Chitosan/Chitin Nanofibrils Composite Films: Effect of Plasticizers on their Mechanical Behavior

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Effect of chitosan on behaviour of wheat B-starch nanocomposite

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Outline

Biopolymer nanofibrils: polymer-polymer composite, biodegradable packaging films

Chitosan/ chitin nanofibrils composite

Effect of plasticizers on CN and CS properties

Plasticized CS/CN films – effect of plasticizer type and composition

Biopolymer nanofibrils + biopolymer matrix

Reinforcement without increase in density

Nonplasticized Chitosan films reinforced with chitin nanofibrils

Merits:

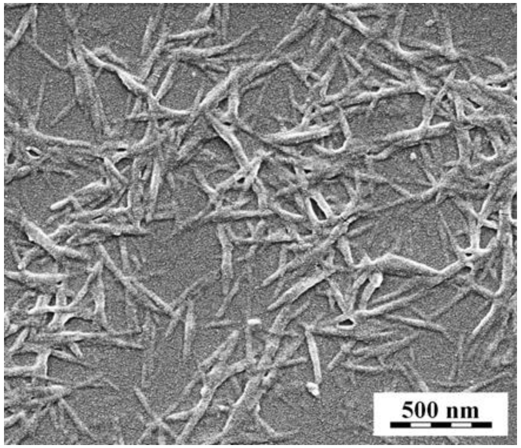
+ rigid and strong single polymer composite
+ easy “green” processing
+ insolubility in water
+ reduced water absorption
+ biodegradability
+ edible
+ antibacterial activity
+ negligible (close to barrier) permeability to oxygen

Demerits:

- range of applications is limited by low elasticity
- limited hydrophobicity

Chitin nanofibrils (CN) MAVI SUD S.r.L.

SEM of dried CN



The deacetylation degree (DD) of D-glucosamine units:
~10 wt% in CN MAVI SUD S.r.L., Italy and
79 wt% in chitosan (CS) Giusto Faravelli, X.p.A., Italy

Modulus of cellulose fibrils ≈ 150 GPa theory: Zeng J-B, He Y-S, Li S-L, Wang Y-Z (2012) Biomacromolecules 13: 1
≈ 10 GPa value calculated using Halpin-Tsai model using experimental values
Halpin J C, Kardos JL (1976) Polym Eng Sci 16: 344

Mechanical properties of CS/CN composites in dependence on CN content

Sample composition CS/CN (wt%)	Stress at break (MPa)	Elongation (%)	E-Modulus (MPa)
100/0	77.0±7.0	6.2±4.0	4230±230
85/15	81.6±7.0	4.8±1.5	5250±500
75/25	83.7±11.0	2.7±1.0	5610±510

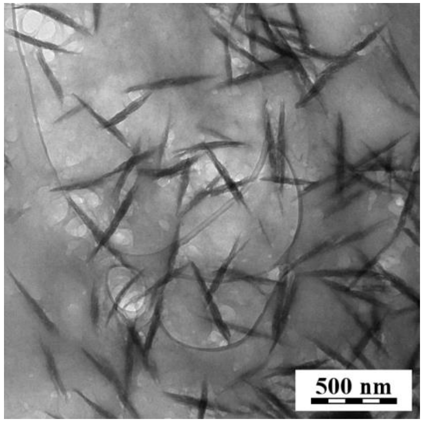
Effect of plasticizers on CS behaviour

Film from	Young's modulus (Mpa)	Break stress (Mpa)	Elongation (%)
Cellulose acetate	127 ± 13	54 ± 5	127 ± 13
Chitosan/glycerol (70/30), wt%	1300	45	28

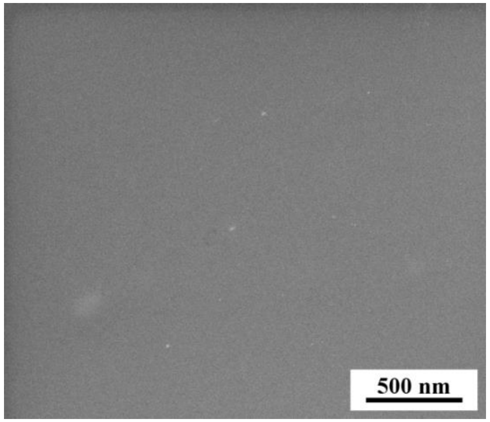
Lubrication theory – internal lubricant, reduction of frictional forces (Di Gioia and Guilbert 1999)
Gel theory – breaking polymer – polymer interactions

