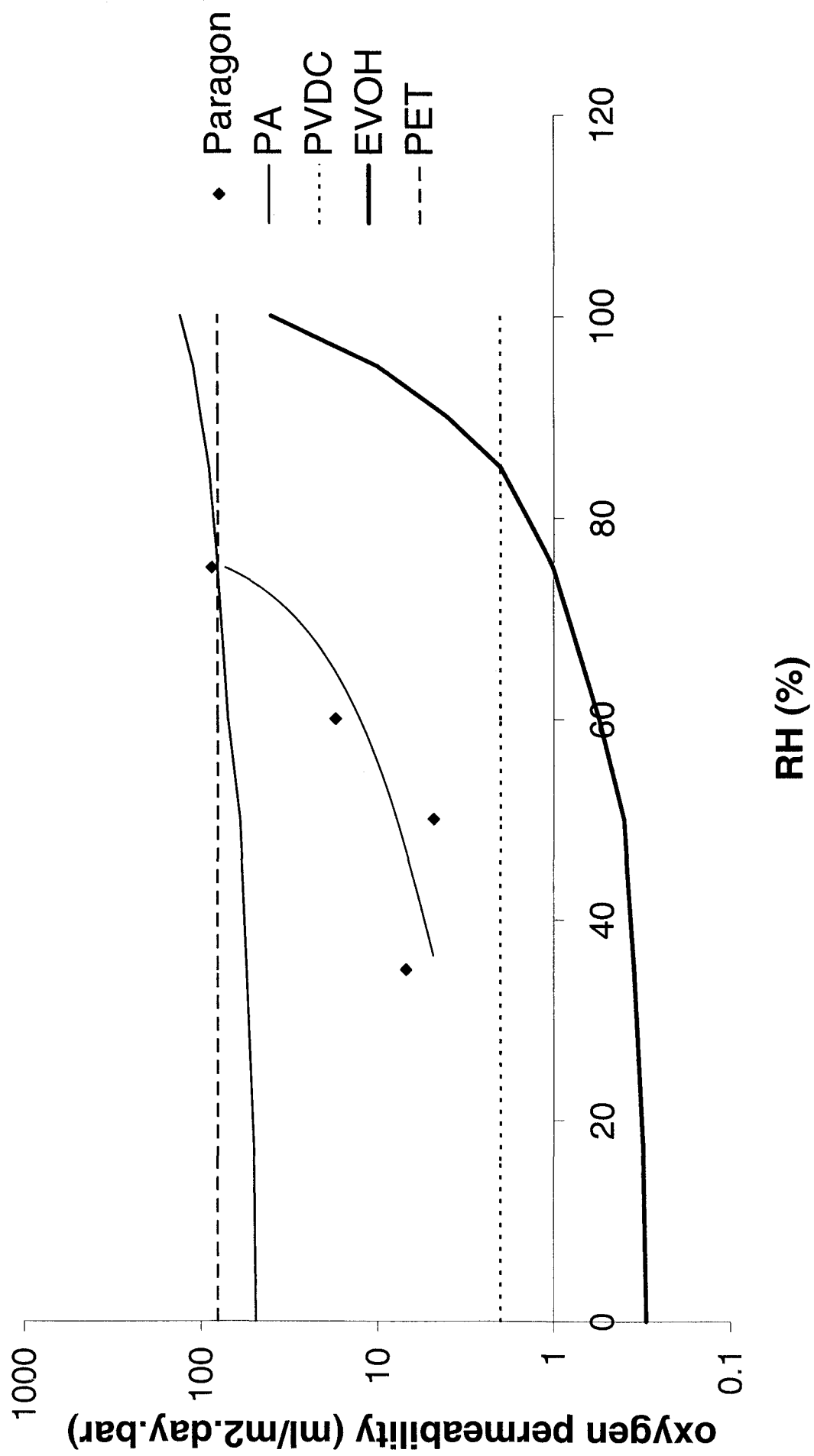
Filename C:\PE\pyris\Data\Aldo Kran... pla4.dsd
Operator ID
Sample ID PLA rubber (7 dec)
Sample Weight 26.000 mg



