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(54) Titre : MATERIAU POLYMERE ET SON PROCEDURE D'ELABORATION
(54) Title: POLYMER MATERIAL AND METHOD FOR THE PRODUCTION THEREOF

(57) **Abrégé/Abstract:**

A method for the production of a polymer material is shown and described, which is characterized by: (a) producing a mixture containing at least 1 to 75 wt.-% starch and/or starch derivative, 10 to 85 wt.-% polyester, and 0.01 to 7 wt.-% of a polymer containing an epoxy group; (b) homogenizing the mixture while supplying thermal and/or mechanical energy; (c) setting the water content of the mixture, so that the end product has a water content of less than approximately 12 wt.-%, in relation to the total composition of the mixture. The polymer material produced with the method according to the invention is characterized by outstanding mechanical properties.

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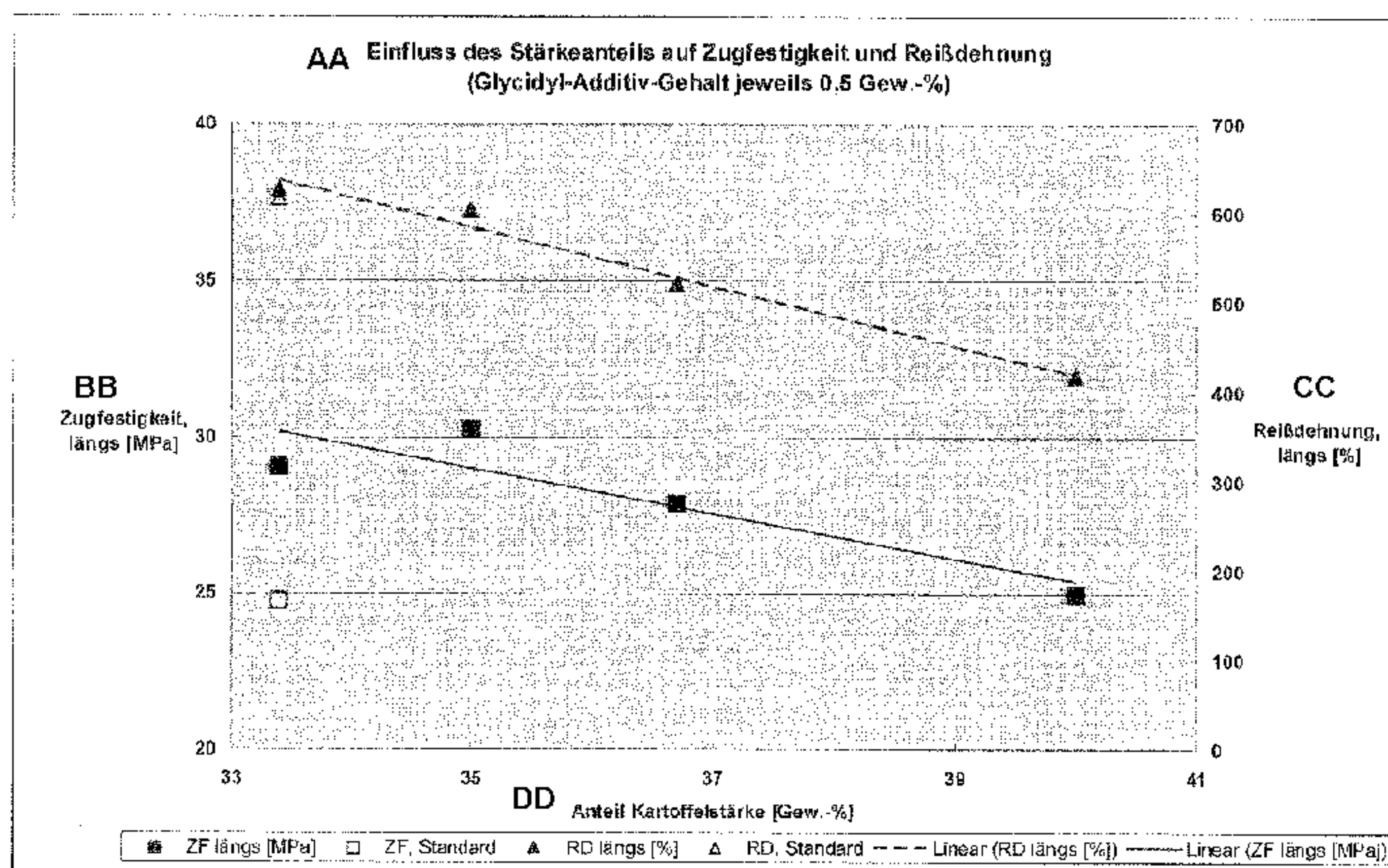
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(54) Title: POLYMER MATERIAL AND METHOD FOR THE PRODUCTION THEREOF

(54) Bezeichnung: POLYMERES MATERIAL UND VERFAHREN ZU DESSEN HERSTELLUNG



EE

Figur 1

AA...Influence of the starch fraction on tensile strength and elongation at tear (glycidyl-additive content 0.5 wt.-% in each case)

BB...Tensile strength, longitudinal

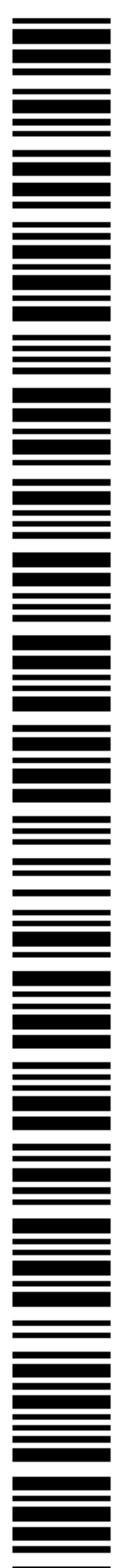
CC...Elongation at tear, longitudinal

DD...Potato starch fraction

EE...longitudinal

(57) Abstract: A method for the production of a polymer material is shown and described, which is characterized by: (a) producing a mixture containing at least 1 to 75 wt.-% starch and/or starch derivative, 10 to 85 wt.-% polyester, and 0.01 to 7 wt.-% of a polymer containing an epoxy group; (b) homogenizing the mixture while supplying thermal and/or mechanical energy; (c) setting the water content of the mixture, so that the end product has a water content of less than approximately 12 wt.-%, in relation to the total composition of the mixture. The polymer material produced with the method according to the invention is characterized by outstanding mechanical properties.

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(57) **Zusammenfassung:** Dargestellt und beschrieben wird ein Verfahren zur Herstellung eines polymeren Materials, welches gekennzeichnet ist durch: (a) Herstellen eines Gemischs enthaltend wenigstens - 1 bis 75 Gew.% Stärke und/oder Stärkederivat, - 10 bis 85 Gew.% Polyester und - 0,01 bis 7 Gew.% eines epoxidgruppenhaltigen Polymers; (b) Homogenisieren des Gemischs unter Zuführen von thermischer und/oder mechanischer Energie; (c) Einstellen des Wassergehalts des Gemischs, so dass das Endprodukt einen Wassergehalt von kleiner etwa 12 Gew.%, bezogen auf die Gesamtzusammensetzung des Gemischs, aufweist. Das nach dem erfindungsgemäßen Verfahren hergestellte polymere Material zeichnet sich durch hervorragende mechanische Eigenschaften aus.

Polymer material and method for the production thereof

The invention relates to a polymer material containing starch, to a method for the production thereof and to moulded parts, films and/or fibres produced from the material.

Polymer materials based on starch, which contain starch in combination with one or more thermoplastic polymers, e.g. polyesters, are generally known. The production and properties of unplasticised polymer blends containing starch are described, for example, in the publications EP 0 596 437 B1 and EP 0 917 540 B1.

Generally, unplasticised polymer blends containing starch contain up to a proportion of at most approximately 33 wt. % based on the total composition of the polymer blend. Although a further increase in the starch proportion would be desirable for economic and ecological reasons, this is not easily possible as an increase in the starch proportion generally is accompanied by a considerable deterioration in the mechanical properties of the polymer.

An unplasticised polymer blend based on starch, which is suitable in particular for blow film extruding, flat film extruding and injection moulding completely biodegradable products, is commercially available under the registered trade name "Bioplast[®] GF 106/02" from Biotec GmbH & Co. KG in Emmerich (Germany).

The invention aims at improving the mechanical properties of the materials containing starch mentioned in the preamble and of the products produced from them (e.g.

moulded parts, films and/or fibres). In particular, the invention aims at providing unplasticised polymer blends based on starch, which have as high a starch content as possible and, at the same time, excellent mechanical properties.