Scanning electron micrographs of

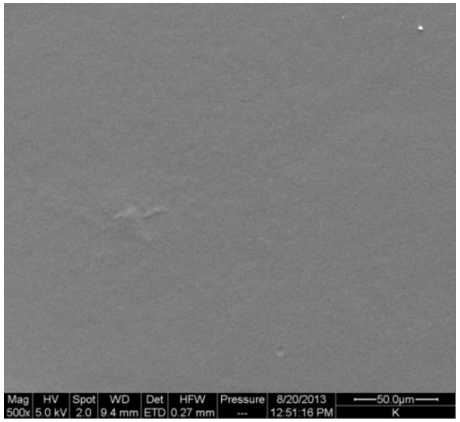
chitin nanofibrils (CN)



dried CN (monolith film)

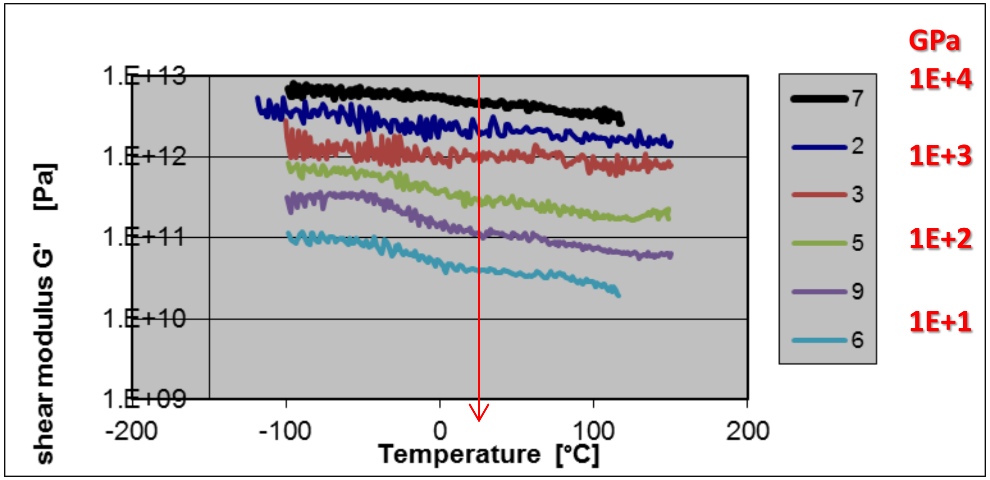


dried (CN/triglycerol)=(70/30) wt%



Effect of plasticizer type on chitosan/CN behaviour

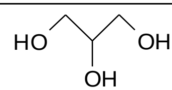
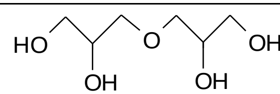
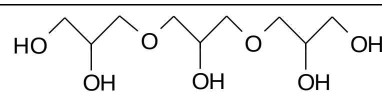
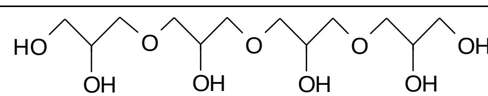
Dynamic mechanical analysis



— 7-(CS/CN)=85/15 (no plasticizer);
— 2- (CS/PEG-600=(70/30wt%) (no CN);
— 3-(CN/glycerol)=65/35wt%;
— 5-(CS/CN)/diglycerol=(85/15)/30wt%;
— 9-(CS/CN)/triglycerol=(85/15)/30wt%;
— 6-(CS/CN)/tetraglycerol=(85/15)/30wt%

The shift of T_g to lower temperatures increased in the range: PEG-600 <glycerol<di- <tri- <tetra-glycerol

