Effect of Grain Husk Microfibers on Physicochemical Properties of Carboxymethyl Polysaccharides-based Composite

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Research Article

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Abstract

Preparation of the novel biodegradable composite based on carboxymethylated starch and cellulose matrix and plant fillers have been described. As a filler milled cereal husks of various origin: rye, spelt, and rice were used. Additionally, softwood flour was used for comparison. Introducing natural filler beneficially affected the mechanical parameters of the CMS/CMC system, as moisture absorption as well as solubility in water decreased (e.g. by ca. 7% and 6%, respectively for CMS/CMC with rice husk filler when compared to the neat system). Moreover the mechanical properties, i.e. Young's modulus and tensile strength increased. The chemical composition and size of natural fillers are essential factors determining the physicochemical properties of obtained composites, and cereal husks are promising raw materials for filling hydrophilic polysaccharide matrix.

Introduction

In the 20th century many composite systems based on petroleum-origin components. In the 21st century, along with the public awareness, great emphasis was placed on the development of biodegradable composites that meet the „5E" principle conditions, i.e.: efficiency, energy saving, enabling, economy and environmental friendly. The materials based on polysaccharide derivatives containing biodegradable fillers may be an alternative to conventional composites [1-4]. Polysaccharides (i.e. cellulose, starch, chitin, glycogen) differ in the chain structure (linear, branched), microstructure (fibrous, globular) and natural function (structural, storage material). They are widely used in food industry, but also in medical and pharmaceutical, paper as well as in coating industries. Chemical modification of polysaccharides widen the areas of their application. Starch and cellulose are renewable, inexpensive and relatively easy to modify natural polymers, thus seem to be the promising raw materials for the biodegradable composite formulations [1-4]. The etherification of starch and cellulose allows to obtain carboxymethyl derivatives which - unlike native polymers - are soluble in cold water. The physicochemical properties of carboxymethyl starch (CMS) and carboxymethyl cellulose (CMC), such as the dissolution rate and viscosity of aqueous solutions, depend greatly on the degree of substitution (DS, average number of substituted hydroxyl groups in the polysaccharide repetitive unit) and their molecular weight [5]. The DS value depends mainly on the type of basic biopolymer (starch or cellulose) as well as the method of its modification [5]. The carboxymethyl derivatives of starch and cellulose have been successfully used for film preparation [3,6-10]. Applying various polysaccharide derivatives composition and ratio allows to obtain films with different properties.

Introducing filler into the polymer matrix is one of the most common method of material modification. The compatibility between filler and matrix is essential for effective reinforcement. Adding the natural filler into polysaccharide derivatives allows to remain the biodegradable character of the final composite. Relatively common biodegradable fillers applied for starch and cellulose-based composites are the nano- or micro-size cellulose crystals [11-13], however their preparation is cost and time consuming. One of the most popular plant fillers used in the plastics industry is wood flour, produced commercially from post-industrial sources such as shavings and sawdust [14]. The scrap wood is sourced for species purity and

then ground to specific particle size distributions. There are many reports on using wood flour as reinforcement for synthetic or biopolymers, e.g. thermoplastic starch- based composites [15-18].

The grain husks are the waste products of food processing (milling). They are available on an annual basis, and could be an alternative for natural fiber industry preserving wood resources [14]. Their chemical composition depends on their botanical origin, but contain mostly cellulose, hemicellulose and lignin. In the field of interest are the husks of rye, rice, barley, spelt and corncobs. They are often introduced into polyolefin matrix [19-22]. In [21] the composites based on PP matrix with grain by-products microfibers were prepared. The plant fillers were also treated enzymatically to remove starch and protein residue, which resulted in higher flexural stress values. However, even unmodified microfibers gave mechanical properties enhancement.

Other approach was using the cereal husk for cellulose nanocrystals preparation [23,24]. They were subsequently used for thermoplastic starch-based composite preparation [25].

Interestingly, unmodified rice husks were used as a macrofiller for cassava starch-based foams for packaging [26].

In this paper the polysaccharide derivatives-based composites were prepared using CMS/CMC matrix and milled cereal husks fillers of various origin: rye, spelt, and rice. Additionally, the most popular plant filler, i.e. softwood flour was used for comparison. The effect of the polymer matrix as well as filler type and content effect on the physicochemical properties (i.e. moisture absorption, solubility in water, thermal and mechanical properties) of the obtained biodegradable composite films have been determined

Experimental

Materials

The potato starch (S) was a product of Nowamyl S.A., Poland. Carboxymethyl cellulose (DS: 0.7, Pollocel AS-2/90) was purchased from Pronicel Sp. o.o. (Poland). Sodium hydroxide (p.a.), chloroacetic acid (p.a.), 2-propanol (p.a.), monohydrate citric acid (CA) (p.a.) and glycerol (p.a.) were purchased form Chempur, Poland. The natural fillers were prepared at the Institute für Lebensmittel und Umweltforschung, Potsdam, Germany, by conditioning and milling spelt, rice husks and rye brans into particles sizes smaller than 600 μm. Microfibers made of the industrial grade softwood flour Jeluxyl Weho500 by Jeluwerk, Germany were used. In Figure 1 the chemical composition of the fillers was presented.