This object is achieved according to the invention by a method for producing a polymer material which is characterised by:

- (a) Producing a mixture containing at least
 - 1 to 75 wt. % of starch and/or starch derivative
 - 10 to 85 wt. % of polyester and
 - 0.01 to 7 wt. % of an epoxide group-containing polymer;
- (b) Homogenising the mixture by supplying thermal and/or mechanical energy;
- (c) Setting the water content of the mixture, so that the end product has a water content of less than approximately 12 wt. % based on the total composition of the mixture.

Advantageous embodiments of the invention are described herein.

A fundamental feature of the method according to the invention is the addition of an epoxide group-containing polymer. Surprisingly, it was found that the presence of epoxide group-containing polymers as an additive during the production of polymer materials containing starch leads to

a significant improvement in the mechanical properties of the material, in particular in its tensile strength, elongation at break and dart drop values.

The polymer material produced according to the method according to the invention is characterised by excellent mechanical properties. Thus, a film produced from the polymer material can have a tensile strength in accordance with DIN 53455 of 5 to 60 N/mm², in particular of 10 to 40 N/mm² and/or an elongation at break in accordance with DIN 53455 of 100 to 1,000 %, in particular of 200 to 800 %.

Furthermore, with the method according to the invention for the first time unplasticised polymer blends based on starch can be produced with a starch content greater or equal to 34 wt. %, wherein films produced from the polymer blends have an elongation at break in accordance with DIN 53455 of at least 300 % and/or a dart drop value in accordance with ASTM D-1709 of at least 10 g/μm.

The method according to the invention makes provision for a mixture containing starch or starch derivative, polyester and epoxide group-containing polymer to be homogenised.

The production of thermoplastic polymers containing starch by homogenising a starting mixture containing starch is generally known and usually takes place in an extruder. Suitable production methods for thermoplastic polymers containing starch are described, for example, in the publications EP 0 596 437 B1 and EP 0 917 540 B1.

The starch and starch derivative used in the method according to the invention are preferably selected from

native potato starch, tapioca starch, rice starch and maize starch.

According to one preferred embodiment of the invention, the mixture contains 5 to 75 wt. %, in particular 10 to 75 wt. %, preferably 15 to 70 wt. %, more preferably 25 to 55 wt. %, most preferably 34 to 51 wt. % of starch and/or starch derivative.

The polyester contained in the mixture is preferably selected from the group consisting of aliphatic-aromatic copolyester, aliphatic polyester, aromatic polyesters, PHA, PLA, PHB and PHBV.

For the method according to the invention, polyesters are in particular (but not exclusively) considered which are biodegradable in accordance with EN13432 and/or have a glass transition temperature (Tg) of less than 0°C, in particular less than -4°C, more preferably less than -10°C, even more preferably less than -20°C and most preferably less than -30°C. The polyesters used in the method according to the invention are furthermore preferably thermoplastic.

According to a particularly preferred embodiment of the invention, a copolyester, in particular a random copolyester, is used as the aliphatic-aromatic polyester, based at least on adipic acid. More preferably, it is a copolyester or random copolyester, based at least on 1,4-butanediol, adipic acid and terephthalic acid or terephthalic acid derivative (e.g. dimethyl terephthalate DMT). This in particular can have a glass transition temperature (Tg) of -25 to -40°C, in particular -30 to

-35°C, and/or a melting range of 100 to 120°C, in particular 105 to 115°C.

Suitable polyesters are, moreover, in particular aliphatic polyesters which are selected from the group consisting of polyhydroxyvalerate, polyhydroxybutyrate-hydroxyvalerate copolymer and polycaprolactone. More preferred aliphatic polyesters are those based on succinate, wherein the polyester can in particular be selected from the group consisting of polybutylene succinate (PBS), polybutylene succinate adipate (PBSA) and polyethylene succinate (PES), or mixtures thereof.

The polyester content in the mixture is preferably 20 to 85 wt. %, in particular 30 to 80 wt. %, more preferably 40 to 80 wt. %, based on the total composition.

The polymer material according to the invention also contains an epoxide group-containing polymer, this preferably being an epoxide group-containing copolymer. Epoxide group-containing polymers or copolymers especially considered are those having a molecular weight (M_w) of 1,000 to 25,000, in particular 3,000 to 10,000.

Preferably, the epoxide group-containing polymer is a glycidyl(meth)acrylate-containing polymer. A suitable glycidyl(meth)acrylate-containing polymer is, for example, a copolymer consisting of (a) styrene and/or ethylene and/or methyl methacrylate and/or methyl acrylate and (b) glycidyl(meth)acrylate. Particularly well suited as the glycidyl(meth)acrylate-containing polymer is a copolymer which is selected from the group consisting of styrene - methyl methacrylate - glycidyl methacrylate, ethylene -

methyl acrylate - glycidyl methacrylate and ethylene - glycidyl methacrylate. Glycidyl(meth)acrylate is preferably contained therein in a quantity of 1 to 60 wt. %, in particular 5 to 55 wt. %, more preferably 45 to 52 wt. % based on the total composition of the glycidyl(meth)acrylate-containing polymer.

Epoxide group-containing copolymers based on styrene, ethylene, acrylic ester and/or methacrylic ester are also considered as epoxide group-containing polymers.

The mixture preferably contains 0.01 to 5 wt. %, in particular 0.05 to 3 wt. %, more preferably 0.1 to 2 wt. % of epoxide group-containing polymer, based on the total composition.

The mixture, in addition to the principal constituents of starch or starch derivative, polyester and epoxide group-containing polymer, can contain conventional additives such as, for example, processing aids, plasticizers, stabilisers, flame retardants and/or fillers.

The method according to the invention provides for the mixture to be homogenised. Homogenisation can be carried out by means of any procedures familiar to the person skilled in the art who is active in the field of plastics technology. Preferably, the mixture is homogenised by dispersing, stirring, kneading and/or extruding. According to a preferred embodiment of the invention, shear forces act on the mixture during homogenisation. Suitable production methods for thermoplastic polymers containing starch, which can also be analogously applied to the production of the polymer material according to the

invention, are described, for example, in the publications EP 0 596 437 B1 and EP 0 917 540 B1.

According to a preferred embodiment of the invention, the mixture is heated during homogenisation (e.g. in the extruder), preferably to a temperature of 90 to 250°C, in particular 130 to 220°C.

According to the invention, it is preferred to keep the water content of the mixture as low as possible.

Preferably, the water content of the mixture is set to less than 10 wt. %, in particular less than 7 wt. %, more preferably less than 5 wt. %, in particular less than 3 wt. %, even more preferably less than 1.5 wt. % and most preferably less than 1 wt. %, based on the total composition.

Preferably, the water content is set by drying during homogenisation. The drying process can be carried out, for example, by degassing the mixture or the melt, advantageously by removing the water vapour during extrusion.

According to another preferred embodiment of the invention, the polymer material produced according to the method according to the invention has thermoplastic properties. Preferably, the material can be thermoplastically processed.

With the method according to the invention, it is possible to produce unplasticised, thermoplastic polymer blends based on starch, which have a starch content of at least 34 wt. % and, at the same time, have excellent mechanical

properties. Unplasticised in this connection means, in particular, that the polymer blends do not contain any glycerol and/or any sorbitol. In particular, films can be produced from the polymer material produced according to the method according to the invention, which have an elongation at break in accordance with DIN 53455 of at least 200 %, and/or a dart drop value in accordance with ASTM D-1709 of at least 5 g/ μ m.

The invention therefore also relates to a starch-containing, thermoplastically processable polymer material, wherein

(a) the polymer material contains less than 10 wt. % low-molecular substances, based on the total composition,

(b) the starch proportion of the polymer material is at least 34 wt. % and

(c) a film produced from the polymer material has an elongation at break in accordance with DIN 53455 of at least 200 % and/or a dart drop value in accordance with ASTM D-1709 of at least 5 g/ μ m.

The starch-containing material according to the invention contains less than approximately 10 wt. % low-molecular substances and is, thereby, essentially unplasticised. In terms of the invention, low-molecular substances are understood to be substances with a molecular weight of less than 500 g/mol, in particular less than 250 g/mol. Low-molecular substances in terms of the invention, are, in particular, water, glycerol, sorbitol and/or mixtures thereof.

According to a preferred embodiment of the invention, the polymer material according to the invention contains less

than 7 wt. %, in particular less than 5 wt. %, preferably less than 3 wt. % low-molecular substances, based on the total composition. According to another preferred embodiment of the invention, the polymer material according to the invention does not contain any glycerol and/or any sorbitol.