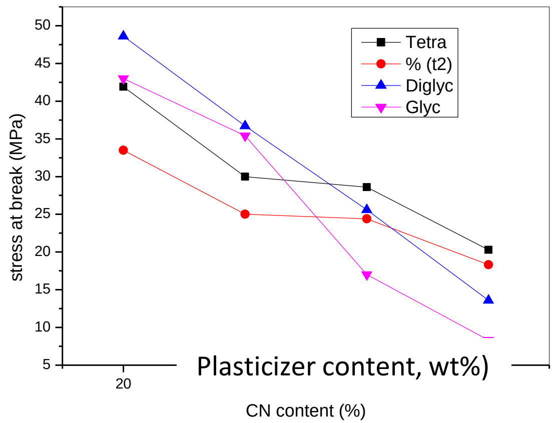
Characteristics of commercial polyglycerols

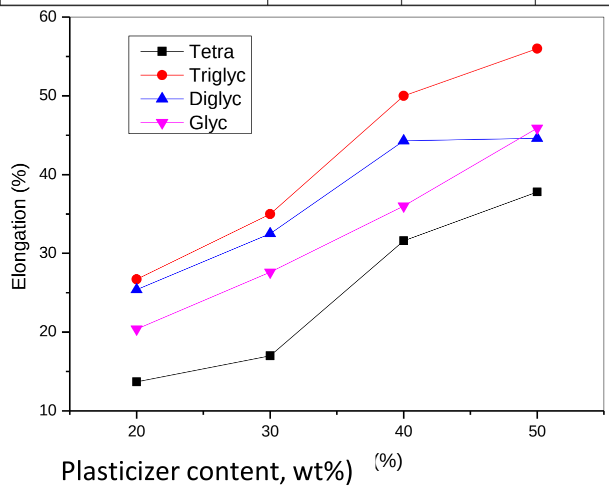
Substance	Chemical structure	Content in the commercial product, wt%
Glycerol		100
Diglycerol		90.3
Triglycerol		43.3
Tetraglycerol		35.2

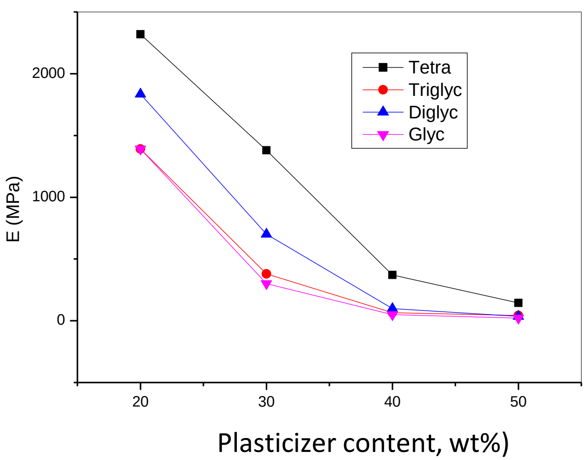
Effect of plasticizer type and its content on mechanical properties of the composite (CS/CN)=(85/15) wt%

The plasticising effect of PEG 600 (Table) is lower in comparison with that of glycerol oligomers due to less decrease in modulus accompanied by relatively low elongation. Figures show the marked effect of the type and content of plasticiser on the basic mechanical parameters of the composite film performance.

