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(71) Applicants:
• **Raiz - Instituto De Investigação Da Floresta E Papel**
3800-783 Eixo, Aveiro (PT)
• **Universidade de Coimbra**
3004-531 Coimbra (PT)

(72) Inventors:
• **Martins Salgueiro Carta, Ana Margarida**
3800-783 Eixo, Aveiro (PT)
• **Coelho Bértolo, Raquel Alexandra**
3800-783 Eixo, Aveiro (PT)
• **De Oliveira Rodrigues Pinto, Paula Cristina**
3800-783 Eixo, Aveiro (PT)
• **Monteiro Valente, Artur José**
3004-531 COIMBRA (PT)
• **Bairrada Murtinho, Dina Maria**
3004-531 COIMBRA (PT)
• **Aguado Garcia, Roberto Juan**
3004-531 COIMBRA (PT)
• **Dos Santos Ferreira, Ana Cláudia**
3004-531 COIMBRA (PT)

(54) **METHOD FOR THE PRODUCTION OF A TISSUE PAPER**

(57) The present invention relates to a tissue paper production method comprising a step of coating a tissue paper with aqueous solutions comprising at least one biopolymer at the converting stage of a tissue product into a finished product.

The aqueous solutions of biopolymers considered in the present invention refer to solutions comprising gum

arabic, cellulose ethers, starch and modified starches, and mixtures thereof.

The method described in this invention results in an increase in the resistance properties of tissue products, a fundamental property in products such as, but not limited to, kitchen rolls, multipurpose rolls, toilet papers, hand towels, napkins, and pocket/face tissues.

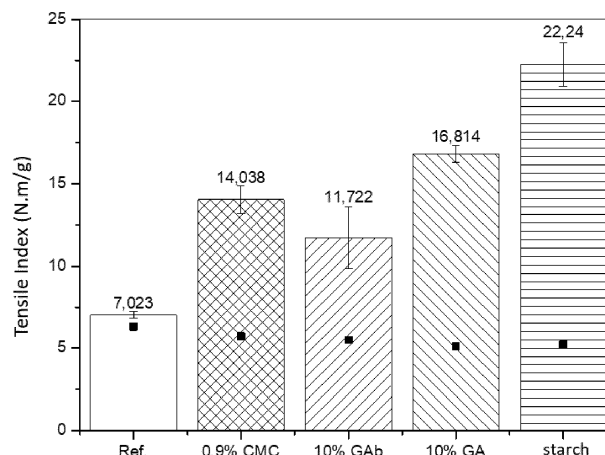


Fig. 1

Description

FIELD OF THE INVENTION

[0001] The present invention relates to the paper industry, namely to the production of tissue paper, and more particularly about a method for the production of tissue paper comprising coating the tissue paper with aqueous biopolymer solutions at the stage of converting the tissue paper into a finished product.

BACKGROUND OF THE INVENTION

[0002] Tissue paper is one of the most popular types of paper in the world. It is a well-established industry with a growing market, covering essential everyday products such as kitchen rolls, multi-purpose rolls, toilet papers, hand towels, napkins, and pocket/facial tissues [1,2]. Competition in this market has led to a constant search for alternatives either to reduce costs or to improve product performance through the use of ecological or "green" raw materials [3-6].

[0003] The main properties of tissue paper are its absorption capacity, softness and strength [3,6]. The importance of each of these properties is related to the specific application of the final product [6,7]. These properties are influenced by the origin and type of fibres, their production process, and the chemical and mechanical treatments to which they are submitted during paper production [7].

[0004] To improve the key properties of tissue papers (softness, absorbency and strength), chemical additives may be used. The development of strength properties occurs mainly in the paper machine through the addition of long fibre (increased fibre content), adjustments in refining or even through incorporation of specialty additives for strength development (for example starches and/or other modified polymers).

[0005] Once the paper reel is formed and ready to be converted, there are no operations during converting into a finished product that in any way promote the development of strength properties, and what most commonly happens is, in fact, the loss of strength due to the processing of the paper during its converting into a finished product.

[0006] The stage of converting into a finished product includes different operations such as unwinding, embossing, lamination, surface treatment (e.g. application of additives as softeners, and/or printing of coloured motifs), perforation, rewinding or folding, and packaging. Among these operations the application of coatings by surface treatment of the paper is predominantly used for developing softness in the finished product. However, there are no known dedicated processes during converting for reinforcement and/or development of strength properties.

