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MODIFICATION OF STARCH PROPERTIES

Thermoplastic starch (TPS) was prepared by thermomechanical treatment of native starch mixed with plasticizer. The influence of the type and amount of plasticizer was investigated. The obtained TPS was then blended in a twin screw mixer with 5 and 10 mass % of poly(ethylene-co-acrylic acid) (EAA), poly(ethylene-co-vinyl acetate) or cellulose acetate (CA) in order to improve the properties of the TPS. The influence of such low amounts of thermoplastic polymer (TPP) on the processability, mechanical properties and water resistance of TPS was investigated. The properties of native starch were changed not only by thermomechanical treatment but also by chemical modification synthesizing carboxymethyl starch (CMS). The influence of the carboxymethylation conditions on the degree of substitution and limiting viscosity number of CMS was studied.

Starch is a polysaccharide which is produced in almost all plants by photosynthesis. Commercially important starch is obtained from corn, wheat, rice, potatoes, tapioca and peas.

Naturally occurring starch consists of two components – amylose and amylopectin. The content of amylose depends on the source plant and can vary from 14 to 27 mass.%. Amylose is a mostly linear α – D – (1→4) glucan, the molar mass of which is several hundred thousand g/mol. Amylopectin is a highly branched α – D – (1→4) glucan with α – D – (1→6) linkages at the branch points, the molar mass of which can be as high as 100 million g/mol [1].

Starch exists in the form of granules in plants. Depending on the plant, the granules range in size from about 3 to 50 or even more μm . Starch is hydrophilic and its moisture content depends on the relative humidity of the atmosphere in which it is stored.

Starch finds very wide application. Its advantages over similar materials are that, being obtained from plants, it is renewable annually. It is biodegradable and its properties can be changed and adjusted to meet various purposes. The properties of native starch can be changed in a directed way by chemical or enzymatic modification. These modifications include chemical and enzymatic catalysed degradation, oxidation, substitution to starch esters and starch ethers, and crosslinking with bifunctional reagents to form diesters and diethers. These means are used to produce modified starches with non-ionic, anionic and cationic substituents. This leads to changes of key properties such as gelatinisation temperature, solubility, viscosity (stability), gel formation, ionic charges and hydrophilic character.

Starch was first used as a biodegradable filler for commercial thermoplastic polymers. Recently, there has

been a growing interest to obtain thermoplastic starch containing relatively low amount of additives which can be used for the production of articles unlikely to be recycled, such as trash and compost bags, mulch films and disposable diapers. These articles are fully biodegradable.

Extrusion cooking of starch, a process during which destructuring of native starch occurs and as a result thermoplastic starch (TPS) is obtained, has been studied extensively during the last decade. The main concern of the studies was the effect of extrusion variables upon molecular degradation, gelatinization, melting, expansion volume and other physicochemical changes in starches [2–7]. The effects of temperature, moisture content and additives on the rheological behaviour of TPS were also investigated [8].

The mechanical properties and stability of thermoplastic starch are not satisfactory. Some approaches for improving the mechanical properties of thermoplastic starch, moisture resistance and temporal stability include chemical modification [9–11], changes in starch morphology [12], and blending with other polymers [13–19], which can be of synthetic or natural origin.

In this study the results of three groups of experiments are presented: 1) the possibilities of obtaining thermoplastic starch by thermomechanical treatment of native corn starch [20]; 2) preparation of TPS blends with some thermoplastic polymers [21] and 3) synthesis of carboxymethyl starch [22]. In the first group of experiments, the influence of low-molecular plasticizers on the success of the thermomechanical treatment was investigated. In the second group of experiments, the properties of the obtained TPS were changed by blending with some commercially available thermoplastic polymers (TPP). Poly(ethylene-co-acrylic acid), poly(ethylene-co-vinyl acetate) (EVA) and cellulose acetate (CA) were chosen to be investigated as components of the blends. Since the ultimate goal of the research efforts is to prepare disposable consumer

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items from substantially pure starch and to exclude non-biodegradable synthetic polymers from the formulation, the content of these polymers in the blends investigated in this work was relatively low – 5, 10 and in one case – 15 mass %. The influence of such low amounts of thermoplastic polymer on the mechanical and rheological properties and water resistance of TPS was investigated.