CMS preparation

The synthesis of carboxymethyl starch was carried out using the one-step method [27]. In the glass reactor, monochloroacetic acid and isopropanol were placed (nitrogen atmosphere), after which the acid was neutralized with an aqueous solution of sodium hydroxide in a molar ratio of 1:1. When the color of reactor content turned opaque white, the system was stirred for 10 min, and subsequently starch and hydroxide were added. The reaction was carried for 2.5 h at 50°C. Then the mixture was neutralized to pH

6. The product was filtered under reduced pressure and washed five times with 80% methanol solution, and the last one with undiluted methanol. The carboxymethyl starch with a degree of substitution of 0.70 was obtained.

Preparation of polysaccharide composites with plant fillers

The CMS/CMC films filled with plant filler were prepared as followed: the aqueous dispersion of plant filler (100 ml, 7 wt. % on a basis of total dry polysaccharide derivatives weight) was prepared and stirred for 30 minutes at room temperature. Then the polysaccharide derivatives and 2 g glycerol were added to this dispersion and stirred for 30 minutes. Subsequently, 2 g citric acid were added and mixed until homogeneity. Then the system was poured into PTFE molds and placed in a dryer for 48 h at 60°C. The obtained films (thickness 200-300 μm) were removed from the mold and tested.

Methods

The size, surface morphology and size distribution of natural fillers were determined using scanning laser microscope KEYENCE, model VK-9700 with equipped with VK Analyzer software.

The FTIR analyses of the natural fillers were performed in Nexus FTIR Spectrometer Thermo Nicolet with Golden Gate ATR attachment. The resulting spectra were converted using the software OMNIC.

The solubility in water of the composites were performed as followed. Three samples (1.5 cm x 1.5 cm) were cut from the film and placed in a desiccator to remove moisture (to constant mass). The samples were then weighed, placed in vials and filled with 50 ml distilled water. After 24 hours the samples were removed, and dried for about 24 hours (60°C) to constant mass. The dry samples were again weighed. The solubility in water values were calculated using the following formula [4]:

$$TSM = [(M_1-M_2)/M_1] \cdot 100\%$$

where: TSM (Total Soluble Mater) - solubility in water [%]; M_1 - mass of the dry sample [g]; M_2 - mass of the sample after drying [g].

For moisture absorption tests of obtained composites three samples (1.5 cm x 1.5 cm) were cut from the film and placed in a desiccator to remove moisture (to constant mass). The samples were then weighed, and placed in a climate chamber (humidity 55 ± 2%, temperature 25 ± 2°C). The samples were weighed 3, 5, 7, 24, 48 and 72 hours after being placed in the climatic chamber. The results obtained in this way were substituted for the formula [7]:

$$A_t = [(M_t-M_0)/M_0] \cdot 100\%$$

where: A_t - sorption of moisture after time t [%]; M_0 - mass of the dry sample [g]; M_t - sample mass after t time: 3, 5, 7, 24, 48 and 72 h [g].

Tensile strength of the composite films was tested using the INSTRON testing machine. The initial length of the sample was 50 mm, 10 mm wide, and about 0.2 mm thick. The speed of the mobile clamp was 10 mm/min. Seven samples of one material type were tested.

Thermal analysis of composites was carried out using the DMTA Q800 (TA Instruments) apparatus in the temperature range -30 to 180°C with a heating rate of 3°C/min and an amplitude of 15 nm.

Results And Discussion

Plant fillers

The morphology of plant fillers performed by laser scanning microscopy were presented in Figure 2. The softwood and spelt fillers exhibited visibly elongated character, whereas rice, and rye fillers were rather irregular. A static analysis of LSM images allowed to evaluate the average particle size and aspect ratio of natural fillers, the results were collected in Table 1. It was revealed that softwood and spelt particles exhibited the highest size and aspect ratio (>270 mm, and >2.7, respectively). The rye and rice fillers exhibited significantly lower average size (up to ca. 80 mm) and aspect ratio below ca. 2. Thus, bearing in mind the aspect ratio, the applied fillers could be considered as microfibers.

In Fig. 3 the FTIR spectra of plant fillers were presented. For all the plant fillers the absorption bands characteristic for starch and cellulose could be observed: the broad band between 3600 and 3000 cm^{-1} assigned to OH stretching (due to hydrogen bonding involving hydroxyl groups on the starch molecules), and at 2900 cm^{-1} to CH_2 symmetrical stretching vibrations. The band at ca. 1000 cm^{-1} is assigned to C-O stretching vibrations, whereas the bands in a range 1650 to 1750 cm^{-1} to carbonyls [28]. For the materials with high lignin content the absorption bands assigned to aromatic ring could be observed at ca. 800 cm^{-1}. Interestingly, for rice filler an intensive band at ca. 490 cm^{-1} could be noticed, that could be assigned to presence inorganic matter associated with high ash content (Fig. 1) [21]. The band in this area was also noticeable for spelt.