According to a further preferred embodiment of the invention, the starch proportion of the polymer material is at least 35 wt. %, in particular at least 36 wt. %, preferably at least 37 wt. %, more preferably at least 38 wt. % and most preferably at least 39 wt. %.

The polymer material according to the invention can also contain a polyester as another constituent, preferably in an amount less than 70 wt. %, in particular less than 65 wt. %, more preferably less than 60 wt. %, most preferably less than 55 wt. %.

The polymer materials according to the invention are suitable for a wide variety of purposes. The materials are, in particular, suitable for producing moulded parts, films or fibres. Consequently, the invention also relates to moulded parts, films or fibres produced from the materials according to the invention.

The invention will be subsequently described more closely by means of exemplary embodiments.

Example 1

Producing glycidyl-modified polymer material containing starch

A mixture consisting of native potato starch, aliphatic-aromatic copolyester and epoxide group-containing polymer in the proportions specified below was filled into a twin-screw extruder.

A random copolyester based on 1,4-butanediol, adipic acid and terephthalic acid having a glass transition temperature (T_g) of -30 to -35°C and a melting range of 105 to 115°C was used as the aliphatic-aromatic copolyester.

A random copolymer based on styrene - methyl methacrylate - glycidyl methacrylate having a molecular weight M_w of approximately 6,800 and an epoxy group equivalent weight of 285 g/mol (additive A) was added as the epoxide group-containing polymer (glycidyl additive).

The mixture was intensively mixed in the extruder within a temperature range from 150 to 190°C, wherein the melt was at the same time degassed in order to dehydrate the mixture. A homogenous melt was formed which could be extracted and granulated. The water content of the compound homogenised in the way described and thermoplastically processed was under 1-wt. %.

By mixing and homogenising the starch with aliphatic-aromatic copolyester a two-phase blend was produced, in which the starch forms the disperse phase and the aliphatic-aromatic copolyester forms the continuous phase. The addition of epoxide group-containing polymer (i.e. glycidyl-containing polymer) caused intra- and inter-molecular chemical cross-linking of starch and aliphatic-

aromatic copolyester, which had a significant effect on the mechanical properties of the thermoplastic blend produced.

From the materials produced, films having a thickness of approximately 40 μm were manufactured by blow film extrusion. To this effect, the granulate was conveyed into a single-screw extruder (L/D = 30, intake cooled, screen 250 μm), melted at 165°C to 190°C, blown up over a tubular die (Mono, die gap 0.8 mm) to form the film bubble (blow-up ratio 3.5) and after flattening was removed.

Example 2

In this example, the effect of glycidyl additive on the mechanical properties of blown films having different starch contents was determined.

Various polymer materials containing starch were produced from aliphatic-aromatic copolyester (59.5 to 66.1 wt. %), native potato starch (33.4 to 40 wt. %) and epoxide group-containing copolymer (0.5 wt. %) according to Example 1. The proportion of native potato starch was varied in the course of this between 33.4 and 40 wt. % step by step at the expense of the aliphatic-aromatic copolyester (see Figures 1 and 2).

As a comparison composition, polymer material was produced without glycidyl additive from aliphatic-aromatic copolyester (66.6 wt. %) and native potato starch (33.4 wt. %) according to the procedure described in Example 1.

After compounding the different composition variants, blown films were produced from the polymer materials produced and

their mechanical properties determined. In particular, the tensile strength (TS), elongation at break (EB), MFR (Melt Flow Rate) and dart drop values (puncture resistance) of the films were determined.

Figure 1 shows the tensile strengths and elongations at break of the films produced with different starch contents.

Compared to a standard film without glycidyl additive produced from the comparison composition, the corresponding glycidyl-modified film with the same starch content (33.4 wt. %) has a considerably higher tensile strength. This difference leads, due to the tension values generally decreasing with an increasing starch proportion, to comparable tensile strengths of standard films with 33.4 wt. % starch and glycidyl-modified films with 40 wt. % starch.

Provided that the starch content is the same, the value for the elongation at break of the glycidyl-modified film does not differ from that of the standard film. By using glycidyl additive, however, even for a film with a starch proportion of 40 % the level of elongation at break (= elasticity) can be maintained at over 400 %.

At the same time, it has to be taken into account that films consisting of polymer material of the same composition without glycidyl additive with a more than 34 % starch proportion are extremely grainy, brittle and fragile, so that determining mechanical characteristics is practically impossible.

In Figure 2 the MFR (Melt Flow Rate) and the dart drop values (puncture resistance) of glycidyl-modified films with increasing starch content are illustrated.

It emerges from Figure 2 that both curves only fall slightly with increasing starch content. While the dart drop values are at the same level for the standard composition without glycidyl additive and for the modified composition, the glycidyl additive brings about a fall in the MFR to less than half of the standard value.

The distinctly lowered MFR level of the formulations treated with glycidyl in comparison to the standard film without glycidyl additive is - without being tied down to one specific theory - to be attributed to the epoxide-induced cross-linking of the polymer chains. The MFR emerges, therefore, as a suitable parameter for evaluating the chemical reaction of corresponding chain lengtheners/cross-linking agents.

What are also striking in Figure 2 are the dart drop values which are stable over the entire starch concentration range. The observation, already made by plotting tensile strength and elongation at break (Figure 1), is confirmed that by adding reactive glycidyl additives to the base composition the brittleness of the material, which usually increases with an increasing starch proportion, can be effectively counteracted.

Example 3

In this example, the effect of different glycidyl additives on the mechanical properties of blown films containing starch was determined.

Example 2 was repeated with three different epoxide-containing polymers (glycidyl additives).

Various polymer materials containing starch were produced from aliphatic-aromatic copolyester (59.5 to 66.1 wt. %), native potato starch (33.4 to 40 wt. %) and epoxide group-containing copolymer (additive A, B or C, see below) (0.5 wt. %) according to the procedure described in Example 1. The proportion of native potato starch was varied in the course of this between 33.4 and 40 wt. % step by step at the expense of the aliphatic-aromatic copolyester (see Figures 3 and 4).

As a comparison composition, polymer material was produced without glycidyl additive from aliphatic-aromatic copolyester (66.6 wt. %) and native potato starch (33.4 wt. %) according to the procedure described in Example 1.

A random copolymer based on styrene - methyl methacrylate - glycidyl methacrylate having a molecular weight M_w of approximately 6,800 and an epoxy group equivalent weight of 285 g/mol was used as additive A.

A random copolymer based on ethylene - methyl acrylate - glycidyl methacrylate having approx. 24 wt. % methyl acrylate, 68 wt. % ethylene and 8 wt. % glycidyl methacrylate and an epoxy group equivalent weight of 1775 g/mol was used as additive B.

A random copolymer based on ethylene - glycidyl methacrylate having approx. 92 wt. % ethylene and 8 wt. % glycidyl methacrylate and an epoxy group equivalent weight of 1775 g/mol was used as additive C.

The glycidyl additives used differ in particular with regard to their content of reactive epoxy units. The mass-related concentration of epoxy units is higher by a factor of 6.23 in additive A than in additives 2 and 3 [sic: B and C?]. Thus, additive B and additive C with the same originally weighted-in quantity contain less than a sixth of reactive epoxy groups compared to additive A.

This significant difference has a correspondingly considerable effect on the properties of comparably produced compositions.

Figures 3 and 4 show, by way of example, the starch-content dependent development of tensile strength and MFR of polymer materials containing starch according to Example 2, offset in each case with 0.5 % of the additives A, B or C.

It emerges from Figure 3 that with additive A the tensile strength of the films increases linearly with increasing starch content, while with additives 2 and 3 it decreases.

It emerges from Figure 4 that the MFR values, which all linearly fall slightly with an increasing starch proportion, are at a very low level for the material treated with additive A. A comparison of the materials treated with additives 2 and 3 with a standard film without glycidyl additive does not, in contrast, show the glycidyl

additive having any perceptible effect on the melt flow rate.

The courses of the curves illustrated in Figures 3 and 4 show that it can hardly be detected that the additives 2 and 3 perceptibly affect the mechanical properties of the films with the concentration of 0.5 wt. % used.

Nevertheless, an improvement in the compatibility of the starch and polyester constituents was also detected with the additives B and C in the concentration used compared to the comparison composition without glycidyl additive.

Example 4

In this example, the effect of different concentrations of epoxide group-containing polymer (glycidyl additive) on the mechanical properties of blown films having a starch content of up to 42 wt. % was determined.