[0007] Patent US8187419B2 [8] discloses the application of surface softening agents, polyhydroxylated com-

pounds, such as glycerols, polyglycerols, polyethylene glycols (PEGs), polyoxyethylenes, polyoxypropylenes, by means of extrusion and in the converting stage, in 2-sheet tissue papers, as a means of obtaining a tissue paper with increased softness and through a process that can be carried out so that strength and absorption properties of the obtained papers are maintained. Strength additives, such as starches and resins are, in the mentioned patent, added to the mixture of fibres that constitute the raw material for producing tissue paper.

[0008] Patent US9347181B2 [9] discloses the mass incorporation of cationically charged polyacrylamides (APAM) and glyoxylated polyacrylamides (GPAM) into the pulp during paper production in the tissue paper machine. Although the patent aims at the development of resistances, it is limited to the application in the paper machine, during the production of tissue paper.

[0009] Patent application EP1627108B1 [10] describes the application of softening agents, via an extruder, to tissue paper sheets. The softening agents mentioned concern silicones, such as polysiloxane. The developed application method allows the application of high viscosity polysiloxane without the use of additional diluents. The softening agents can be applied at different points in the paper production process, either before the drying section, in the drying section, and after the drying section or in, but not specified, post-process steps of paper production. The strength agents mentioned in the invention described in the text of patent application EP1627108B1 are described as being added in their typical applications, i.e. added to the cellulosic fibre mixture before the tissue paper sheet is formed. Thus, mentioned polymers, such as starch and carboxymethylcellulose, are used in the invention described in EP1627108B1 as mixed into the cellulose pulp from which the tissue paper is produced.

[0010] In fact, starch is a biopolymer widely used in paper production. This polymer can be used in its native or modified form, with usually cationic starches being used in paper production, and of different origins (corn, potato, tapioca, among others), as retention agents or resistance agents.

[0011] Typically, starches are used in paper production for the development of their dry strengths and for the development of their surface properties. This polymer is traditionally added as a gluing agent in the paper production process step. It can be added at the internal sizing stage, where the polymer is added to the pulp that will originate the paper product, or at the surface sizing stage, where the polymer is used to coat the partially dried paper product. Its application is intended to improve the interaction of the paper surface with, for example, printing inks and to promote fibre bonds [11-13].

[0012] Carboxymethyl cellulose is the most widely used water-soluble cellulose derivative in paper production, usually used in the form of sodium salt. This is used for the purpose of improving the strength properties of a paper, printing quality of the paper, and/or grease resist-

ance. Like starch, it is also applied in the internal and surface bonding stages of a paper production process [11-13].

[0013] Another polymer of interest is gum arabic which has characteristics of relevance such as being natural, amorphous, non-toxic, odourless, colourless and tasteless [11-13], water soluble, amphiphilic and with a low viscosity in aqueous solution. This polymer is commonly used in applications involving food and pharmaceutical products [14].

[0014] This state-of-the-art review demonstrates the need for a tissue paper production method that allows an improvement of the strength properties of the finished tissue paper product, as an alternative to the traditional pulp incorporation approach in the wet end of the paper machine, and that allows the use of biocompatible biopolymers for sanitary, personal hygiene, household, and industrial use.

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SUMMARY OF THE INVENTION

[0016] The present invention relates to a method for the production of a tissue paper comprising the step of coating a tissue paper, at the converting stage into a finished product, with 0,5 a 14 g/m² of an aqueous solution comprising at least one biopolymer.

[0017] According to a preferred embodiment the biopolymer is selected from the group consisting of gum arabic, cellulose ethers, starch, modified starches, and mixtures thereof.

[0018] According to a preferred embodiment the gum arabic is alkalinized gum arabic.

[0019] According to a preferred embodiment the cellulose ethers are selected from the group consisting of carboxymethylcellulose, hypromellose, hydroxypropylcellulose, hydroxyethylcellulose and mixtures thereof.

[0020] According to a preferred embodiment the cellulose ether is carboxymethylcellulose.

[0021] According to a preferred embodiment the

starches are selected from the group consisting of cationic starches, starches with quaternary ammonium functional groups, starches with phosphate functional groups, starches with sulfate functional groups, starches with sulfonate functional groups and starches with carboxyl functional groups and mixtures thereof.