Finally, in the third group of experiments, chemical modification of starch was performed by etherification of starch with monochloroacetic acid, MCA, in the presence of sodium hydroxide. As a product of this reaction, carboxymethyl starch (CMS) was obtained. The carboxymethylation can be performed in water as a solvent [23–26] or in a water-miscible organic solvent containing small amounts of water [27–29]. Carboxymethyl starches are reported to have increased water solubility as the degree of substitution, DS, increases, so organic solvents are to be used when a granular product is desirable. In this work, the carboxymethylation was performed in an ethanol/water mixture and the influence of the reaction mixture composition, reaction time and temperature and type of starch being carboxymethylated on the degree of substitution, DS, and limiting viscosity number, $[\eta]$, was studied. Carboxymethyl starch, as a water-soluble polysaccharide, is widely employed as an additive in the paper industry [30], and as a thickener in the formulation of textile printing pastes. The application of CMS is also growing in enhanced oil recovery [31].

EXPERIMENTAL

Materials

Native starch (S) and WX – starch, i.e., native starch enriched with amylopectin (S_0) were used for thermomechanical treatment. They were produced by the "Jabuka", Starch Industry, Serbia. Native starch, oxidized starch (Starch Industry, Zrenjanin, Serbia, starch oxidized by hypochlorite solution, content of carboxyl groups between 0.40 – 0.60 mass %) and starch enriched with amylose ("BAGKF" Institute, Germany, 70% of amylose) were used for carboxymethylation.

All the other chemicals used for CMS synthesis (NaOH, ClCH_2COOH , $\text{CH}_3\text{CH}_2\text{OH}$, CuSO_4 , FeCl_3 , EDTA, CaCl_2 , NaCl, HCl, Murexid) were produced either by Carlo Erba or Zorka (Šabac, Yugoslavia).

Ethylene glycol (EG), propane triol (glycerine) (G) and poly (ethylene glycol) (PEG) with a molar mass of less than 1000 g/mol were used as plasticizers without any purification. Irganox 1076 (IX) was used as the thermostabilizer. Before mixing with the additives, the starch was dried in a vacuum oven for four hours at 80°C. The moisture content of the starch was determined by thermogravimetric analysis and it was found to be 2% after drying.

The thermoplastic polymers, poly(ethylene-co-acrylic acid) (LUWAX EAS-2, BASF, $M_w=20000$ g/mol, 20 % acrylic acid), poly(ethylene-co-vinyl acetate) (BASF, $M_w=20000$ g/mol, 30% vinyl acetate) and cellulose acetate (Eastman, 39.8±0.5% acetate groups) were used as obtained from the producers.

Thermomechanical treatment

Thermomechanical treatment of the starch with additives (plasticizer and thermostabilizer) was performed in a twin screw mixer Rheomix – 600 which was connected to a Rheocord 90 (HAAKE). This mixer enabled thermomechanical treatment of the starch at different temperatures and screw speeds. All the TPS blends were prepared in the same mixer with a screw speed of 100 rpm and a starting temperature of 165°C. Thermoplastic starch obtained from native starch with 20 mass % glycerine as plasticizer and 1 mass % of stearic acid as lubricant was used for blending with the chosen polymer.

Molding

For tensile studies and water absorption, the blends and TPS obtained from the mixer had to be molded. After thermomechanical treatment they were in the form of chunks irregular shaped. In order to avoid weld lines, these chunks had to be broken into small pieces and then ground in a coffee-grinder before being filled into the molds.