Firstly, the effectiveness of different additive concentrations was tested at a manufacturing plant (ZSK 70/7). For this purpose, materials with three different additive concentrations were compounded (0.1 wt. % glycidyl additive, 0.5 wt. % glycidyl additive and a comparison composition (standard) without additive). Additive A from Example 3 was used as the epoxide group-containing polymer.

Various polymer materials containing starch were produced from aliphatic-aromatic copolyester (57.5 to 66.5 wt. %), native potato starch (33.4 to 42 wt. %) and epoxide group-containing polymer (0.1 and 0.5 wt. %) according to Example 1. The proportion of native potato starch was varied in the course of this between 33.4 and 42 wt. % step by step at

the expense of the aliphatic-aromatic copolyester (see Figures 5 and 6). Equally, the proportion of epoxide group-containing polymer (additive A) was varied at the expense of the aliphatic-aromatic copolyester.

As a comparison composition, polymer material was produced without glycidyl additive from aliphatic-aromatic copolyester (66.6 wt. %) and native potato starch (33.4 wt. %) according to the procedure described in Example 1.

Figure 5 shows the course of the melt flow rate (MFR) of blown films produced from the materials, dependent on the starch content and the concentration of additive. It is evident from the values that the melt flow rate (MFR) (i.e. the flowability) reduces with increasing starch content and increasing glycidyl concentration. In comparison to the standard composition (circle) the MFR value of the formulation with 42 wt. % starch and 0.5 wt. % glycidyl additive falls to less than a fifth (triangle), an indication of extensive cross-linking of the contained polymers.

Without being tied down to one specific theory, this course can be explained by a cross-linking reaction of the glycidyl additive with the polyester and the starch. The sudden halving of the MFR at 40 wt. % starch in the change-over from the continuous line to the dashed line shows that the falling MFR value cannot be solely attributed to an increase in the starch content (as is so in the case of the continuous curve between 33 and 40 wt. %) but can also be significantly attributed to an increased reaction of the glycidyl additive used in more concentrated form.

In Figure 6, the course of tensile strength (TS), elongation at break (EB) and dart drop (DD) is illustrated for films with different contents of starch and glycidyl additive. While TS and EB decrease with an increasing starch content, the DD value remains at a constant level.

It is evident from Figure 6 that the elongation at break, linearly decreasing with increasing starch content, is not perceptibly affected by adding glycidyl additive. Even at a 0.5 wt. % proportion of additive (continuous curve), the value falls further after exceeding 40 wt. % starch. The puncture resistance (DD value) maintains itself at a constant level over the entire investigated range.

Without being tied down to one specific theory, it is assumed that the effect of a DD value normally decreasing with an increasing starch content (i.e. the film becomes more brittle) is compensated for by polymer cross-linking with the glycidyl additive. The strand cross-linking, more extensive with a higher glycidyl additive content, can be substantiated by a significantly higher tensile strength with the same starch content (sudden change-over of the dash-dotted curve at 40 wt. % starch).

Example 5

In this example, the glycidyl additives 1 and 2 from Example 3 with equivalent glycidyl proportions were compared.

Firstly, a polymer material containing starch was produced from aliphatic-aromatic copolyester (59.9 wt. %), native

potato starch (40 wt. %) and *additive A* from Example 3 (0.1 wt. %) according to the procedure described in Example 1.

Subsequently, a polymer material containing starch was produced from aliphatic-aromatic copolyester (59.4 wt. %), native potato starch (40 wt. %) and *Additive B* from Example 3 (0.6 wt. %) according to the procedure described in Example 1.

The two materials produced in this way and the two blown films produced from them were compared with one another. Figure 7 shows the results:

Figure 7 shows that the additives 1 and 2, with quantitatively equivalent glycidyl proportions (0.1 wt. % *additive A* versus 0.6 wt. % *additive B*), produce comparable material properties in the polymer material. Only the value for the elongation at break (EB) is perceptibly higher with the film containing *additive B*.

From the results, the following can be established based on the tests carried out:

The material properties of generic polymer materials containing starch can be significantly altered by adding glycidyl-containing additives. While conventional polymer materials containing starch without glycidyl additive have inadequate mechanical properties above approximately 34 wt. %, just a content of 0.1 % of glycidyl additive enables a polymer material to be produced with a starch content of 40 wt. % with, at the same time, excellent mechanical properties.

While the increase in the starch content inevitably is at the expense of the elasticity of the glycidyl-modified material, the puncture resistance of the glycidyl-modified material is not affected by an increase in the starch proportion.

Without being tied down to one specific theory, it is assumed that the glycidyl additive acts as a compatibiliser between the otherwise incompatible starch and polyester polymers. The efficiency of the polymer cross-linking is exhibited in increased tensile strength values with, at the same time, a lower melt flow rate (MFR).

The invention has been described above by means of exemplary embodiments. At the same time, it is to be understood that the invention is not limited to the exemplary embodiments described. Rather, varied options for modification and refinement arise within the scope of the invention for the person skilled in the art.

What is claimed is:

1. A method for producing a polymer material containing starch, characterised by:

(a) producing a mixture containing at least

- 1 to 75 wt.% starch, starch derivative, or a mixture thereof,
- 10 to 85 wt.% polyester, and
- 0.01 to 7 wt.% of a polymer containing epoxide groups;

(b) homogenising the mixture by supplying thermal energy, mechanical energy or mechanical and thermal energy; and

(c) setting the water content of the mixture to less than 1.5 wt.% based on the total composition of the mixture.

2. The method according to claim 1, wherein the mixture contains 5 to 75 wt.% of the starch, the starch derivative, or the mixture thereof.

3. The method according to claim 2, wherein the mixture contains 10 to 75 wt.% of the starch, the starch derivative, or the mixture thereof.

4. The method according to claim 3, wherein the mixture contains 15 to 70 wt.% of the starch, the starch derivative, or the mixture thereof.

5. The method according to claim 4, wherein the mixture contains 25 to 55 wt.% of the starch, the starch derivative, or the mixture thereof.
6. The method according to claim 5, wherein the mixture contains 34 to 51 wt.% of the starch, the starch derivative, or the mixture thereof.
7. The method according to any one of claims 1 to 6, wherein the mixture contains 20 to 85 wt.% of the polyester.
8. The method according to claim 7, wherein the mixture contains 30 to 80 wt.% of the polyester.
9. The method according to claim 8, wherein the mixture contains 40 to 80 wt.% of the polyester.
10. The method according to any one of claims 1 to 9, wherein the mixture contains 0.01 to 5 wt.% of the polymer containing epoxide groups.
11. The method according to claim 10, wherein the mixture contains 0.05 to 3 wt.% of the polymer containing epoxide groups.
12. The method according to claim 11, wherein the mixture contains 0.1 to 2 wt.% of the polymer containing epoxide groups.

13. The method according to any one of claims 1 to 12, wherein the polymer material is biodegradable according to EN 13432.
14. The method according to any one of claims 1 to 13, wherein the polyester is an aliphatic-aromatic co-polyester, aliphatic polyester, aromatic polyester, PHA, PLA, PHB or PHBV.
15. The method according to any one of claims 1 to 14, wherein the polyester has a glass transition temperature (Tg) of less than 0°C.
16. The method according to claim 15, wherein the polyester has a glass transition temperature (Tg) of less than -4°C.
17. The method according to claim 16, wherein the polyester has a glass transition temperature (Tg) of less than -10°C.
18. The method according to claim 17, wherein the polyester has a glass transition temperature (Tg) of less than -20°C.
19. The method according to claim 18, wherein the polyester has a glass transition temperature (Tg) of less than -30°C.
20. The method according to claim 14, wherein the aliphatic-aromatic polyester is a copolyester based on at least adipic acid.

21. The method according to claim 20, wherein the copolyester is a random copolyester.
22. The method according to claim 14, wherein the aliphatic-aromatic polyester is a copolyester based on 1,4-butanediol, adipic acid, and terephthalic acid or a terephthalic acid derivative.
23. The method according to claim 22, wherein the terephthalic acid derivative is dimethyl terephthalate (DMT).
24. The method according to claim 22 or 23, wherein the copolyester is a random copolyester.
25. The method according to any one of claims 22 to 24, wherein the polyester has a glass transition temperature (T_g) of -25 to -40°C.
26. The method according to claim 25, wherein the polyester has a glass transition temperature (T_g) of -30°C to -35°C.
27. The method according to claim 25 or 26, wherein the polyester has a melting range of 100°C to 120°C.
28. The method according to claim 27, wherein the polyester has a melting range of 105°C to 115°C.
29. The method according to any one of claims 1 to 19, wherein the polyester is an aliphatic polyester which is polyhydroxyvalerate, polyhydroxybutyrate-hydroxyvalerate

copolymer or polycaprolactone.