[0022] According to a preferred embodiment the modified starch is cationic starch.

[0023] According to a preferred embodiment the tissue paper comprises fibers selected from the group consisting of virgin fibers, recycled fibers and mixtures thereof.

[0024] According to a preferred embodiment the finished product is selected from the group consisting of kitchen rolls, multipurpose rolls, toilet papers, hand towels, napkins and handkerchiefs.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025]

Figura 1. Results for the tensile index of tissue paper sheets treated with carboxymethyl cellulose (CMC), alkalinized gum arabic (GAb), natural gum arabic (GA-without treatment) and cationic starch (starch), and comparison with sheets without treatment or "Ref.". Percentages refer to the concentration in w/v of the solution applied on the paper.

Figure 2. Results for the water absorption capacity of tissue paper sheets treated with carboxymethyl cellulose (CMC), alkalinized gum arabic (GAb), natural gum arabic (GA-without treatment) and cationic starch (starch), and comparison with sheets without treatment or "Ref.". Percentages refer to the concentration in w/v of the solution applied on the paper.

Figure 3. Air permeability obtained for tissue papers treated with carboxymethylcellulose (CMC), alkalinized gum arabic (GAb), natural gum arabic (GA-without treatment) and cationic starch (starch), and comparison with sheets without treatment or "Ref.". Percentages refer to the concentration in w/v of the solution applied on the paper.

Figure 4. Results obtained for the various softness parameters analyzed in tissue sheets treated with carboxymethylcellulose (CMC), alkalinized gum arabic (GAb), natural gum arabic (GA-without treatment) and cationic starch (starch), and comparison with sheets without treatment or "Ref.". The parameters referred to are for each series the following: "HF" or "Handfeel", first column; "TS7", second column; and "TS750", third column.

Figure 5. Capillarity obtained, according to the Klemm method, for tissue sheets treated with carboxymethylcellulose (CMC), alkalinized gum arabic (GAb), natural gum arabic (GA-without treatment)

and cationic starch (starch), and comparison with sheets without treatment or "Ref.".

DETAILED DESCRIPTION OF THE INVENTION

[0026] It is here described a method for the production of tissue paper comprising coating a tissue paper, in the step of converting a tissue paper into a finished product, with an aqueous solution comprising at least one biopolymer, according to what is described in this patent application and claim 1.

[0027] This method allows the significant development of dry strength properties in tissue products and is an alternative when this effect is not possible to be developed in the paper machine (the production stage of the base paper, where this property is normally developed), or to obtain additional levels of strength.

[0028] The method of the present invention makes possible the development and/or the correction of this property in papers previously produced, to higher levels, in what it is a highly valued and differentiating requirement in tissue products such as kitchen rolls, multi-purpose rolls, toilet paper, hand towels, napkins and handkerchiefs, among others. This surprising effect is also achieved through the use of biocompatible, hydrophilic, water-soluble biopolymers obtained from natural products.

[0029] The present invention thus comprises a method for the production of tissue papers by coating, during the converting step into a finished product, from 0.5 to 14 g/m² of an aqueous solution comprising at least one biopolymer, such as gum arabic, cellulose ethers, starches, modified starches or mixtures thereof. The resulting finished products consist of, and are not limited to, kitchen rolls, multi-purpose rolls, toilet papers, hand towels, napkins and pocket/ facial tissues.

[0030] In the context of the present invention a tissue paper corresponds to low grammage, creped and/or uncreped papers, used for hygienic and sanitary purposes, either in domestic environment or in public places.

[0031] In the context of the present invention, the stage of converting tissue paper into a finished product, also referred to in this patent application as just the converting stage, includes all the processes to which the already produced tissue paper reels are subjected until the finished product is obtained. Depending on whether the final product is a roll or a folded product, the unit processes vary and may include unrolling operations, embossing, laminating, surface treatment (for example, application of additives such as softeners, or printing of motifs), perforation, rewinding, folding and packaging.

[0032] In the context of the present invention, biopolymers are polymers produced from natural sources, chemically synthesized from a biological material, or fully biosynthesized by living organisms. In this invention biopolymers such as gum arabic, cellulose ethers, starch, modified starches, or mixtures thereof are used.

[0033] In the context of the present invention, the coat-

ing with biopolymers is carried out by coating means that are commonly applied in the converting of tissue paper by transferring the components to the paper through rollers (such as, but not limited to, flexography and/or roto-gravure) or by spraying. The coating comprises aqueous solutions of biopolymers.