- 1) Hold for 5.0 min at -50.00°C
- 2) Heat from -50.00°C to 200.00°C at 10.00°C/min
- 4) Hold for 5.0 min at -50.00°C
- 5) Heat from -50.00°C to 200.00°C at 10.00°C/min

Mechanical properties of PLA's

Material	RH (%)	E-Modulus (N/mm ²)	Stress-max (N/mm ²)	L at stress-max (%)	Stress at fract. (N/mm ²)	Strain at fract. (%)
PLA amorf (6 dec) Hycail	60% RH	3253 [138]	57.8 [1.1]	2.0 [0.1]	45.5 [3.2]	4.4 [1.2]
	90% RH	3168 [142]	55.8 [0.5]	1.9 [0.1]	44.4 [6.7]	4.6 [2.1]
	Water	3176 [58]	52.1 [1.6]	1.8 [0.1]	33.4 [1.6]	8.5 [2.8]
PLA thermoform (29 nov) Hycail	60% RH	3134 [232]	60.6 [1.7]	2.1 [0.1]	47.6 [7.7]	4.6 [2.2]
	90% RH	3207 [41]	58.0 [0.7]	2.0 [0.1]	46.9 [5.3]	3.2 [0.7]
	Water	3044 [66]	54.5 [0.8]	2.1 [0.1]	35.6 [2.3]	7.0 [1.1]
PLA treated thermoform (23 jan) Hycail	60% RH	2959 [196]	59.7 [1.4]	2.2 [0.1]	40.5 [2.6]	6.6 [2.7]
	90% RH	2985 [110]	55.9 [0.6]	2.1 [0.1]	28.5 [6.1]	10.2 [3.5]
	Water	2688 [113]	53.8 [0.3]	2.3 [0.1]	36.0 [0.9]	6.2 [1.4]
PLA rubber (7 dec) Hycail	60% RH	299 [93]	10.0 [0.7]	9.4 [0.5]	10.4 [0.4]	9.8 [0.1]



Sealenergy of polyesters on PLA amorf

Material	Cool	Seal	Energy (N/mm)	Remarks
BAK	1	1	0.023	Broke on seal
	3	1	0.015	Broke on seal
	5	1	0.048	Broke on seal
	1	3	0.057	Broke on seal
	1	2	0.087	Broke on seal
Ecoflex	1	1	1.053	Broke on seal+foil
	3	1	1.002	Broke on seal+foil
	5	1	0.998	Broke on seal
	1	3	0.510	Broke on seal+foil
	1	2	0.843	Broke on seal+foil
Tie layer	1	1	0.312	Broke on seal
	3	1	0.391	Broke on seal
	5	1	0.473	Broke on seal
	1	3	0.677	Broke on seal
	1	2	0.917	Broke on seal

Sealenergy of polyesters on PLA treated thermoform

Material	Cool	Seal	Energy (N/mm)	Remarks
BAK	1	1		Broke before measurement
	3	1	0.176	Broke on seal
	5	1	0.061	Broke on seal
	1	3	0.063	Broke on seal
	1	2	0.089	Broke on seal
Ecoflex	1	1	0.790	Broke on seal
	3	1	0.650	Broke on seal
	5	1	0.881	Broke on seal+foil
	1	3	0.820	Broke on seal+foil
	1	2	0.961	Broke on seal+foil
Tie layer	1	1	0.661	Broke on seal
	3	1	0.695	Broke on seal
	5	1	0.434	Broke on seal
	1	3	0.728	Broke on seal
	1	2	0.938	Broke on seal+foil