30. The method according to any one of claims 1 to 19, wherein the polyester is an aliphatic polyester based on succinate, wherein the polyester is polybutylene succinate (PBS), polybutylene succinate adipate (PBSA) or polyethylene succinate (PES).

31. The method according to any one of claims 1 to 30, wherein the polyester is biodegradable according to EN 13432.

32. The method according to any one of claims 1 to 31, wherein the polymer containing epoxide groups is a copolymer.

33. The method according to any one of claims 1 to 31, wherein the polymer containing epoxide groups is a polymer containing glycidyl (meth)acrylate.

34. The method according to claim 33, wherein the polymer containing glycidyl (meth)acrylate is a copolymer comprising:

(a) one or more of styrene, ethylene, methyl methacrylate, methyl acrylate; and

(b) glycidyl (meth)acrylate.

35. The method according to claim 33 or 34, wherein the polymer containing glycidyl (meth)acrylate is a copolymer containing epoxide groups based on one or more of styrene, ethylene, acrylic ester, and methacrylic ester.

36. The method according to any one of claims 33 to 35, wherein the polymer containing glycidyl (meth)acrylate is a copolymer which is styrene - methyl methacrylate - glycidyl methacrylate; ethylene - methyl acrylate - glycidyl methacrylate; or ethylene - glycidyl methacrylate.

37. The method according to any one of claims 33 to 36, wherein the polymer containing glycidyl(meth)acrylate contains glycidyl (meth)acrylate in a quantity from 1 to 60 wt.%, based on the total composition of the polymer containing glycidyl (meth)acrylate.

38. The method according to claim 37, wherein the polymer containing glycidyl (meth)acrylate contains glycidyl (meth)acrylate in a quantity from 5 to 55 wt.%, based on the total composition of the polymer containing glycidyl (meth)acrylate.

39. The method according to claim 38, wherein the polymer containing glycidyl (meth)acrylate contains glycidyl (meth)acrylate in a quantity from 45 to 52 wt.%, based on the total composition of the polymer containing glycidyl (meth)acrylate.

40. The method according to any one of claims 1 to 39, wherein the polymer containing epoxide groups has a molecular weight (M_w) from 1,000 to 25,000.

41. The method according to claim 40, wherein the polymer containing epoxide groups has a molecular weight (M_w) from

3,000 to 10,000.

42. The method according to any one of claims 1 to 41, wherein the mixture is homogenised by one or more of dispersing, stirring, kneading and extruding.

43. The method according to claim 42, wherein the mixture is homogenised by extrusion.

44. The method according to any one of claims 1 to 43, wherein the mixture is homogenised by the action of shear forces on the mixture.

45. The method according to any one of claims 1 to 44, wherein the mixture is heated to a temperature from 90 to 250°C, during homogenisation or extrusion.

46. The method according to claim 45, wherein the mixture is heated to a temperature from 130°C to 220°C.

47. The method according to any one of claims 1 to 46, wherein the water content of the mixture is set to less than 1 wt.%, based on the total composition.

48. The method according to any one of claims 1 to 47, wherein the water content of the mixture is set during homogenisation.

49. The method according to any one of claims 1 to 48, wherein the water content of the mixture is set by degassing

the mixture.

50. The method according to claim 49, wherein the water content of the mixture is set by degassing the melt.

51. The method according to any one of claims 1 to 50, wherein the water content of the mixture is set by drying the mixture during homogenisation or extrusion.

52. The method according to any one of claims 1 to 51, wherein a film produced from the polymer material has a tensile strength according to DIN 53455 from 5 to 60 N/mm².

53. The method according to claim 52, wherein a film produced from the polymer material has a tensile strength according to DIN 53455 from 10 to 40 N/mm².

54. The method according to any one of claims 1 to 53, wherein a film produced from the polymer material has an elongation at break according to DIN 53455 from 100 to 1000%.

55. The method according to claim 54, wherein a film produced from the polymer material has an elongation at break according to DIN 53455 from 200 to 800%.

56. A polymer material which contains starch and can be thermoplastically processed, wherein:

(a) the polymer material contains less than 3 wt.% water, based on the total composition;

(b) the proportion of starch in the polymer material is

at least 34 wt.%;

(c) the polymer material contains a polyester, wherein the polyester is an aliphatic-aromatic copolyester, aliphatic polyester, aromatic polyester, PHA, PLA, PHB or PHBV; and

(d) the polymer material contains a copolymer containing epoxide groups which has a molecular weight (M_w) from 1,000 to 25,000.

57. The polymer material according to claim 56, wherein the polymer material contains less than 7 wt.% glycerol, sorbitol, or mixtures thereof, based on the total composition.

58. The polymer material according to claim 57, wherein the polymer material contains less than 5 wt.% glycerol, sorbitol, or mixtures thereof, based on the total composition.

59. The polymer material according to claim 58, wherein the polymer material contains less than 3 wt.% glycerol, sorbitol, or mixtures thereof, based on the total composition.

60. The polymer material according to any one of claims 56 to 59 wherein the proportion of starch in the polymer material is at least 35 wt.%.

61. The polymer material according to claim 60, wherein the proportion of starch in the polymer material is at least 36 wt.%.

62. The polymer material according to claim 61, wherein the proportion of starch in the polymer material is at least 37 wt.%.

63. The polymer material according to claim 62, wherein the proportion of starch in the polymer material is at least 38 wt.%.

64. The polymer material according to claim 63, wherein the proportion of starch in the polymer material is at least 39 wt.%.

65. The polymer material according to any one of claims 56 to 64, wherein a film produced from the polymer material has at least one of: an elongation at break according to DIN 53455 of at least 300%; and a dart drop value according to ASTM D-1709 of at least 10 g/ μm .

66. The polymer material according to any one of claims 56 to 65, wherein the polymer material contains the polyester in a quantity of less than 70 wt.%.

67. The polymer material according to claim 66, wherein the polymer material contains the polyester in a quantity of less than 65 wt.%.

68. The polymer material according to claim 67, wherein the polymer material contains the polyester in a quantity of less than 60 wt.%.

69. The polymer material according to claim 68, wherein the polymer material contains the polyester in a quantity of less than 55 wt.%.

70. The polymer material according to any one of claims 56 to 69, wherein the polyester is a polyester according to any one of claims 15 to 31.

71. The use of a polymer material according to any one of claims 56 to 70 for producing formed parts, films or fibres.

72. Formed parts, films or fibres containing a polymer material according to any one of claims 56 to 71.

Effect of starch proportion on tensile strength and elongation at break
 (Glycidyl additive content in each case 0.5 wt. %)