[0034] In the context of the present invention, gum arabic is used in its natural form or in its alkalized form, i.e., treated with an excess of NaOH, KOH or another water-soluble hydroxide. The alkalized gum arabic is precipitated in acetone, separated by filtration, sedimentation, centrifugation and/or decantation, and redissolved in water.

[0035] In the context of the present invention, the used cationic starches include chemically modified starches, with quaternary ammonium groups or tertiary amino groups, which are examples of commercial products used in the paper industry. These have cationic charge.

[0036] In the context of the present invention, in addition to cationic starches, modified starches are used, i.e., starches with quaternary ammonium functional groups, starches with phosphate functional groups, starches with sulfate functional groups, starches with sulfonate functional groups, starches with carboxyl functional groups and other starches synthesized by etherification, esterification or oxidation, in order to obtain the desired functional groups to be used. Their mixtures are also considered.

[0037] In the context of the present invention, used cellulose ethers include, and are not limited to, carboxymethylcellulose, hypromellose, hydroxypropylcellulose and hydroxyethylcellulose. Their mixtures are also considered.

[0038] In the context of the present invention, the coating pick-up is defined as the grammage difference between the coated paper and the base paper.

[0039] In the context of the present invention, the aqueous solutions of biopolymers have concentrations in biopolymers which can vary from 0.1 to 90% in w/v or in vivo

[0040] In the context of the present invention, both virgin fibers and recycled fibers can be used in the constitution of the tissue paper to be coated in the converting step. Their mixtures are also considered. Virgin fibers refer to fibers that have only been chemically or mechanically processed once to produce pulp and paper. Recycled fibers refer to fibers that have previously been used in pulp and paper production and which are processed again for integration into subsequent pulp and paper production processes.

Examples

Example 1

I) Preparation of materials

[0041] Tissue sheets with a grammage of 20 g.m⁻² were prepared in accordance with an adaptation of the

ISO 5269-1 standard, for the formation of sheets of lower grammage and without pressing and considering a fibrous composition of 30% long fibers and 70% short fibers. The sheets were dried under controlled conditions of temperature ($23 \pm 1^\circ\text{C}$) and humidity (50 \pm 2%). The moisture content was $<0.2 \text{ g}_{\text{water}}/\text{g}_{\text{paper}}$, thus ready to be processed in the next step of converting into a finished product.

[0042] For the coatings that were applied during the following step of converting dried tissue paper sheets, a solution of carboxymethylcellulose (CMC) (CAS 9004-32-4) was prepared by dissolving it in water at a concentration of 0.9% (m/v). This solution was applied by spraying, on the surface of the sheets, until the complete and uniform coating of the sheet, obtaining a pick-up of 2 g/m². The gum arabic solution (CAS 9000-01-5) was applied in the same way but using a concentration of 10% (w/v), both in its natural form and in its alkalized form (treated with excess sodium hydroxide and precipitated with acetone). When using gum arabic in its natural form, a pick-up of 9 g/m² is obtained, and in the case of its alkalized form, a pick-up of 14 g/m² is obtained. Cationic starch (CAS 56780-58-6) was diluted in water in a ratio of 1:3 (v/v) and applied in the same way on the sheets, obtaining sheets with a pick-up of 14 g/m².

[0043] After application by spraying the biopolymers, the sheets were again dried under controlled conditions, under the same conditions mentioned above. This adopted step could have been dispensed and the drying could have been carried out naturally.

II) Paper properties

[0044] The grammage and bulk of the sheets were determined following the ISO 12625:6 and 12625:3 standards, respectively. Tensile index was determined according to ISO 12625:4 using a vertical tensile analyzer. The smoothness was analyzed using a smoothness analyzer (TSA) from Emtec, considering the QAI algorithm. This equipment makes it possible to determine the smoothness through the handfeel index (HF) and the parameters TS7 (related to the inherent smoothness of the material) and TS750 (related to the topography and roughness of the paper). The capillary rise was analyzed following an adaptation of the ISO 8787 standard, while the water absorption capacity was determined according to the ISO 12625-8 standard. Air permeability was analyzed on a FEXTES Instruments FX3300 LabAir III equipment with a pressure drop of 200 Pa.

III) Results

[0045] Figures 1 to 5 show the results obtained for the main paper properties analyzed.