Test	Formula	Code	Vocht (%)	Layer profile (%)	Extruder	Extruder temperature profile	Die temperature	Extruder pressure (Bar)	Extruder Amps	Screw speed (RPM)	Feed rate (kg/h)	Line Speed (M/min)	Comment
682	PLA Amorf	Hycail		17.5	2	151/150/144/150		233	11	29			Stripes in the foil. Foil not completely stable
	ATO tie layer			7.5	3	187/180/180/180/185		73	11	16			
	ATO SE 1620	ATO		50	1	175/160/135/110/110	155/144/138/135/140	164	26	19			
	ATO tie layer			7.5									
683	PLA Amorf	Hycail		17.5									No problems while processing
	PLA Treated Thermofilm				2	145/185/180/175/175		212	12	30			
	ATO tie layer			7.5	3	163/180/180/180/185		108	15	24			
	ATO SE 1620	ATO		65	1	175/160/135/110/110	164/160/150/147/150	268	33	23			
684	PLA Treated Thermofilm	Hycail		17.5									No problems while processing
	PLA Treated Thermofilm				2	145/185/180/175/175		211					
	ATO tie layer			7.5	3	185/180/180/180/185		117					
	ATO SE 1620	ATO		25	1	175/160/135/110/110	184/160/150/147/150	235					
685	PLA Treated Thermofilm	Hycail		7.5									No problems while processing
	PLA Treated Thermofilm				2	145/185/180/175/175		181					
	ATO tie layer			7.5	3	185/180/180/180/185		105					
	ATO SE 1620	ATO		70	1	175/160/135/110/110	164/160/150/147/150	335					
686	PLA Treated Thermofilm	Hycail		7.5									Bubbles in the foil because of bad adhesion
	PLA Treated Thermofilm				2	145/185/180/175/175		169					
	ATO tie layer			7.5	3	145/186/180/175/175		115					
	ATO SE 1620	ATO		70	1	175/160/135/110/110	164/160/150/144/147	357					

Mechanical properties of PLA/starch laminates

Foil	Materials	RH (%)	E-Modulus (N/mm ²)	Stress-max (N/mm ²)	L at stress-max (%)	Stress at fract. (N/mm ²)	Strain at fract. (%)
682	PLA amorf	60 %	1459 [258]	22.9 [2.8]	2.8 [1.0]	19.5 [2.6]	7.0 [3.3]
	Tie layer (ATO)	7.5					
	SE 1620 (ATO)	50					
	Tie leyer (ATO)	7.5	956 [61]	16.4 [1.2]	18.5 [12.0]	8.7 [4.7]	22.1 [12.9]
683	PLA amorf	60 %	1459 [258]	22.9 [2.8]	2.8 [1.0]	19.5 [2.6]	7.0 [3.3]
	Tie layer (ATO)	7.5					
	SE 1620 (ATO)	50					
	Tie leyer (ATO)	7.5	956 [61]	16.4 [1.2]	18.5 [12.0]	8.7 [4.7]	22.1 [12.9]
684	PLA amorf	60 %	1459 [258]	22.9 [2.8]	2.8 [1.0]	19.5 [2.6]	7.0 [3.3]
	Tie layer (ATO)	7.5					
	SE 1620 (ATO)	50					
	Tie leyer (ATO)	7.5	956 [61]	16.4 [1.2]	18.5 [12.0]	8.7 [4.7]	22.1 [12.9]
685	PLA amorf	60 %	1459 [258]	22.9 [2.8]	2.8 [1.0]	19.5 [2.6]	7.0 [3.3]
	Tie layer (ATO)	7.5					
	SE 1620 (ATO)	50					
	Tie leyer (ATO)	7.5	956 [61]	16.4 [1.2]	18.5 [12.0]	8.7 [4.7]	22.1 [12.9]
686	PLA amorf	60 %	1459 [258]	22.9 [2.8]	2.8 [1.0]	19.5 [2.6]	7.0 [3.3]
	Tie layer (ATO)	7.5					
	SE 1620 (ATO)	50					
	Tie leyer (ATO)	7.5	956 [61]	16.4 [1.2]	18.5 [12.0]	8.7 [4.7]	22.1 [12.9]