CMS/CMC composite films with plant fillers

In Figure 4 the FTIR spectra of citric acid, neat CMS and CMC as well as CMS/CMC film were collected. For neat CMS and CMC the absorption band between 3600 and 3000 cm^{-1} and at 2900 cm^{-1} could be attributed to hydroxyl groups and to CH_2 stretching vibrations, respectively. The strong peaks at 1415, and 1315 cm^{-1} were assigned to CH_2 scissoring and OH bending vibrations, and at 1060 cm^{-1} to ether groups, respectively [5,6]. Protonated carboxylic groups (CA) give a C-O band at about 1700 cm^{-1}, whereas carboxylate (COO^-) of neat CMS and CMC give strong absorption band at about 1600 cm^{-1} [29], however in case of CMS/CMC films the carbonyl group bands are observed at 1720 cm^{-1} indicating chemical linkages between polysaccharide derivatives and citric acid (crosslinking agent) via ester bonds.

In Figure 5 the moisture absorption of CMS/CMC films and CMS/CMC/S composites containing 7 wt.% of various plant filler were presented. Water absorption depends on filler-matrix interphase as well as filler hydrophilic/hydrophobic character [30]. For polyolefin-based composites it was reported that wood fibers were primarily responsible for water absorption [31]. However, in case of CMS/CMC-based composites it was also associated with the type of raw material (i.e. strongly hydrophilic) used for the formation of the polymer matrix. Introducing plant filler resulted in reduction of moisture absorption of all CMS/CMC composite films. However, in case of rye filler the decrease was rather low (ca. 2%) when compared to other filler types, when the decrease was in a range of 5-7% (after 72 hours).

Moisture is mainly absorbed by starch, hemicellulose, and non-crystal cellulose on the microfiber surface [14]. Thus, the probable reason of that was the composition of rye filler, i.e. high starch content (ca. 28%, whereas for others it did not exceed 5%), and hemicellulose (ca. 18%) as well as low lignin content (ca. 4%, and >12, respectively). Starch exhibits strongly hydrophilic character – higher than cellulose where the hydrogen bonds hinder the penetration of water molecules into the fibrous structure of the filler [6].

The results are consistent with the reports on thermoplastic starch containing wood flour [30].

Solubility in water of CMS/CMC based composites containing various plant origin fillers was collected in Fig. 6. The composite films after solubility test maintained their integrity, and did not break apart. That indirectly indicates the successful crosslinking reaction of the polymer matrix. The presence of the filler reduced the solubility of the composite in water. The lowest values of this parameter was recorded for foil filled with softwood, and rice (ca. 57%). The general trend correlate to absorption moisture measurements result, i.e. the composite systems with higher cellulose and lignin content exhibited reduced solubility in water. Similar results, i.e. reduction of solubility in water after wood fiber addition was reported for chayotextle starch-based foams [16, 32].

In Figure 7 the mechanical parameters: elongation at break, Young's modulus and tensile strength of the composites based on CMS/CMC containing various plant origin filler has been collected. Adding the plant filler resulted in enhanced mechanical performance of composite: increased tensile strength and Young’s modulus, with elongation at break reduction. The plant fibrous act as mechanical reinforcement of CMS/CMC attributed to well-formed interfacial interaction between the filler and polysaccharide matrix allowing stress transfer from the matrix to the filler [30]. Moreover, reduction of the material flexibility could have occurred due to formation of the hydrogen bonds between the hydroxyl and carboxyl groups of CMS/CMC and natural particles [9, 33]. Additionally, limiting mobility of CMS and CMC chains could also be affected by cross-linking with CA.

The highest tensile strength value (ca. 18 MPa) was noted for the composite containing rice fillers. Generally, it could be observed that higher reinforcing effect was noted for the composites containing smaller particles (rye and rice). The mechanical properties of composites strongly depend on the particles diameter [34]. Above certain diameter value the possibility of surface defect and microcracks occur reducing the possibilities of efficient reinforcement [34]. Similar trend, i.e. enhanced mechanical

properties with plant fibers addition was observed for thermoplastic starch based system containing walnut [30] or banana leaf fibers [35].

The DMTA measurements were performed to evaluate the loss factor (tan d) as a function of temperature for CMS/CMC based composites. The loss factor is sensitive to molecular motion and its peak relates to the glass transition temperature [36]. All the curves of CMS/CMC based composites revealed one broad transition at ca. 40°C indicating good compatibility between the polymer matrix and the fillers (no phase separation) – Fig. 8. From the chemical point of view, polysaccharide, i.e. cellulose or starch (for rye) is the dominant compound in the fillers, thus compatibility with starch and cellulose derivatives-based matrix is apparent. The Tg noted for the neat CMS/CMC system was 28.4°C. Introducing natural filler resulted in slight Tg increase, which was the result of hydrogen bonds formation between hydroxyl and carboxylic groups pf CMS/CMC and fillers. However, the value of Tg for all the samples tested was in a narrow range ca. 33 - 38°C, which suggested that the filler type had slight influence on the transition maxima of the composite. Referring to the research carried out on the effect of microcellulose on the thermal transformation of polysaccharide systems, the results are analogous [7,13].

Conclusion

The natural composites based on CMS/CMC system containing milled cereal husks fillers of various origin:, rye, spelt, and rice, as well as softwood flour have been prepared.

Introducing natural filler beneficially affected the mechanical parameters of the CMS/CMC system, as moisture absorption as well as solubility in water decreased (e.g. by ca. 7% and 6%, respectively for CMS/CMC with rice husk filler when compared to the neat system). Moreover the mechanical properties, i.e. Young's modulus and tensile strength increased.

It seems that the chemical composition and size of natural fillers are essential factors determining the physicochemical properties of obtained composites.