[0046] The paper converted by the coating of aqueous solutions of biopolymers, as described in the present invention, showed increases in the tensile index that, in the case of gum arabic at 10% (w/v) reached values of

up to +140%, with gum arabic treated with 10% of a base (m/v) reached values up to +67%. With starch, values up to +217% were reached and with 0.9% (w/v) CMC values up to +100% were reached, as shown in Figure 1.

[0047] There was a decrease in the values of properties such as absorption capacity (figure 2), air permeability (figure 3) and capillarity (figure 5). However, these values are acceptable for the use of tissue paper, considering that according to the type of finished product, the resistance requirements will be more valued compared to the other properties, for its function.

[0048] Softness parameters also showed a decrease, although not relevant for tissue paper applications where strength properties are given the most importance.

Example 2

[0049] Tissue sheets of 20 g.m⁻² were prepared as described in section I) Preparation of materials, as described in Example 1.

[0050] Aqueous solutions of carboxymethylcellulose (CMC), gum arabic (CAS 9000-01-5) and cationic starch (CAS 56780-58-6) were also prepared by diluting them in water and applying them in previously prepared sheets, as also described in Example 1, and in order to obtain sheets with a pick-up of 0.5 g/m².

[0051] Increases in the tensile index of the prepared sheets were also observed, by coating with aqueous solutions of biopolymers, in line with the results of example 1.

ified starches are selected from the group consisting of cationic starches, starches with quaternary ammonium functional groups, starches with phosphate functional groups, starches with sulfate functional groups, starches with sulfonate functional groups, and starches with carboxyl functional groups, and mixtures thereof.

7. The method according to the previous claim, wherein the modified starch is cationic starch.

8. The method according to any one of the preceding claims, wherein the tissue paper comprises fibers selected from the group consisting of virgin fibers, recycled fibers, and mixtures thereof.

9. The method according to any of the preceding claims, wherein the finished product is selected from the group consisting of kitchen rolls, multipurpose rolls, toilet papers, hand towels, napkins, and handkerchiefs.

Claims

1. A method for the production of a tissue paper comprising a step of coating a tissue paper, at the converting stage into a finished product, with 0,5 a 14 g/m² of an aqueous solution comprising at least one biopolymer.
2. The method according to the previous claim, wherein the biopolymer is selected from the group consisting of gum arabic, cellulose ethers, starch, modified starches, and mixtures thereof.
3. The method according to the previous claim, wherein the gum arabic is alkalinized gum arabic.
4. The method according to claim 2, wherein the cellulose ethers are selected from the group consisting of carboxymethylcellulose, hypromellose, hydroxypropylcellulose, hydroxyethylcellulose, and mixtures thereof.
5. The method according to the previous claim, wherein the cellulose ether is carboxymethylcellulose.
6. The method according to claim 2, wherein the mod-