For tensile measurements and dynamic mechanical analysis, specimens were prepared in a special mold which was filled with ground TPS or TPS blend, kept at 140°C for 10 min under a pressure of 2.5 kPa and then allowed to cool to 50°C under pressure before the pressure was relaxed and the mold removed from the press. The obtained samples, in the form of thin strips with dimensions 63x12.5x1.3 mm, were used directly for dynamic mechanical analysis. The dogbone specimens for tensile measurements were mold cut from the thin strips.

For water absorption determination, the specimens were obtained in a similar way, but in the form of discs with a diameter of 25.0 and a thickness of 2.0 mm. [KJ1]

Methods

Dynamic mechanical analysis of the TPS and its blends was performed using a mechanical spectrometer Rheometrics RMS-605. The specimens were subjected to dynamic torsion at a constant frequency of 6.28 rad/s, in the temperature range from 30 to 170°C. The temperature was increased stepwise in 5 K increments with a thermal soak time 0.5 min. The strain range was from 0.3% at the lowest temperature (30°C) increasing gradually to 0.6% at the highest temperature (170°C) in order to obtain an optimum response domain of the transducer.

The tensile strength and modulus of the dogbone specimens were determined using a Model TT-CM tensile strength tester (Instron Inc., Canton, Massachusetts) at a crosshead speed of 1 mm/min. The definitions of the parameters are outlined in ASTM D-638-68 test. The properties reported are the average of five specimen. Starch is very hydrophilic and its moisture content depends on the relative humidity. Thus, before testing, the samples were conditioned in a closed chamber at room temperature and known relative humidity for seven days. The relative humidity was adjusted by glycerine/water mixture to be 45, 67 and 85 %RH.

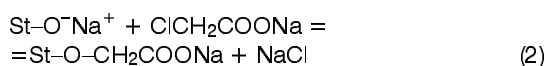
The swelling of TPS and the investigated blends was determined gravimetrically.

Synthesis and characterization of carboxymethyl starch

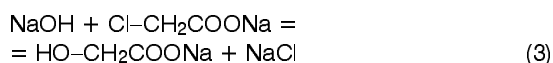
The synthesis of CMS was performed by a partially modified procedure for the carboxymethylation of cellulose/starch mixtures developed by Samer and Bochof [32]. It was performed in two steps. In the first step:



alkalization was achieved by mixing starch, ethanol and aqueous 11.5 M NaOH solution at room temperature. The reaction mixture was stirred for 20 min. Afterwards, MCA dissolved in 11.5 M NaOH solution (the molar ratio of MCA and NaOH was always equal to 6.83) was added and the reaction mixture heated up to the desired temperature and stirred at that temperature for a designated time. In this second step etherification occurs:



Additionally, the following side reaction is possible:



The synthesized CMS samples were purified by dissolving in water, neutralizing the solution with dilute NaOH or HCl solution and precipitating with ethanol. The precipitated CMS was filtered and dried under vacuum at 40°C.

The DS was defined as the molar ratio of -CH₂COONa groups to anhydroglycose units (AGU) of the starch molecule. The method developed by von H. Kessel [33] was used for the DS determination. In this analysis method, the CH₂COONa groups of CMS are determined by precipitating their copper salt and back titrating the excess copper in the filtrate with ethylenediaminetetraacetate (EDTA) using Murexid as the indicator.

An Ubbelohde dilution viscometer was used for determining the limiting viscosity number of starch in water and CMS in 1.0 % NaCl (w/w) at 25°C. The values of $[\eta]$ were determined graphically in the usual way [34].

RESULTS AND DISCUSSION

Thermoplastic starch preparation

Six samples were prepared from native starch (S1 – S6) and six from WX-starch (S₀1 – S₀6) by mixing the starch with different amounts and types of plasticizer. The thermostabilizer Irganox 1076 was added to some of them. In addition, one more sample was prepared in which 0.8 mass. % of stearic acid (SA), a lubricant, was added. The compositions of all the samples are given in Table 1.