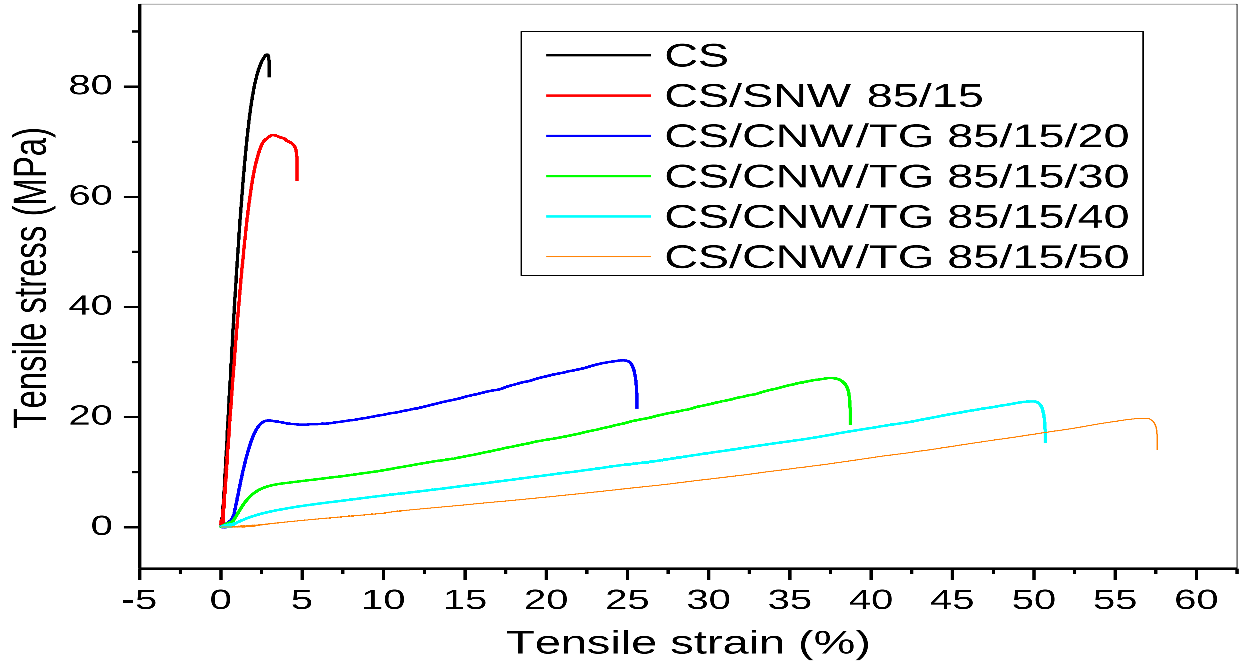
Sample Plasticized with PEG-600	Composition, wt%			Maximum tensile stress	Strain at break	Young's Modulus
	CS	CN	P1	MPa	%	MPa
3	46	20	34	37±5	18±3	852±166
6	47	20	33	51±3	23±3	905±191
9	48	21	30	43±4	24±4	729±164
St	Celulose Acetate			54±5	84±14	127±13





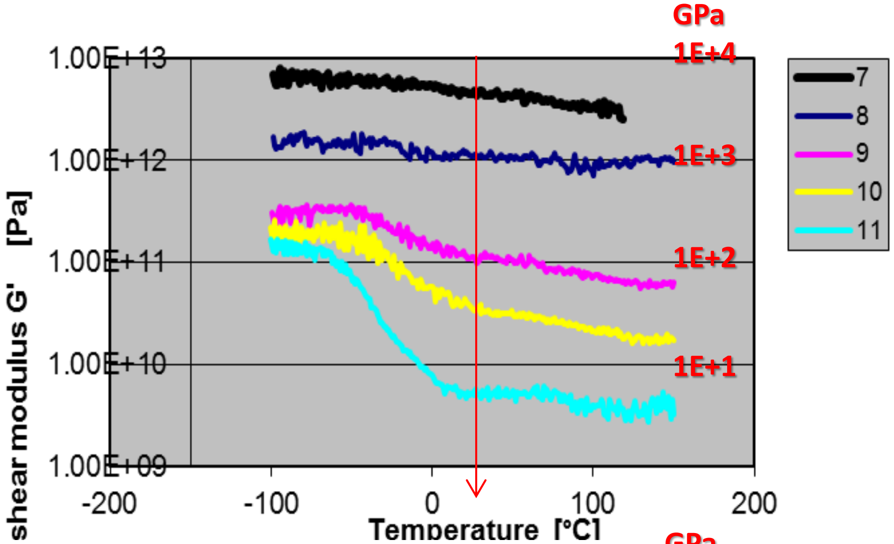


Effect of triglycerol content on the mechanical properties of the films with CS/CN proportion =(85/15) wt%



The stress-strain curves demonstrate altering of mechanical behaviour with triglyceride content.

Dynamic mechanical analysis



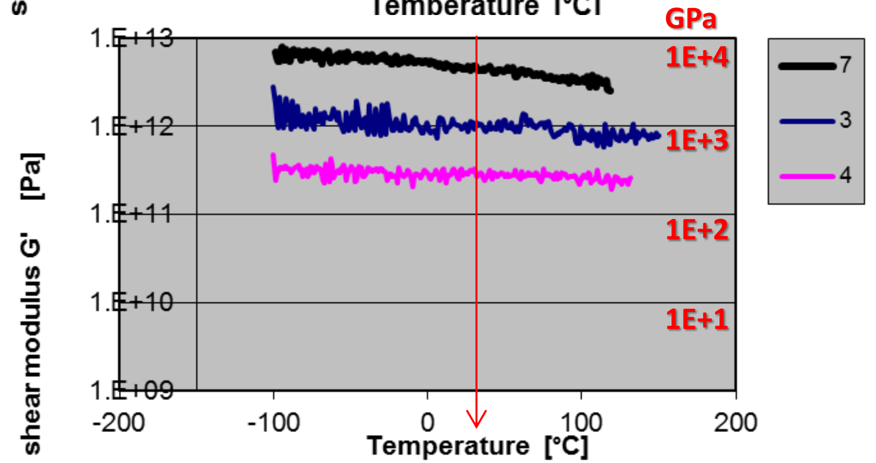
– 7-CS/CN=85/15 (no plasticizer);