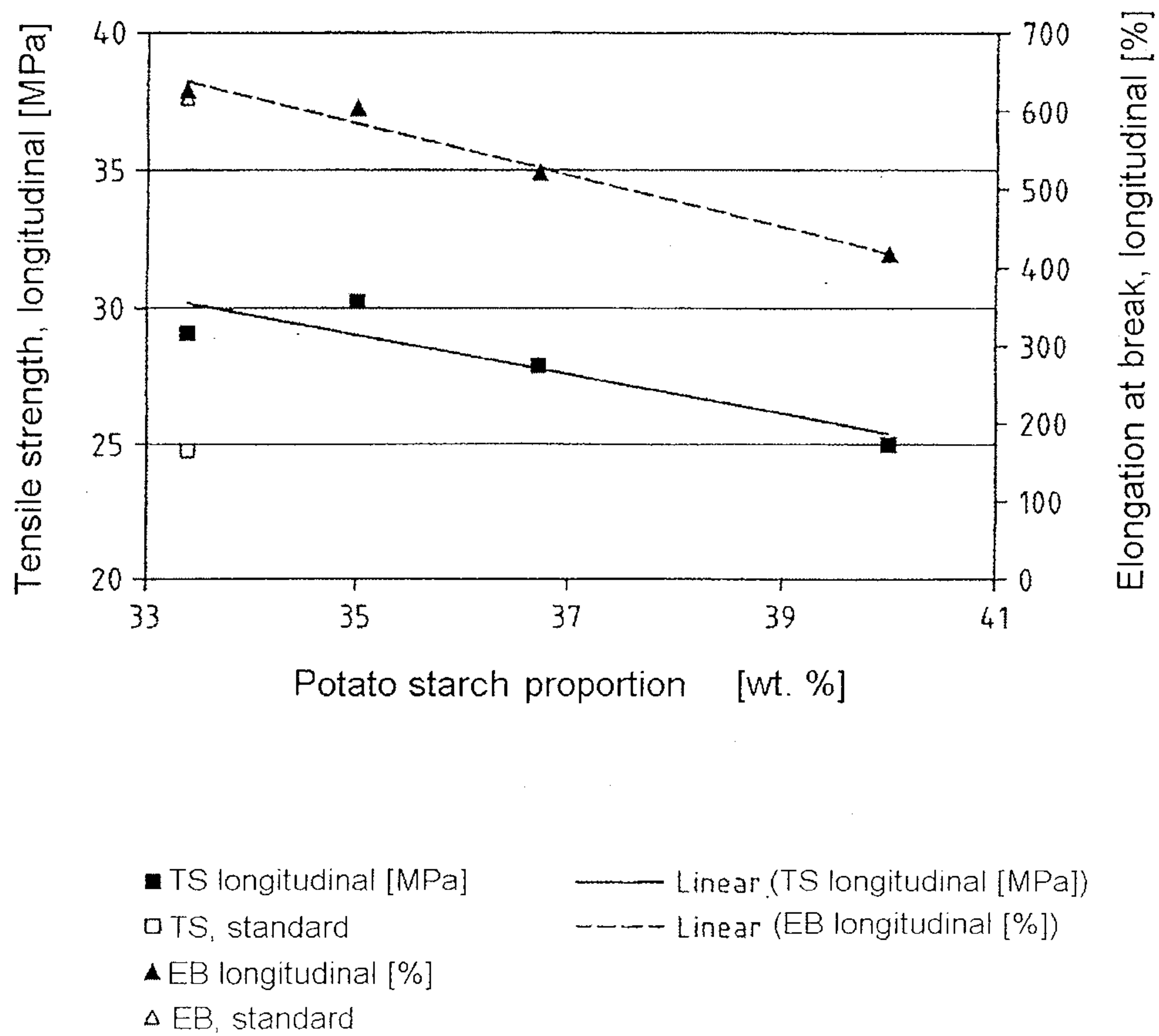


Fig.1

Effect of starch proportion on MFR and Dart Drop

(Glycidyl additive content in each case 0.5 wt. %)

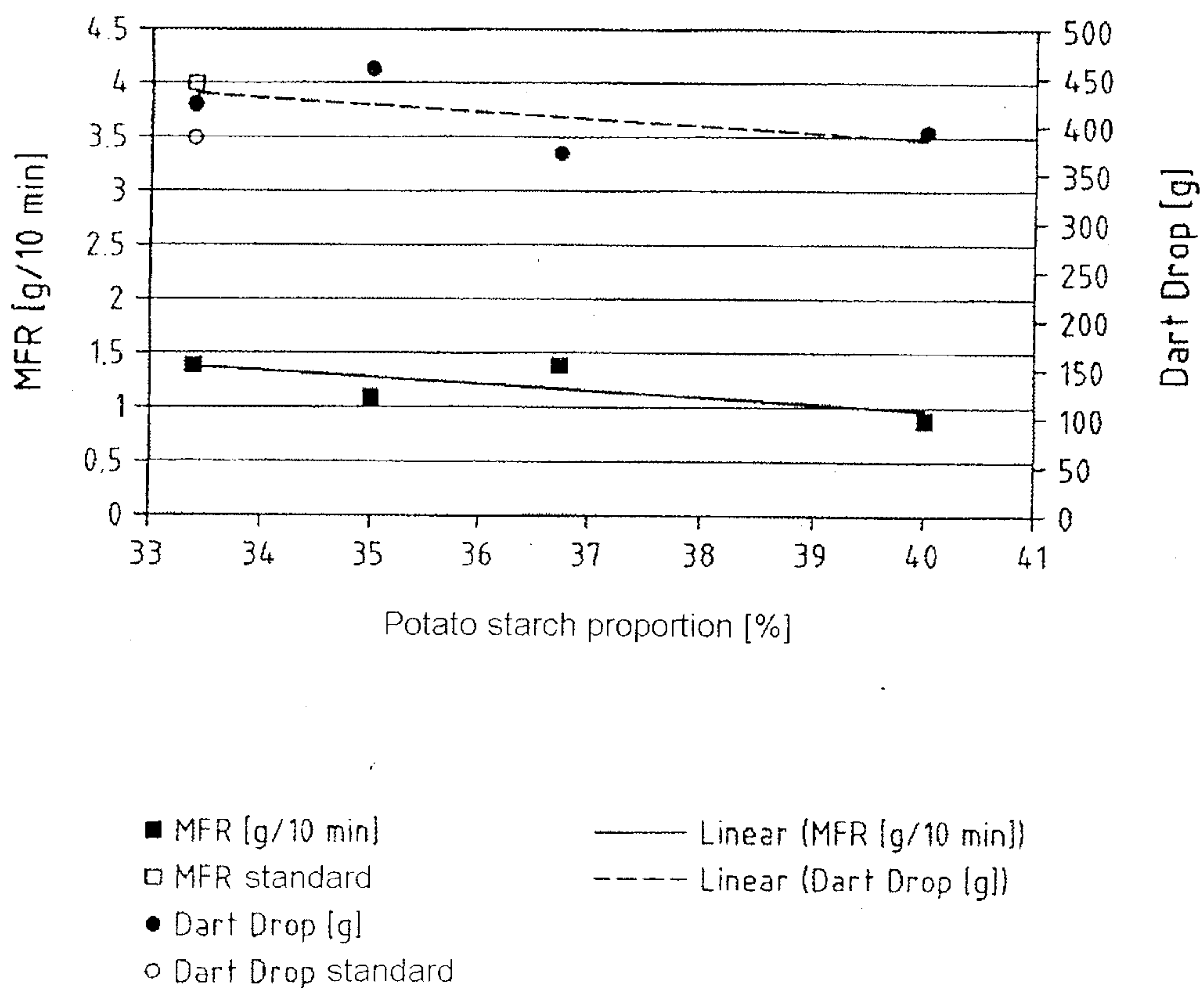


Fig.2

Effect of different glycidyl additives on tensile strength
 (Glycidyl additive content in each case 0.5 wt. %)