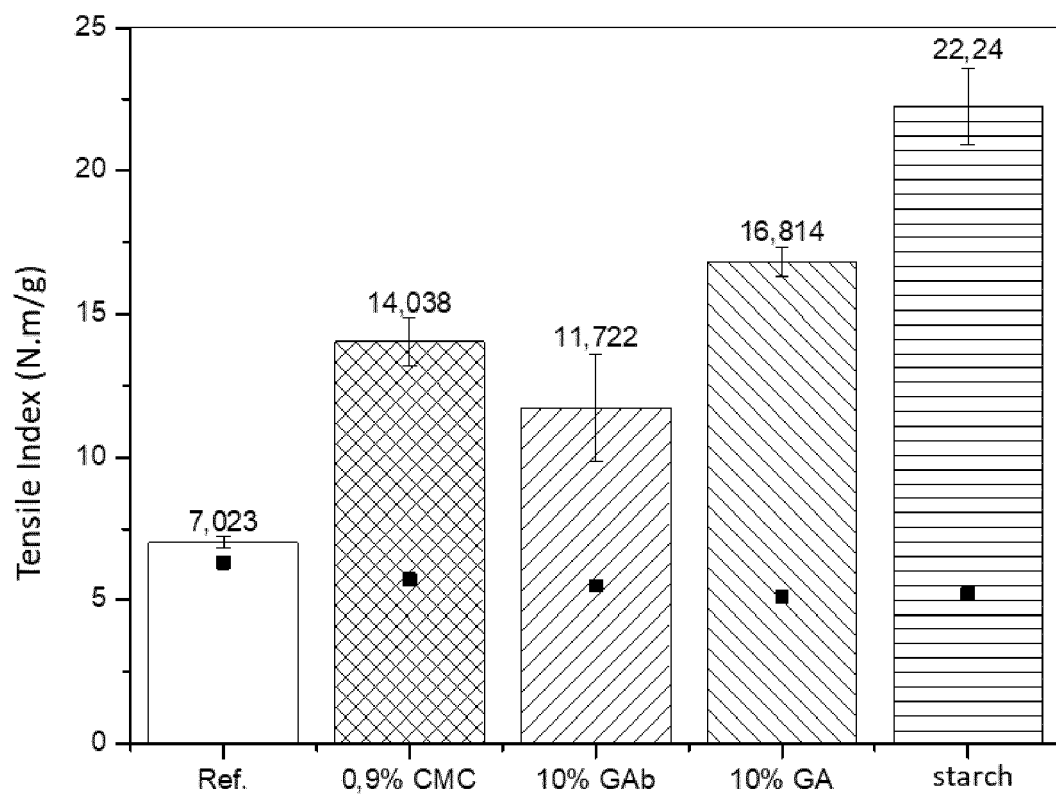


Fig. 1

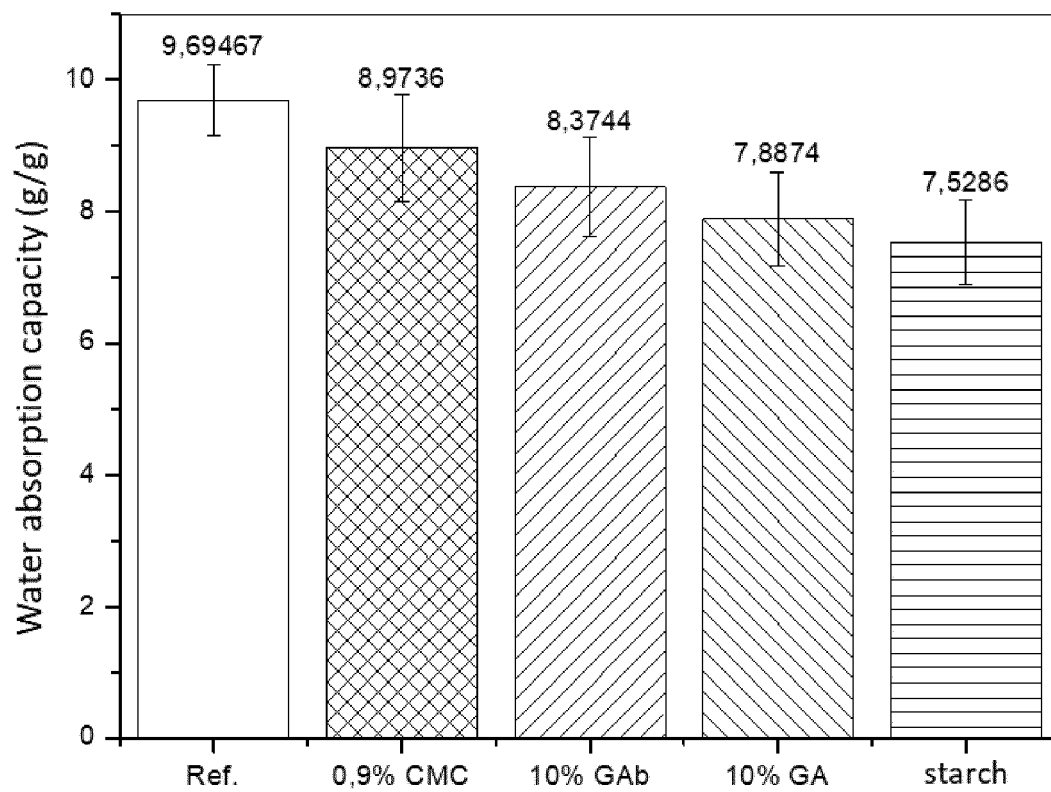


Fig. 2

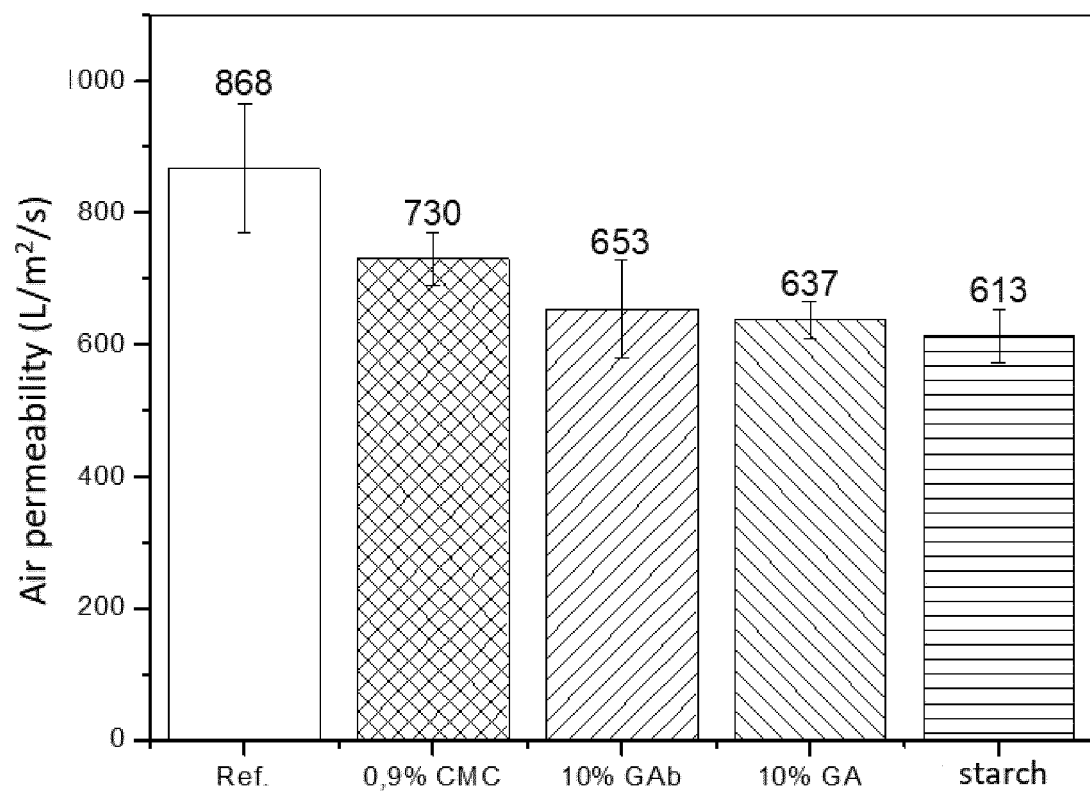