Bearing the above in mind it could be concluded that cereal husks are promising raw materials for loading into hydrophilic polysaccharide matrix. Moreover, the obtained composites met the sustainability requirements as the were made from renewable resources, thus they contribute to a lower environmental footprint.

Declarations

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Declarations

Funding - not applicable

Conflicts of interest/Competing interests –no conflict of interest

Availability of data and material

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code availability -Not applicable

Authors' contributions

Conceptualization: K. Wilpiszewska, A.K. Antosik; Methodology: K. Wilpiszewska, A.K. Antosik; Formal analysis and investigation: K. Wilpiszewska, A.K. Antosik; Writing - original draft preparation, and review: K. Wilpiszewska; Editing: K. Wilpiszewska, A.K. Antosik

Ethics approval - not applicable

Consent for publication

The Authors declare consent for publication.

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Tables

Tab. 1 Particle size of plant fillers

Filler	Average size [µm]	Aspect ratio (l/d)
Rye	84 ± 5	1.80
Rice	52 ± 3	2.03
Spelt	271 ± 21	2.71
Softwood	293 ± 25	2.93

Figures

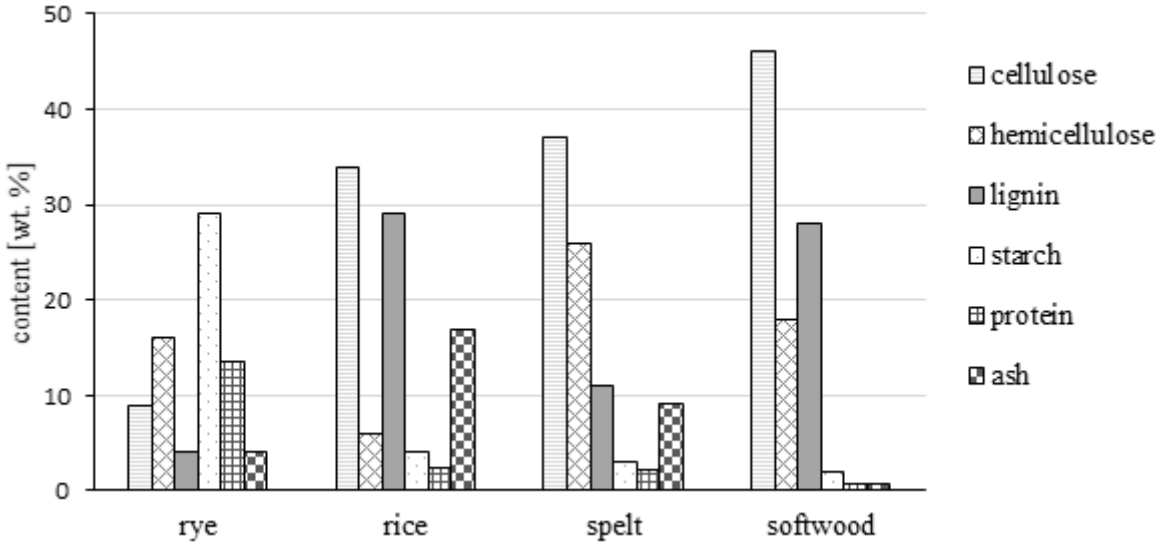

Figure 1

The chemical compositions of natural fibers [21,22]