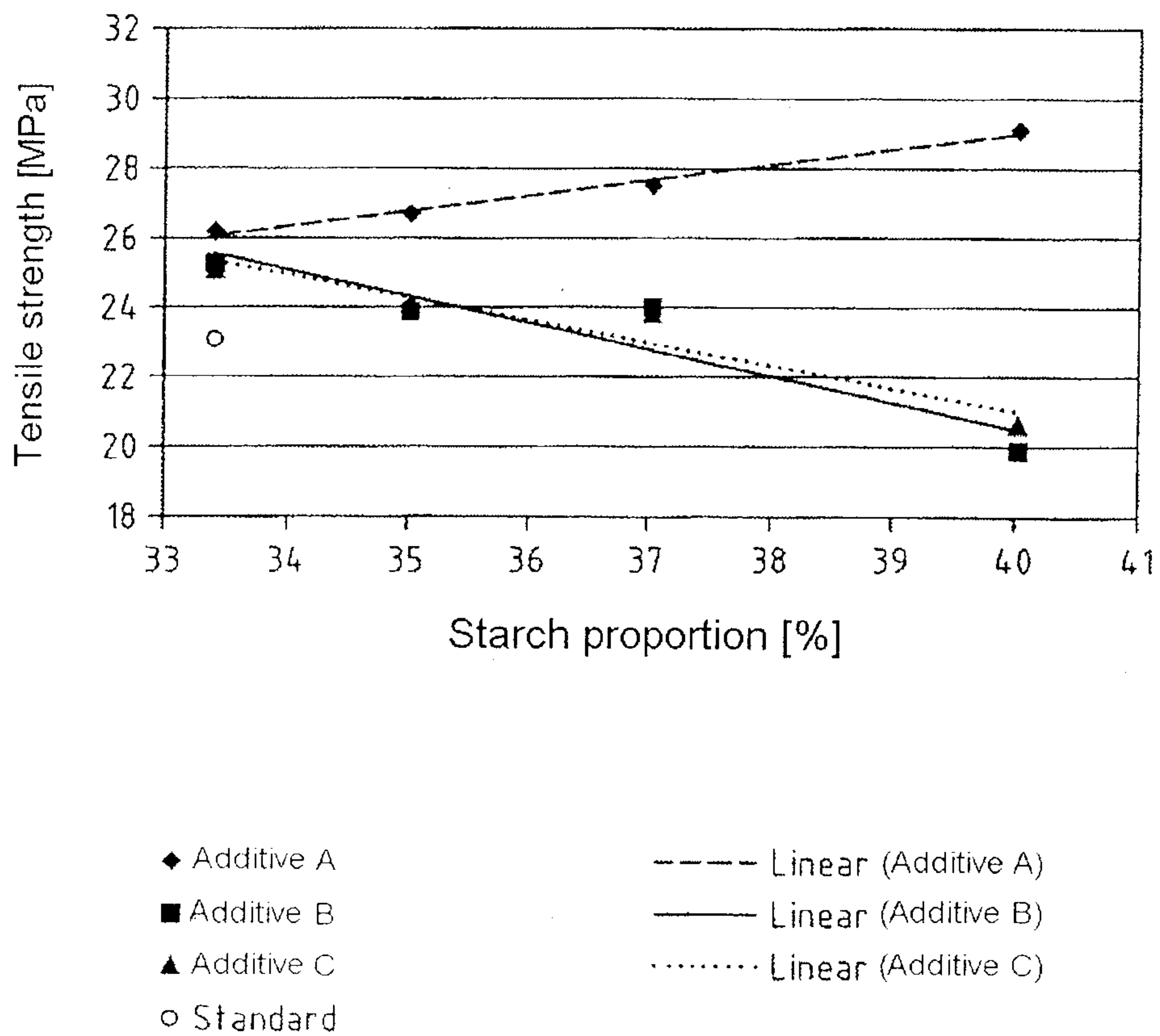


Fig.3

Effect of different glycidyl additives on MFR curve

(Glycidyl additive content in each case 0.5 wt. %)

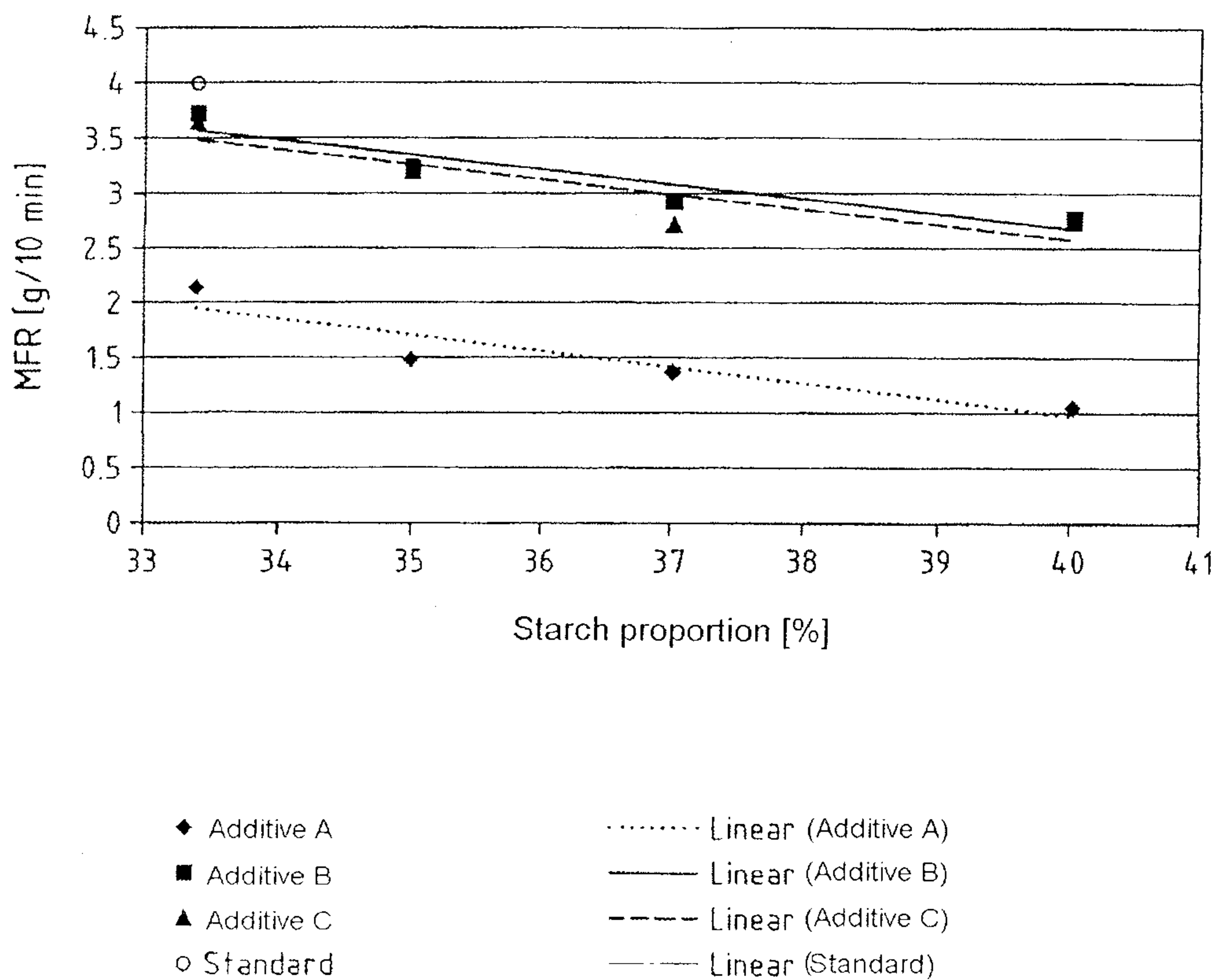
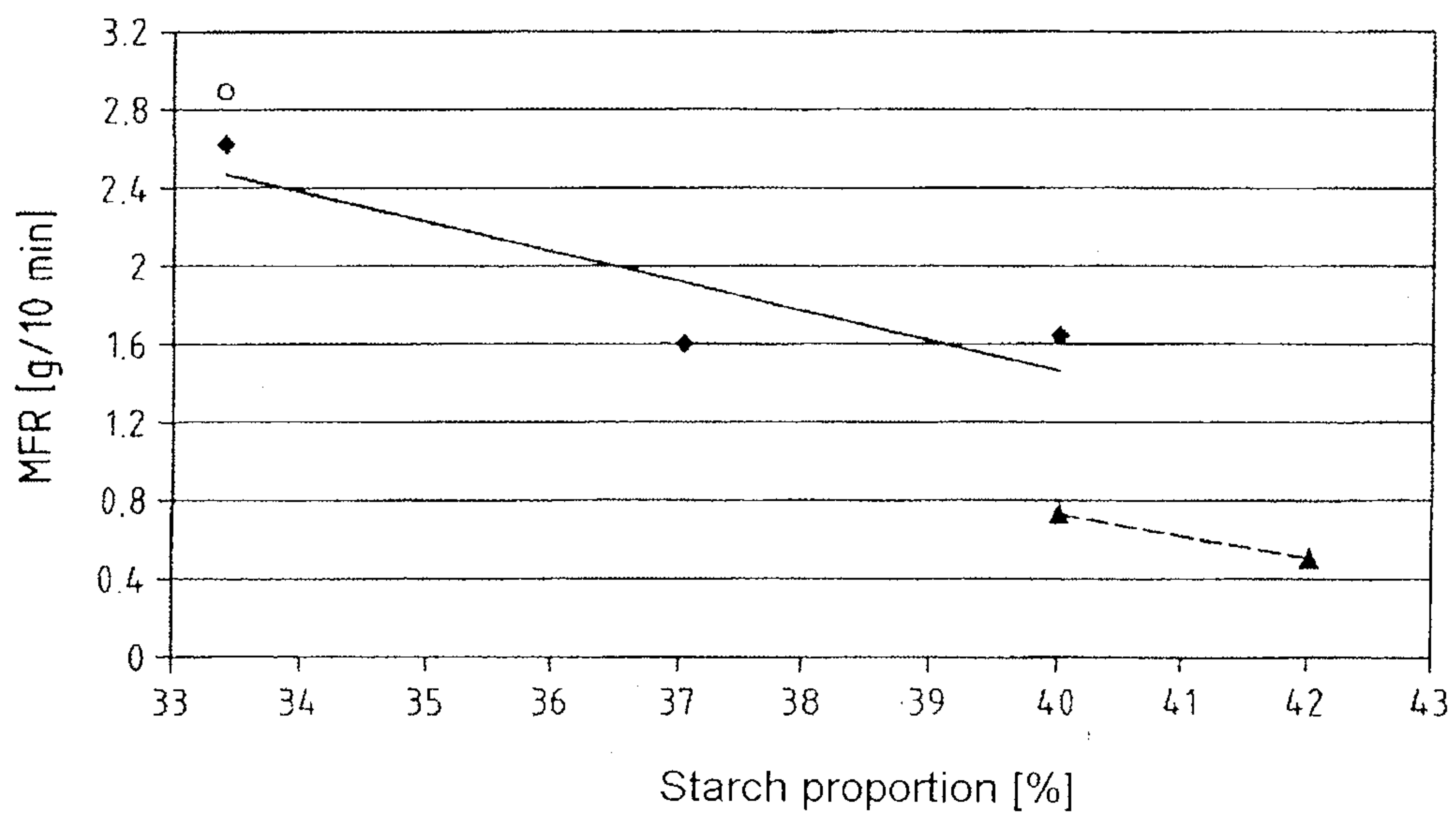