Fig. 3

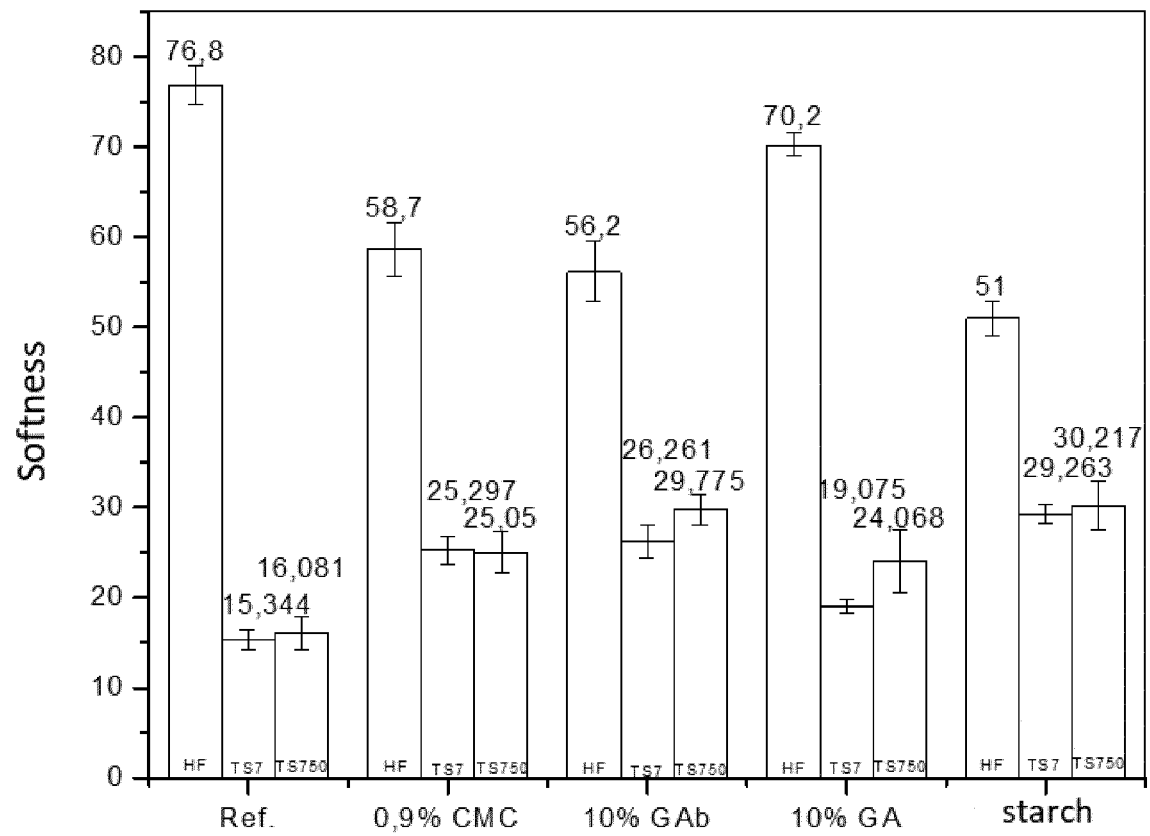


Fig. 4

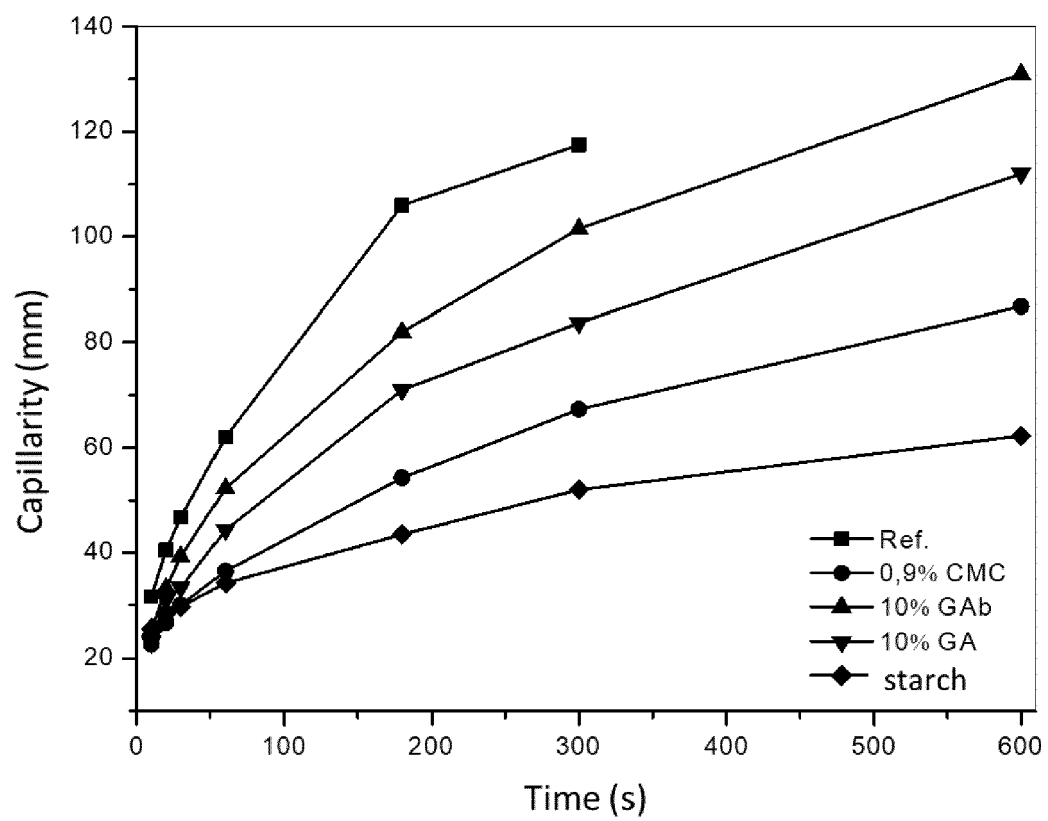


Fig. 5



EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 11 July 2023	Examiner Karlsson, Lennart
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