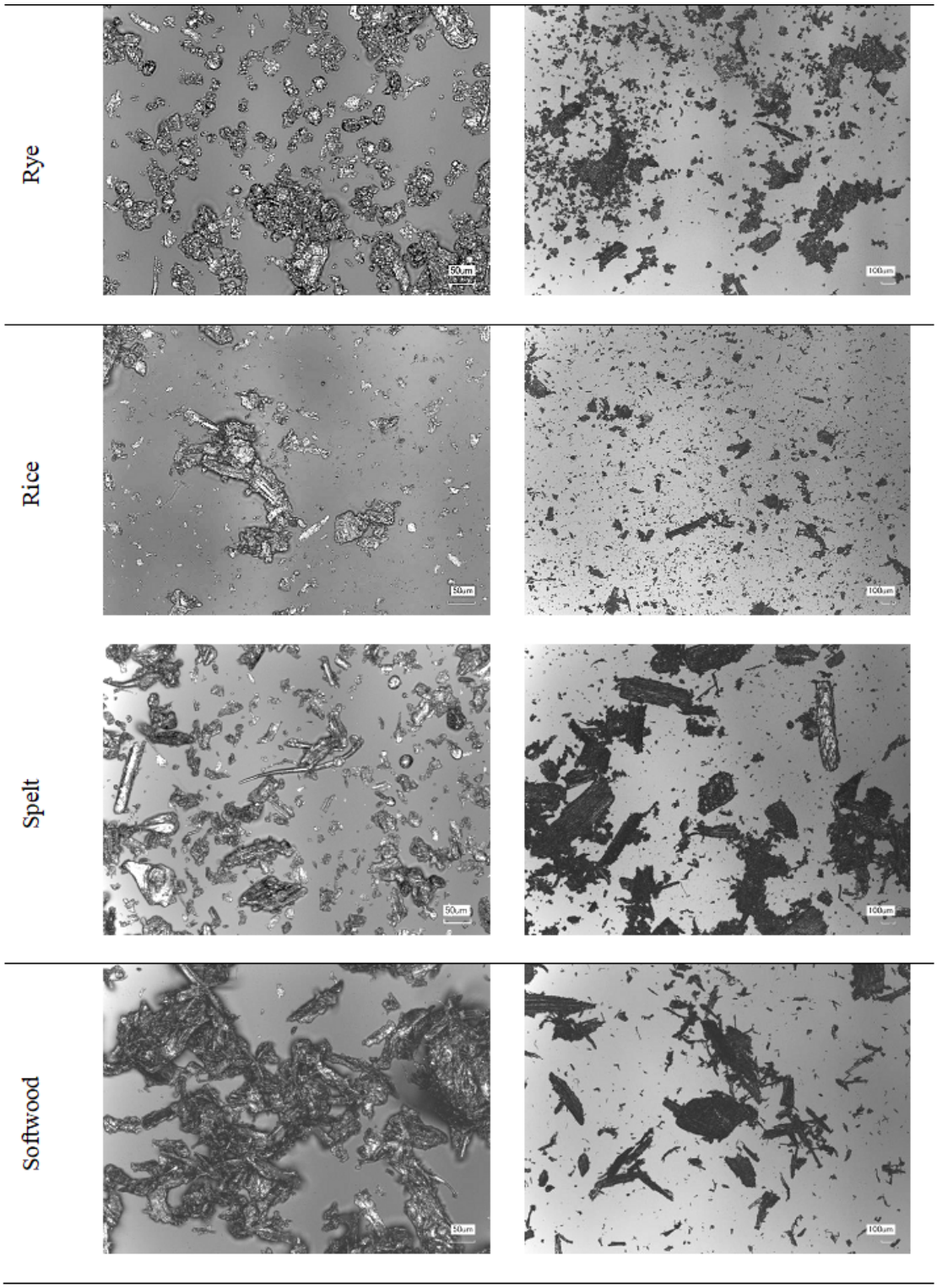

Figure 2

The LSM images of plant fillers

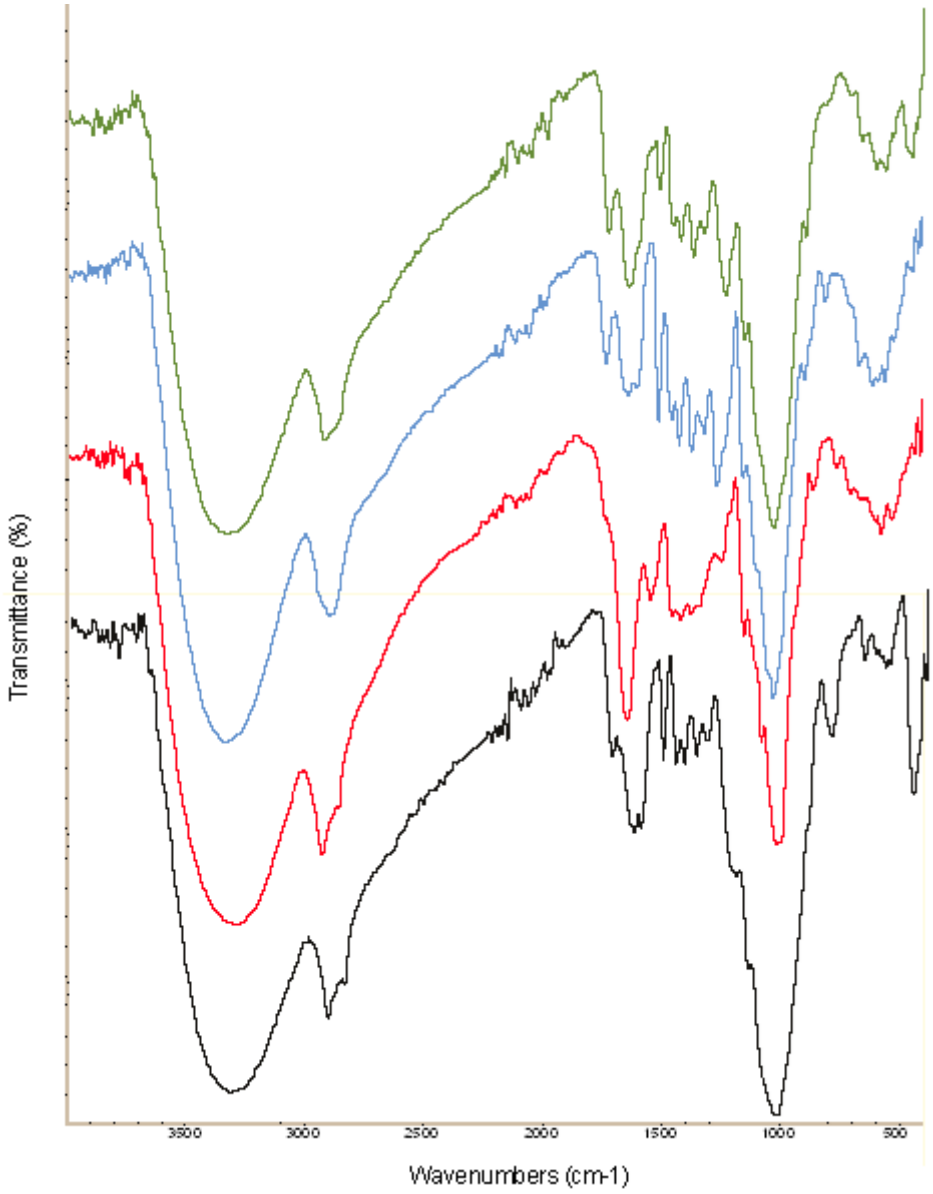

Figure 3

FTIR spectra of plant fillers

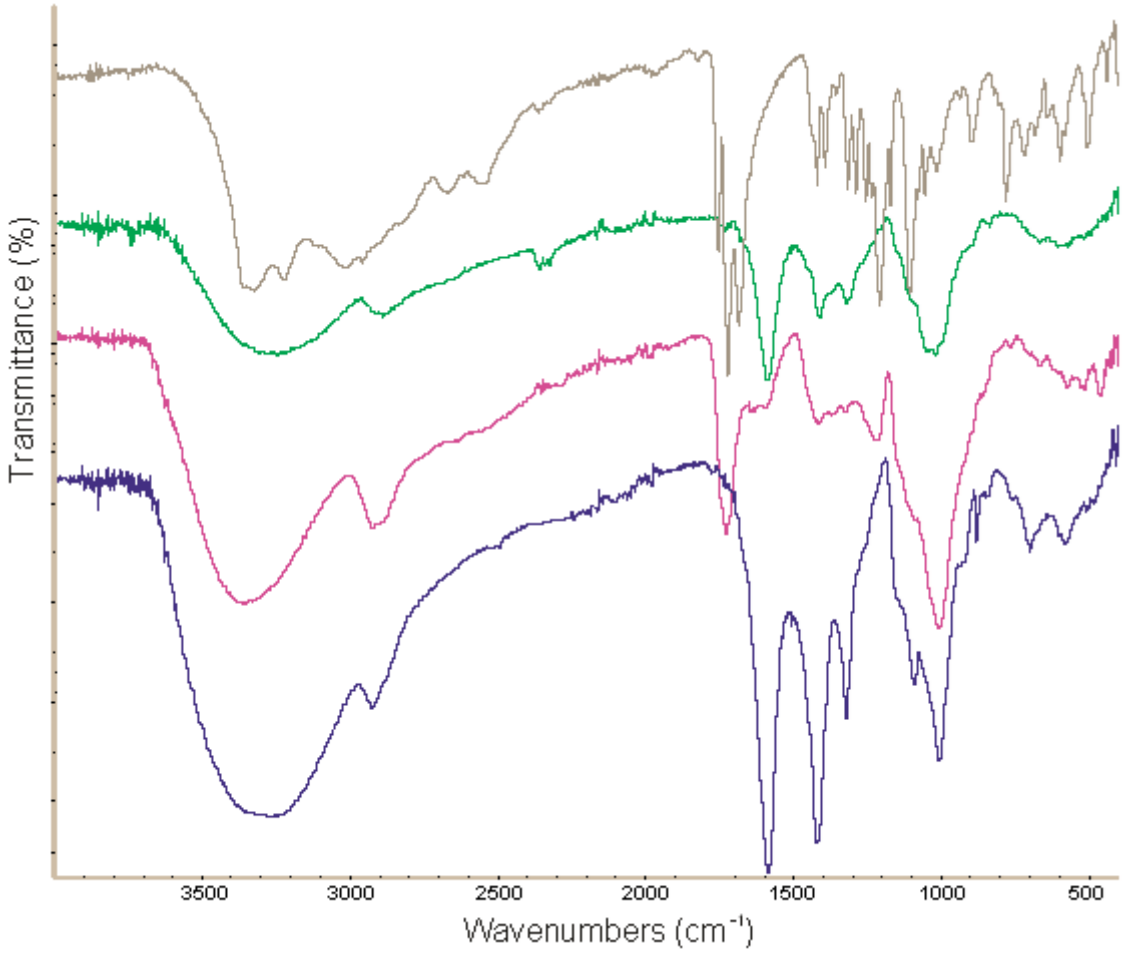