Table 1. Sample composition, conditions and successfulness of transformation of native to thermoplastic starch

Sample	Content, mass %			T _{st} , °C	τ _{max} , ^{a)} Nm	SOT ^{b)}
	Starch	Plasticizer	Stabilizer			
S1-G-20	80,0	20,0	–	165	60.7	(+)
S2-G-30	70,0	30,0	–	165	26.8	(+)
S3-G-20+PEG	72.7	18.2+9.1 PEG	–	165	8.7	(–)
S4-G-20	72.8	27.2	–	160	68.0	(+)
S6-G-20-IX	79,6	19,9	0,50	160	38.1	(+)
S5-E-20	80,0	20,0	–	130	–	(–)
S ₀ 1-E-10	90,0	10,0	–	160	9.3	(–)
S ₀ 2-E-20	80,0	20,0	–	140	29.6	(+)
S ₀ 3-E-30	70,0	30,0	–	130	9.4	(+)
S ₀ 4-G-20–	80,0	20,0	–	140	–	(–)
S ₀ 5-E-20	80,0	20,0	–	150	37.2	(+)
S ₀ 6-G-20+IX	82,4	17,1	0,50	160	34.5	(+)
S-G-20+SA	79,4	19,8	0,80	140	–	(+)

^{a)} τ_{max} – torque maximum

^{b)} SOT – successfulness of transformation

Thermomechanical treatment of the samples was performed in a twin screw mixer Rheomix 600 with a screw speed of 100 rpm. The temperature was chosen according to the plasticizer type and ranged from 120 to 165°C. Variation of the temperature, torque and mechanical energy used during the thermomechanical treatment of the starch samples with the time of treatment was automatically registered. The values of the starting temperature, T_{st}, and of the maximum torque, read from the diagram, are also presented in Table 1. The samples that were not successfully transformed into thermoplastic starch are indicated in Table 1 by a minus sign.

The results from Table 1 show that when glycerine was added as plasticizer to native starch (S1-G-20, S2-G-20, S4-G-20 and S6-G-20-IX), a starting temperature of 160°C led to a successful transformation of starch. The maximum value of the torque decreases with increasing content of plasticizer. It is equal to 60.7 Nm for the sample S1-G-20 (20 mass.% of glycerine) and 26.8 Nm for the sample S2-G-30 (30 mass. % of G). It is interesting to note that for the sample additionally

containing poly (ethylene glycol) (S3-G-20-PEG), the transformation to thermoplastic starch was not successful although it contained 18.2 mass.% of glycerine and T_{st} was 165°C. The most probable reason for this is that the glycerine solvated not only the starch macromolecules but also the poly(ethylene glycol) ones. Thus, the critical amount of 16 mass.% of glycerine, which, according to Tomka [35], is necessary to successfully transform native to thermoplastic starch at $T_{st} = 165^\circ\text{C}$, was not available.

Sample S5-E-20 (20 mass.% of ethylene glycol) was thermomechanically treated at a T_{st} equal to 130°C. Such a low starting temperature was chosen because it was expected that the starch macromolecules would be better solvated by the smaller ethylene glycol molecules than by glycerine, which would allow transformation to occur at lower temperatures. However, the transformation of this sample was not successful.

The influence of ethylene glycol was investigated in more detail with WX-starch. It was found that a sample containing only 10 mass.% of EG (S₀1-E-10) was not successfully transformed into thermoplastic starch even at 160°C. The addition of 20 mass.% of ethylene glycol (S₀2-E-20) plasticized the WX-starch enough to enable transformation to occur at 140°C. When the content of ethylene glycol was 30 mass.% the transformation already occurred at the $T_{st} = 130^\circ\text{C}$, but the torque was very low (9,4 Nm) and the obtained thermoplastic starch was very soft.