— 8-(CS/CN)/Triglycerol=(85/15)/20wt%;

—9- (CS/CN)/Triglycerol=(85/15)/30wt%;

— 10- (CS/CN)/Triglycerol=(85/15)/40wt%;

— 11-(CS/CN)/Triglycerol=(85/15)/50wt%;



— 7- CS/CN-85/15 (no plasticizer);

—3-(CS/CN)/glycerol=(65/35)/30wt%;

– 4-(CS/CN)glycerol=(65/35)/50wt%

The DMA curves confirm significant effect of the plasticizer content on the modulus of the CS/CN films. At the same plasticizer content (30 or 50 wt%) but about twice higher content of CN in the films with CS/CN proportion (75/15) or (65/35) wt%, glycerol influence on modulus values considerably less than triglycerol. The G‘ = f(T) curves are deliberately shifted for the sake of easier comparison.

chitopack

Effect of CS/CN proportion on mechanical properties of plasticized films

Composition	Young's modulus (Mpa)	Break stress (Mpa)	Elongation (%)
Cellulose acetate	127 ± 13	54 ± 5	127 ± 13
CS/CN/triglycerol 85/15/30	120 ± 55	29,3 ±3,4	47,0 ± 5,5
CS/CN/triglycerol 75/25/30	105 ± 55	24,0 ± 6,5	37,5 ±7,0
CS/CN/triglycerol 65/35/30	130 ± 38	23,4 ± 5,8	41,8 ± 7,9
CS/CN/diglycerol 85/15/30	450 ± 55	33,0 ± 7,0	32,3 ± 8,4
CS/CN/diglycerol 75/25/30	250 ± 62	34,6 ± 6,2	35,3 ± 5,9
CS/CN/diglycerol 65/35/30	190 ± 53	29,5 ± 6,8	35,0 ± 7,5

The mechanical properties of the films with the CS/CN proportion of 85/15, 75/25 and 65/35 wt% plasticized with the same amount of di-glycerol or tri-glycerol depended on the plasticizer type more than on the CN content. The plasticizing effect of tri-glycerol was higher than that of di-glycerol.

Conclusions

1. **Both glycerol and polyglycerols-2-4 influenced on the mechanical properties of CS/CN nanocomposite films significantly. The reason consists obviously in the ability of the plasticisers to bind with CS chains disrupting the intra- and inter-chains bonds in CS matrix and between CS and CN.**

2. **Incorporation of plasticizers allows producing the nanocomposite biodegradable films from chitin nanofibrils and chitosan with balanced mechanical properties. Their applications in food packaging could help in solving environmental problems of utilization of the huge quantities of waste of the sea food industry – exoskeletons of crustaceans, from which chitin nanofibrils and chitosan are produced.**

Acknowledgement

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Effect of chitosan on behaviour of wheat B-starch nanocomposite

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Goal

Application of chitosan modified montmorillonite in thermoplastic B starch
Polyfunctionality of CS – "linking" of MMT platelets

Solution: "in situ" MMT modification inside the TS system

State of the art

Combination of nanofillers and CS to upgrade thermoplastic starch
Example: Cassava starch-based materials.