Figure 4

FTIR spectra of citric acid, neat CMS and CMC, and CMS/CMC film

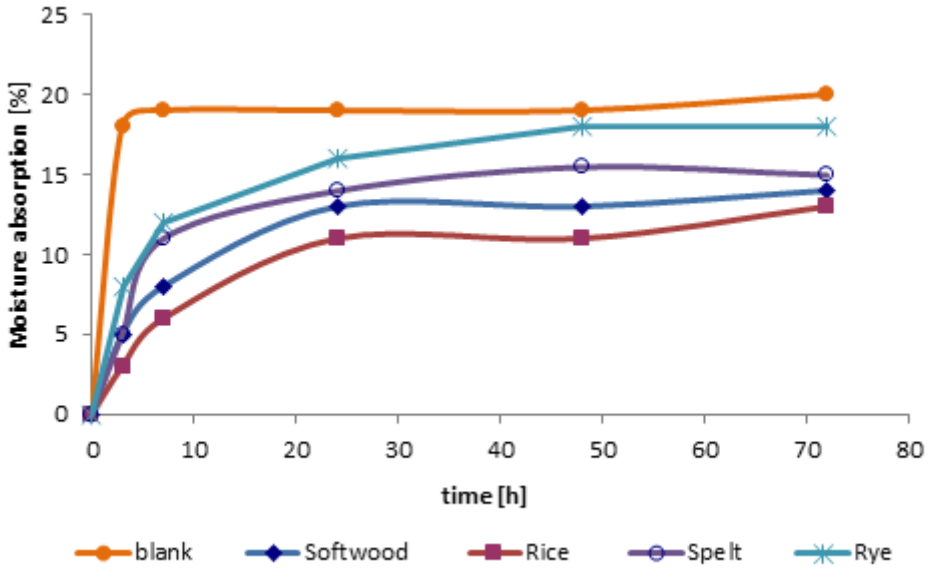

Figure 5

The moisture absorption of composite films