BLENDS OF TPS AND SOME THERMOPLASTIC POLYMERS

Dynamic mechanical analysis

The TPS and all the investigated blends conditioned at three RH, were subjected to dynamic mechanical analysis. As a result, the storage, G' , and loss, G'' , moduli and $\tan\delta$ as function of temperature at constant frequency (6.28 rad/s) were obtained. The temperature dependence of the storage modulus and $\tan\delta$ for TPS blends with 10 mass % of EAA conditioned at 45, 67 and 85 %RH is shown in Fig.1. The sample

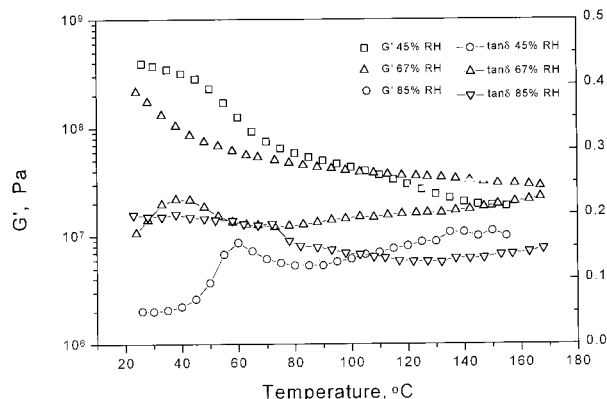


Figure 1. Temperature dependence of G' and $\tan\delta$ for TPS blends with 10 mass % of EAA conditioned at 45, 67 and 85 %RH

conditioned at 85 %RH was already in the rubbery state at room temperature, whereas the samples conditioned at 45 and 67 %RH exhibited a well-defined transition from glassy to rubbery state. Similar results were obtained for all blends investigated in this work. The glass transition temperature, determined as the temperature of the $\tan\delta$ peak, was about 20 degrees higher for the samples conditioned at 45 %RH than for the samples conditioned at 67 %RH, which was expected knowing that water acts as a plasticizer.

The influence of the type of the investigated TPP on the Tg of the TPS, all samples being conditioned at 67 %RH, is shown in Fig. 2 where the temperature dependence of G' and $\tan\delta$ is given for TPS and TPS blends with 10 mass % of EAA, EVA or CA. They all exhibit a transition from the glassy to the rubbery state but the Tg values for the samples are very similar so no conclusion can be made about the specific influence of any of the investigated TPP. Similar results were obtained for blends conditioned at 45 %RH. It is obvious that RH, i.e. moisture content, of the TPS blends has a much larger influence on the Tg than the TPP.

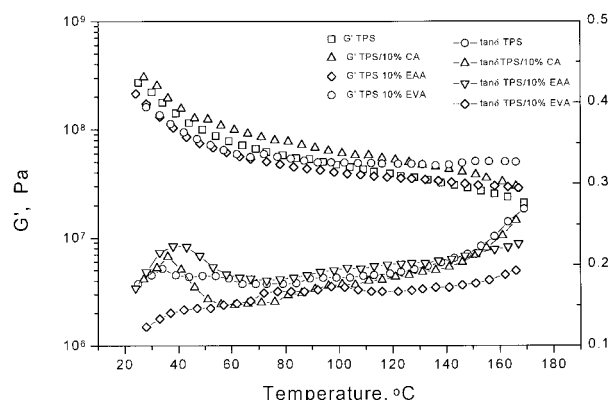


Figure 2. Temperature dependence of G' and $\tan\delta$ for TPS and TPS blends with 10 mass % of EAA, EVA or CA conditioned at 67 %RH

The influence of the TPP concentration on the Tg was investigated for TPS/EAA blends containing 5, 10 and 15 mass % of EAA. The temperature dependence of G' and $\tan\delta$ for TPS and these blends conditioned at 67 %RH are presented in Fig. 3. It can be seen that, quite unexpectedly, the Tg increases with increasing content of EAA. This might be explained by the "anti-plasticizing" effect of this TPP compared to water.