Srikultit et al. found moderate increase in mechanical parameters and reduction of water uptake in nanocomposite contaning 0-15% CS. The reason seems to be the fact that CS did not increase interlamellar distance significantly and also did not support degree of exfoliation. CS acts as a compatibilizer only (Kampeerapappun, Piyaporn; Aht-ong, Duangdao; Pentrakoon, Duanghathai; Srikulkit K, Carbohydr Polym, 67, 155-163 (2007)

Materials

Wheat B-starch “Soltex P6” of dry matter (DM) 91.3% and of mean average diameter 5.9μm was provided by the Amylon Havlíčkův Brod starch company (Czech Republic)

Glycerol, analytical grade, Lachner (Czech republic)

Cloisite C30 B -montmorillonite (MMT) modified with methyl tallow bis(2-hydroxyethyl) quaternary ammonium chloride was obtained from Southern Clay Products, Inc. (Texas, USA).

Chitosan, average molecular weight ~400 000, deacetylation degree 68%, Aldrich

Preparation of films

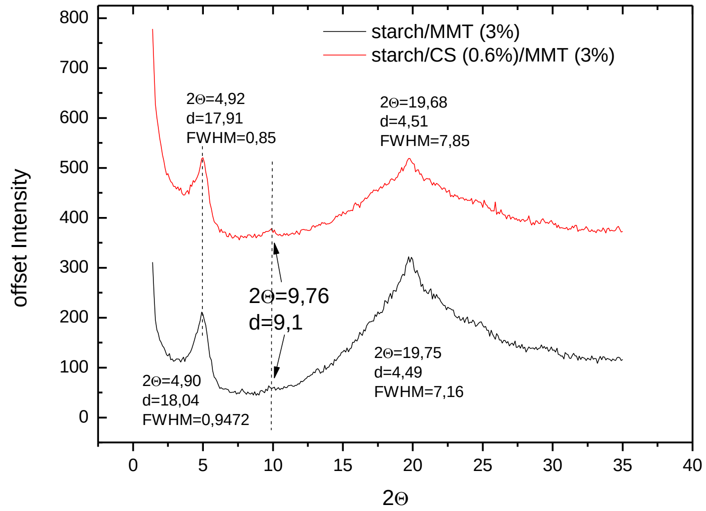
A mixture of starch and glycerol at a ratio 4:1 by mass was dissolved in distilled water (4x the mass of starch), MMT and 1 % solution of chitosan in 1% (w/w) aqueous acetic acid solution were added. All components were mixed for 30 min at ambient temperature and gelatinized at 80°C for 30 min.

Films were prepared by casting the solution to glass surface and dried at ambient temperature for 48 hours, the uniform thickness of 0.1 mm was adjusted by a knife.

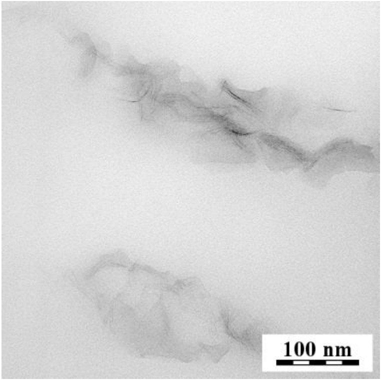
Mechanical properties of starch films containing glycerol (20 %)

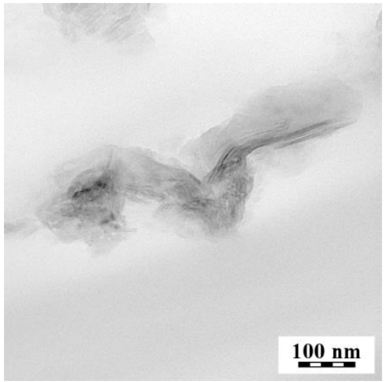
Sample composition	Max. stress (MPa)	Elongation (%)	Modulus (MPa)
Starch	21.7±2.3	4.5±0.7	1074±190
Starch/CS (0.6%)	32.5±1.7	4.1±0.5	1420±80
Starch/MMT (3%)	32.2±4.0	2.9±0.4	1570±140
Starch/MMT (3%)/CS (0.6%)	34.2±1.7	3.7±0.3	1580±75

A pronounced effect of small amount of chitosan on mechanical properties of thermoplastic B-starch reflected in significant increase in both strength and modulus with negligible decrease in ductility. The nanocomposites both from starch containing CS (0.6%) and MMT (3%) had the similar tensile strength but the latter was more rigid and less elastic. The starch nanocomposite containing both additives (CS and MMT) had the best mechanical properties.