based on CMS/CMC containing 7 wt.% of plant fillers

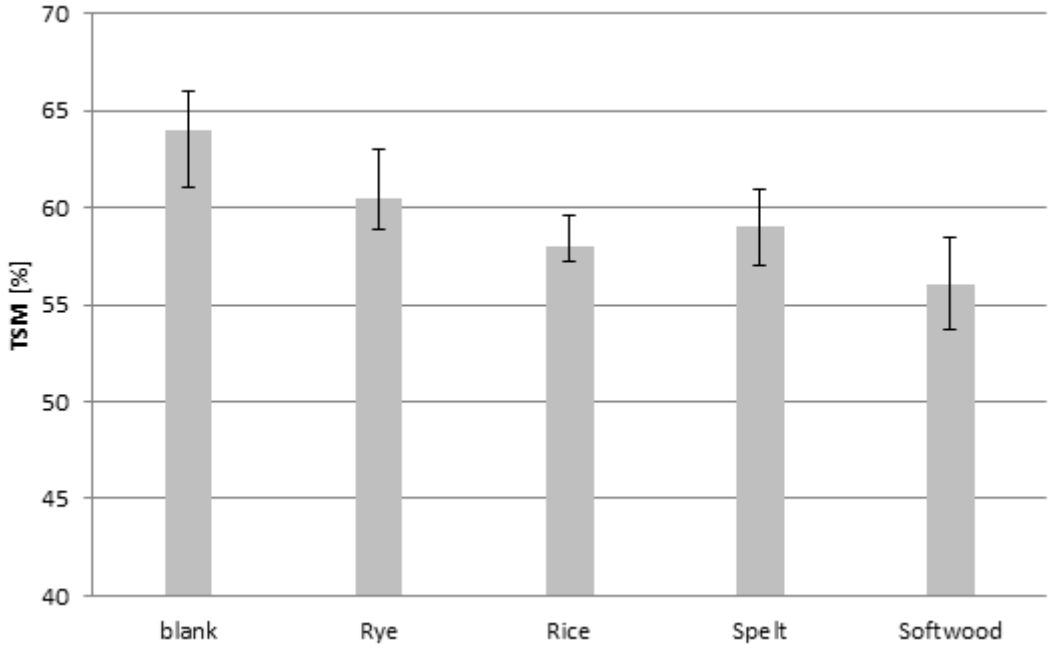

Figure 6

Influence of plant origin flour addition on solubility in water of CMS/CMC based films