It should be noted here that no attempt was made to determine the Tg values from the temperature dependence of G' for the investigated blends because there were not enough data for all samples at temperatures below the Tg. The temperature dependence of G' is presented in the figures just as a confirmation of glass transition since G' decreases by an order of magnitude in going from the glassy to the rubbery state.

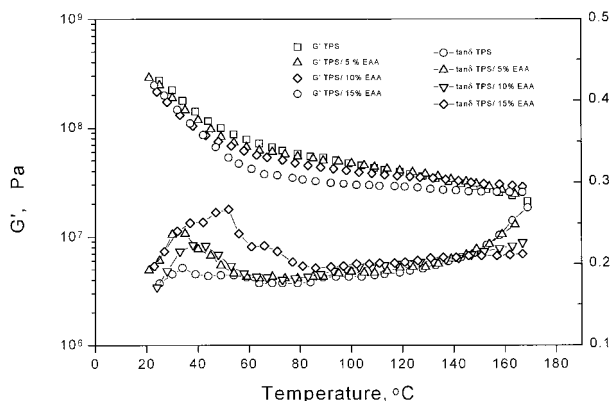


Figure 3. Temperature dependence of G' and $\tan\delta$ for TPS and TPS blends with 5, 10 and 15 mass% of EAA conditioned at 67 %RH

Tensile measurements

Only TPS blends with 10 mass% of EAA, EVA or CA were used for tensile measurements. The tensile properties of the test specimens were measured after they had been conditioned at the required relative humidity (45 and 85 %RH) at room temperature for 7 days. The tensile properties of TPS and its blends depend greatly on the moisture content (MC), water acting as a plasticizer, and the MC changes considerably with relative humidity.

The stress (σ) – strain (ϵ) curves for TPS and its blends conditioned at both RH are presented in Fig. 4. The tensile strength (σ_s) and elongation at break (ϵ_b) for all samples are shown in Table 2, together with the values of the tensile modulus, E.

The main conclusion which can be drawn on the basis of the presented data is that 10 mass% of the investigated TPP does not influence the tensile properties of TPS significantly. The moisture content has a much larger influence. The tensile strength and tensile modulus values for TPS and its blends which were conditioned at 45 %RH are an order of magnitude larger than the values for the corresponding samples kept at 85 %RH, whereas elongation at break values are approximately ten times smaller. In other words, TPS and its blends with lower MC are strong and brittle and with increasing MC they become more soft and ductile.

The three TPP used as blend components did have some influence on the tensile properties. For the

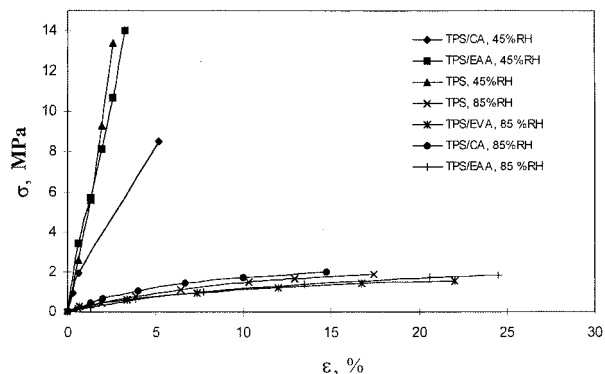


Figure 4. $\sigma - \epsilon$ curves for TPS and TPS blends with 10 mass% of EAA, EVA or CA conditioned at 45 and 85 %RH

blends conditioned at 45 %RH, the tensile strength and modulus are approximately the same for TPS/EAA and TPS and larger than for the TPS/CA blends, while elongation at break decreases in the following order: TPS/CA > TPS/EAA > TPS. The tensile strength for blends conditioned at 85 %RH have quite low values with TPS/CA and TPS/EAA having similar values to the value for TPS, all of them being larger than the value for TPS/EVA. The TPS/EAA and TPS/EVA blends have similar ϵ_b values which are larger than the values for TPS and TPS/CA, the two of them being alike. The highest modulus was obtained for TPS/CA blend and the lowest one for TPS/EVA. It is difficult to discuss unambiguously the influence of TPP on the tensile properties since moisture has such a large effect.