XRD patterns of starch/MMT and starch/MMT/CS nanocomposite





Starch/MMT (3%) **Starch/CS (0.6%)/MMT(3%)**

Transmission electron microscopy observations

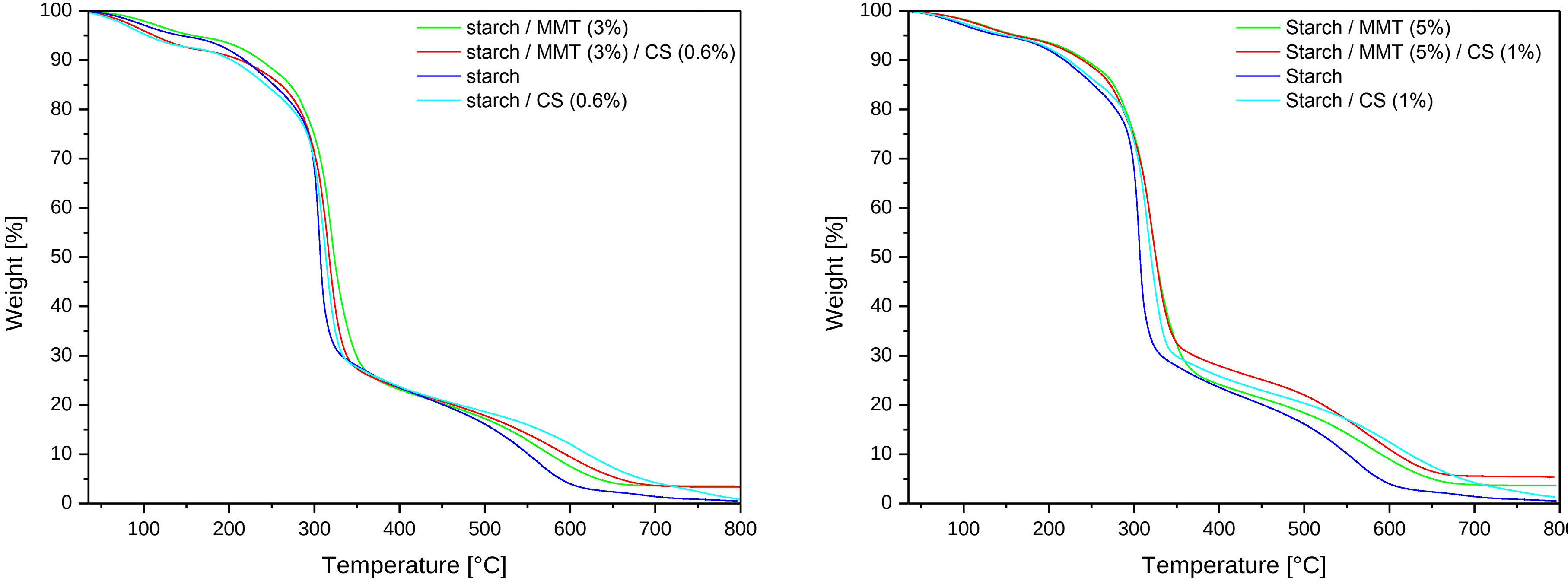
Oxygen permeability at 30°C in dependence on composition

Sample	Permeability		Diffusion Coefficient	Solubility
	mol/(m.Pa.s)	Barrer	m^2/s	mol/(m^3 Pa)
Starch*	-	-	-	-
Starch/CS (0.6%)	$3.617.10^{-17}$	0.108	$5.810.10^{-13}$	$6.225.10^{-5}$
Starch/MMT (3%)	$3.606.10^{-17}$	0.107	$6.194.10^{-13}$	$5.822.10^{-5}$
Starch/CS (0.6%)/MMT (3%)	$5.225.10^{-18}$	0.016	$4.732.10^{-13}$	$1.104.10^{-5}$