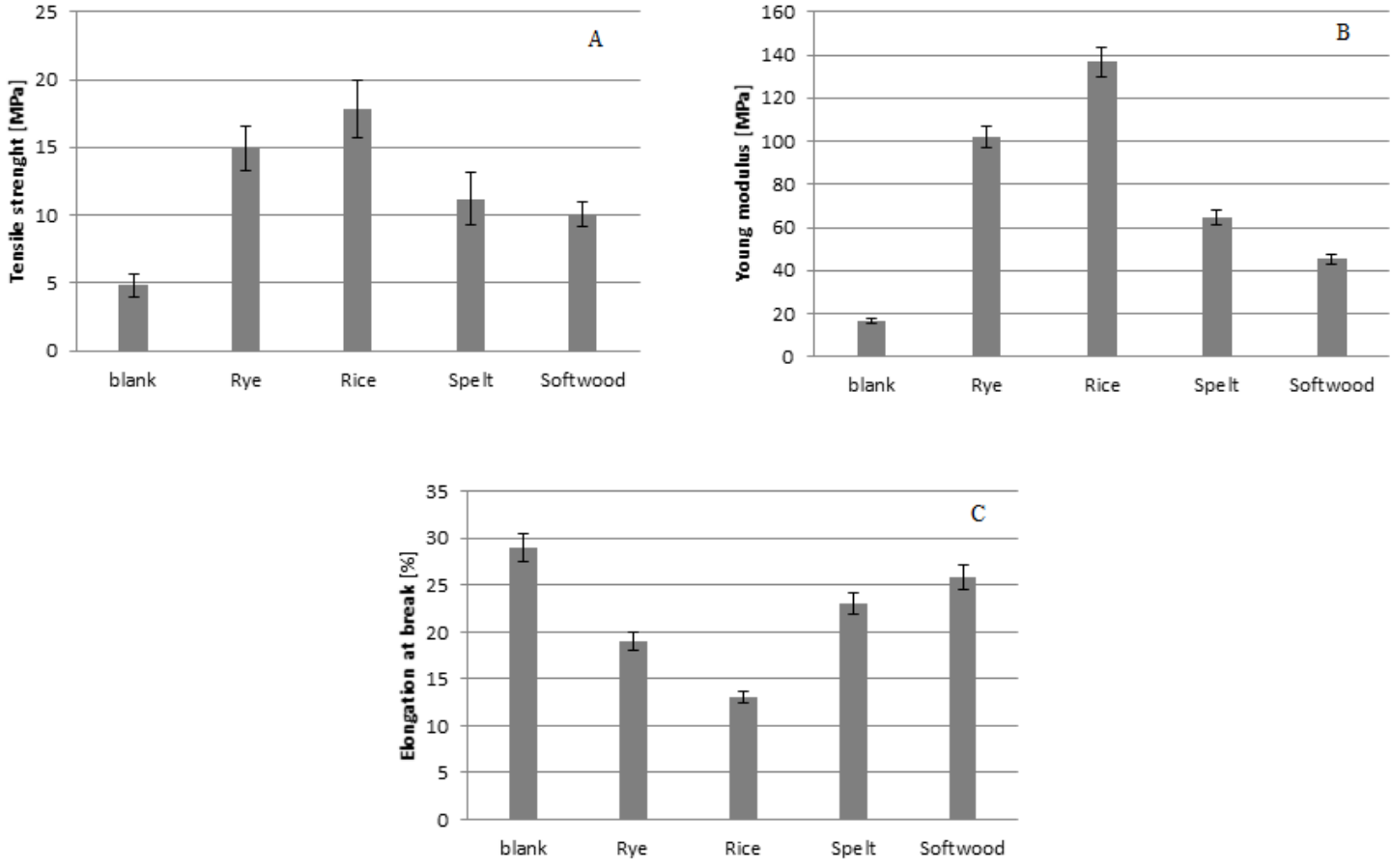

Figure 7

Tensile strength (A), Young's modulus (B) and elongation at break (C) of CMS/CMC-based composites

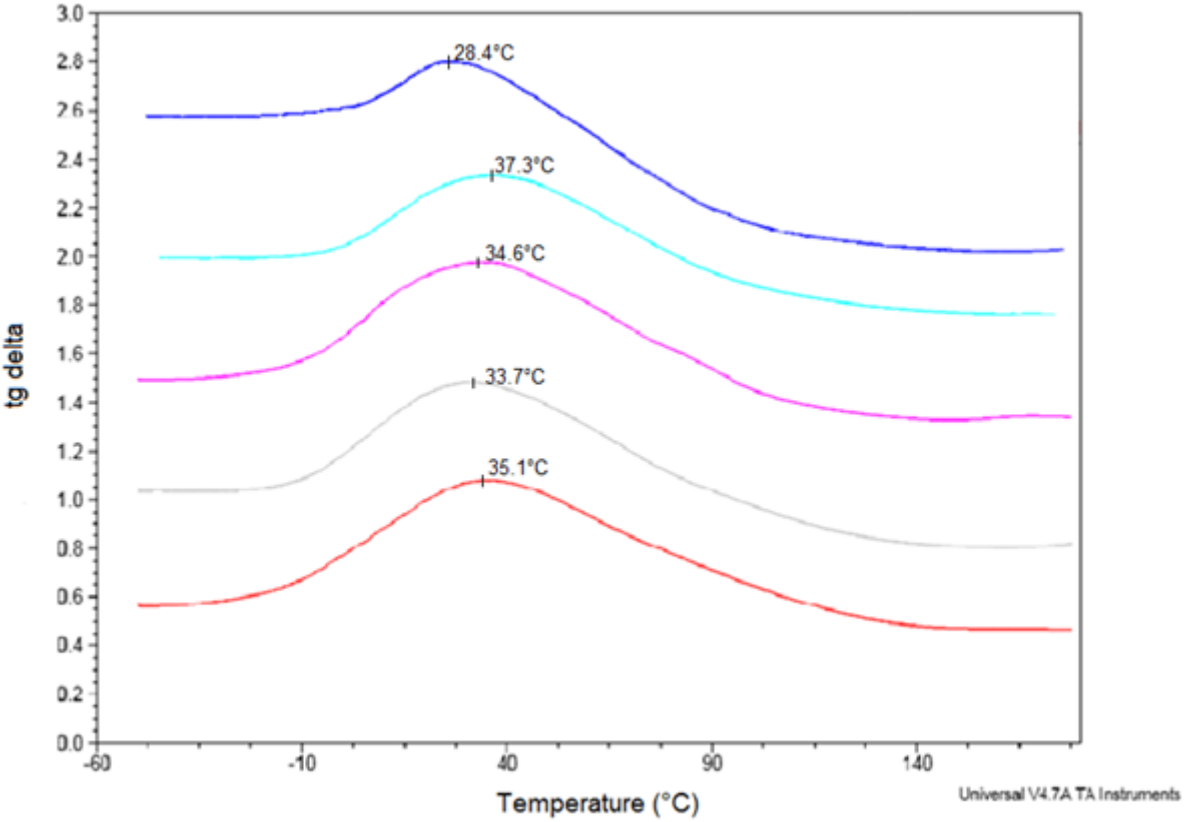

Figure 8

DMTA curves of CMS/CMC based films with various plant fillers

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Graphicalabsract.jpg