Fig.4

Effect of different quantitative proportions of glycidyl additives on the MFR curve

(190 °C, 5 kg)



- ◆ 0.1% additive A
- Standard
- ▲ 0.5% additive A
- Linear (0.1% additive A)
- - - Linear (0.5% additive A)

Fig.5

Effect of different quantitative proportions of glycidyl additives on elongation at break and strength

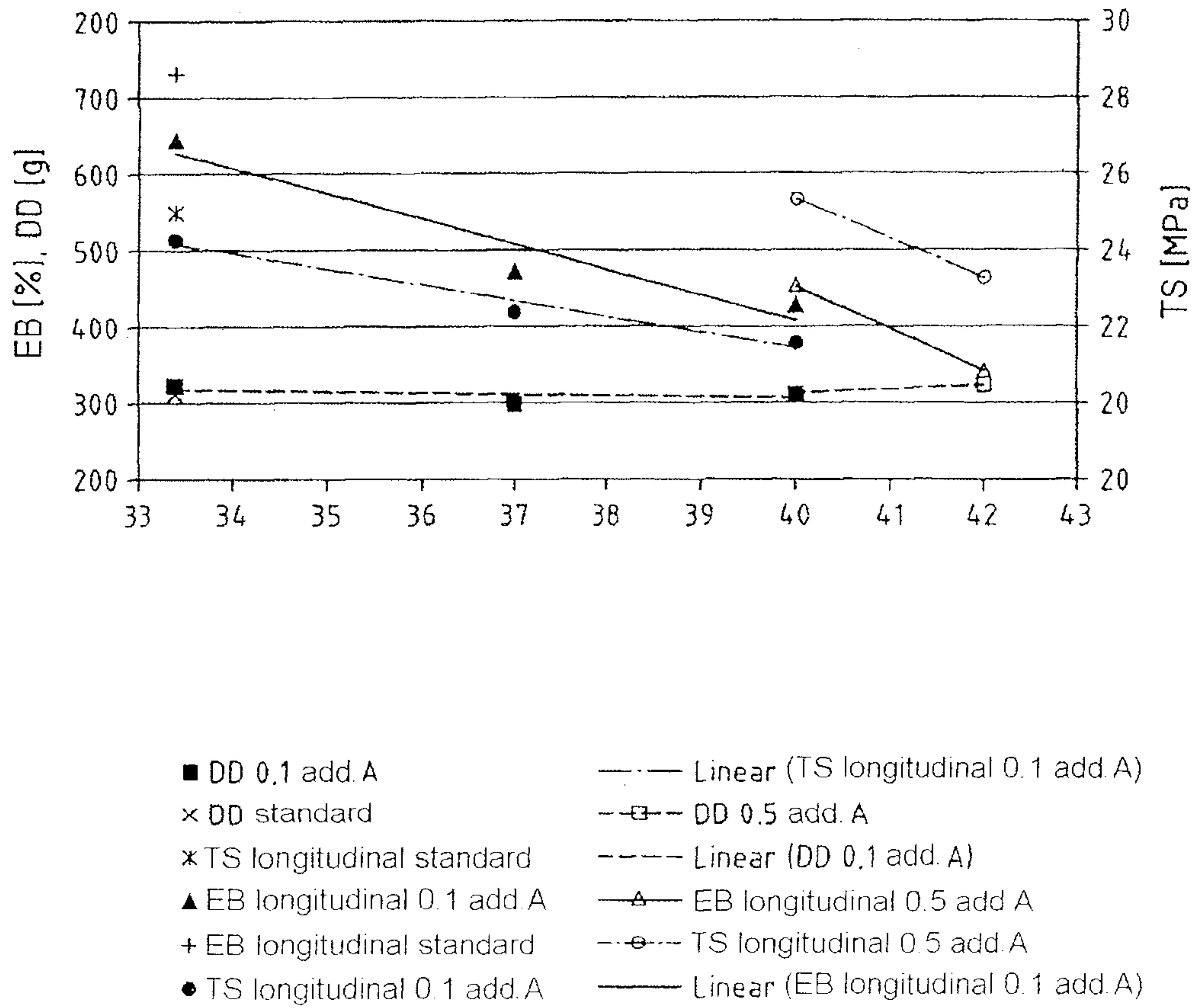


Fig.6

Comparison of different glycidyl additives at equivalent glycidyl proportions

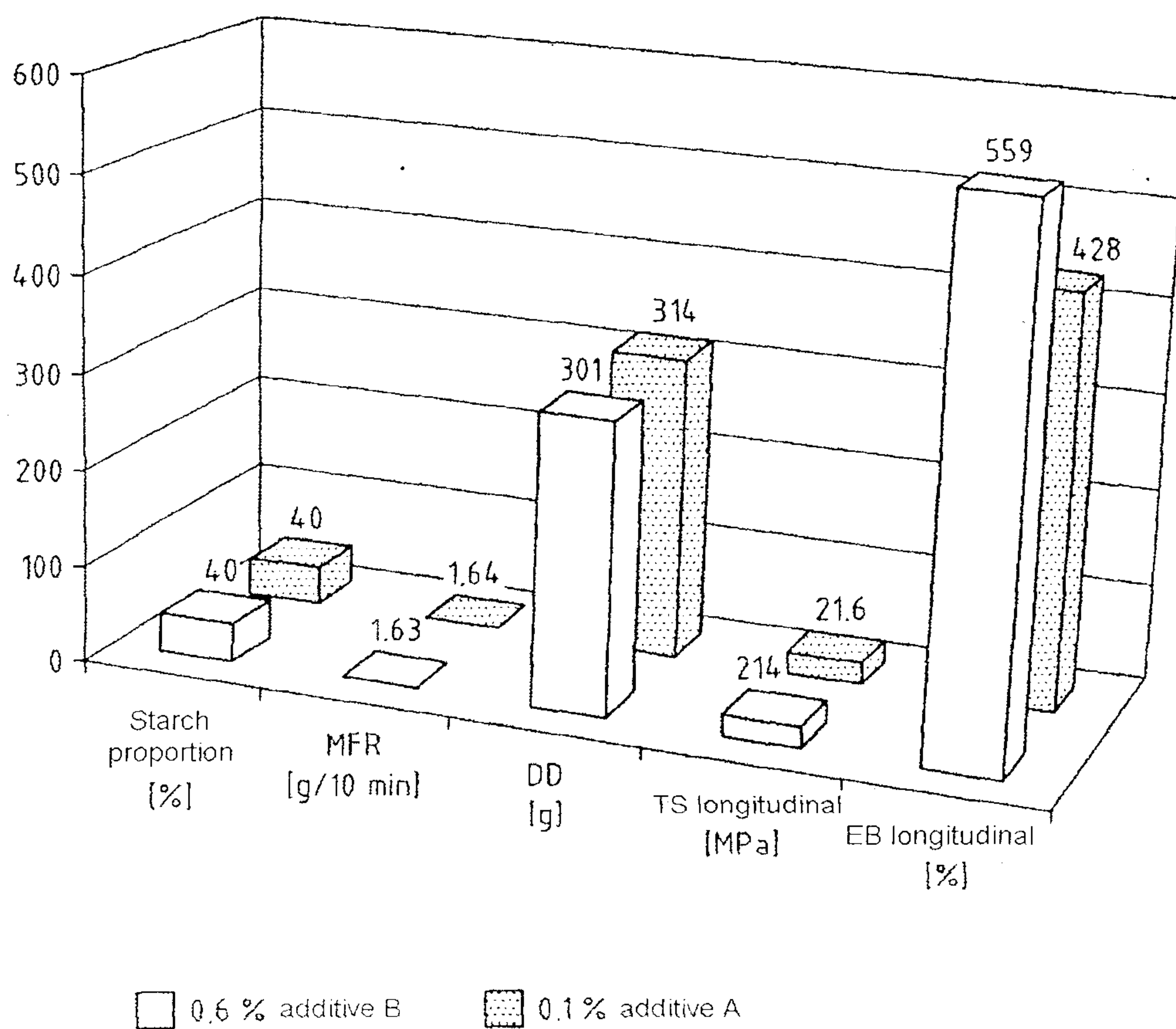


Fig.7