1 Barrer = 10^{-10} cm^3 (STP) cm/ (cm^2 s cmHg)
* starch film failed at test conditions

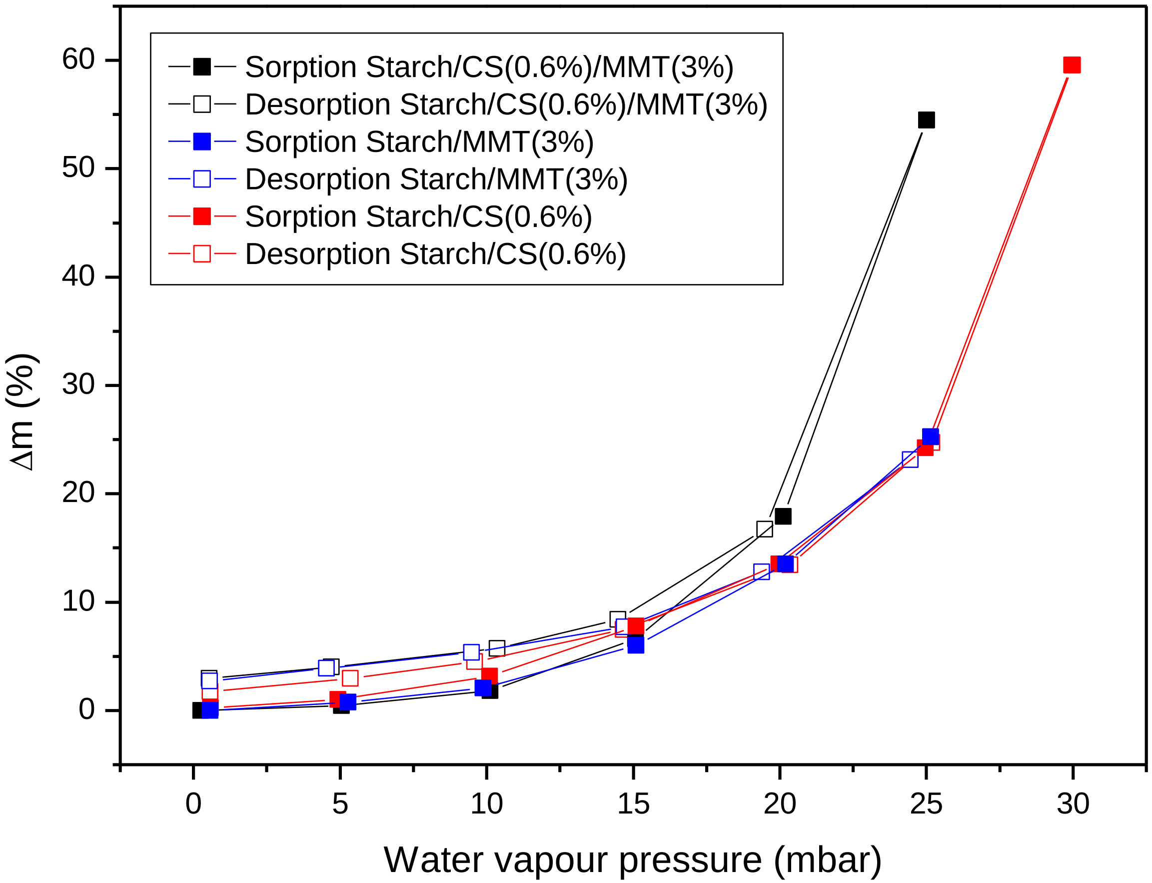
The oxygen permeability of the starch composites containing CS (0.6 %) or MMT (3 %) was almost the same. Both modifications improved barriers properties of the composites substantially. The starch composite containing both additives exhibited an order less permeability to oxygen than the former ones.

Thermogravimetric analysis of starch derived materials: Effect of CS and MMT on thermal stability of starch



The lowest mass loss was found for starch/MMT composite in temperature range below ~350°C. The relatively lower stability of starch/CS/MMT composite was in agreement with its higher moisture content.

Water vapors sorption/desorption at 25°C



Rather peculiar property of starch/MMT/CS composite is its most significant water vapors absorption in comparison with the starch/CS and starch/MMT ones at the same pressure of water vapors. Antagonistic effect arising from combination of there hydrophilic components is subject of further work. This enhanced water absorption is in line with some results of published by others.

Conclusions

1. Obtained results indicate high effect of small amount of chitosan (< 1%) on mechanical properties of both B-starch- and montmorillonite-containing nanocomposites.

1. Due to simultaneous significantly reduced permeability for oxygen in the nanocomposites, the starch/CS/MMT composite obtained using a simple one-step preparation represents a promising material to upgrade parameters of thermoplastic wheat B-starch for food protection/packaging applications. However, the lack of antimicrobial activity of starch can be a serious obstacle in its application as food packaging material.