The tensile measurements showed that the tensile properties of TPS cannot be significantly changed by adding up to 10 mass% of investigated TPP. Much larger changes are achieved by varying the moisture content of TPS or its blends. In order to control the modulus, strength and ductility of TPS blends by adding a TPP, the amount of the TPP should be much larger than 10 mass%.

Water absorption

The water absorption of all the investigated TPS blends and pure TPS was studied by immersing sample discs in water and observing the weight gain with time. The samples of TPS, TPS/CA and TPS/EVA blends disintegrated after a few minutes. Similar behavior was displayed by the sample of TPS/EAA blend with 5

Table 2. Tensile strength (σ_s), elongation at break (ϵ_b) and tensile modulus (E) for TPS and its blends with 10 mass % EVA, CA or EAA conditioned at two relative humidities (RH)

Sample	45 %RH			85 %RH		
	σ_s , MPa	ϵ_b , %	E, MPa	σ_s , MPa	ϵ_b , %	E, MPa
TPS	13.4 ± 1.3	2.58 ± 0.57	479 ± 96	1.86 ± 0.20	17.4 ± 3.8	28.2 ± 5.6
TPS/EVA	–	–	–	1.55 ± 0.17	22 ± 4.8	17.8 ± 3.6
TPS/CA	8.51 ± 0.94	5.16 ± 1.1	298 ± 60	1.97 ± 0.22	14.7 ± 3.2	40.8 ± 8.2
TPS/EAA	14.0 ± 1.5	3.22 ± 0.71	419 ± 84	1.82 ± 0.20	24.5 ± 5.4	20.2 ± 4.0

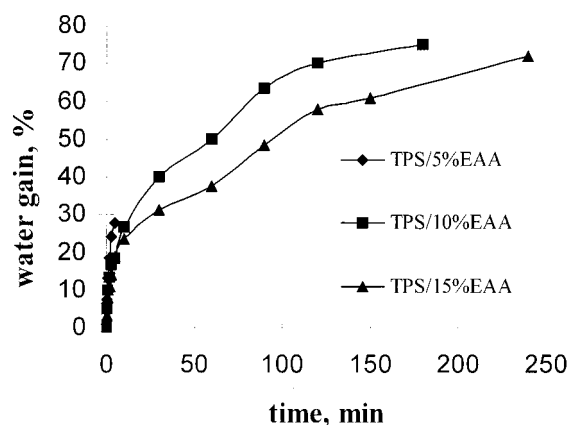


Figure 5. Water gain of TPS blends with 5, 10 and 15 mass% of EAA vs time at room temperature

mass% of EAA which disintegrated after 5 min. The only samples which absorbed water without losing some pieces were samples which contained 10 and 15 mass % of EAA. The water gains for these two samples and for the sample with 5 mass% of EAA as a function of time are shown in Fig. 5. The smallest water gain was for the TPS/EAA blend with 15 mass % of EAA.

CARBOXYMETHYLATION OF STARCH

Three types of starch were used for carboxymethylation. They were characterized by determining the values of their $[\eta]$ and the obtained results are presented in Table 3 together with their designation.

Table 3. Types, designations and limiting viscosity numbers, $[\eta]$, of the starches used for carboxymethylation

Starch type	Designation	$[\eta]$, g ⁻¹ cm ³
Native starch	NS	70.5
Oxidized starch	OS	49.5
Starch enriched with amylose	SA	31.5

Optimisation of the process of carboxymethylation was performed by varying the process parameters, such as reaction medium, starch: liquor ratio, concentration of NaOH and MCA, temperature and duration of reaction. Each parameter was varied keeping the other parameters constant as shown in the different sets of experiments A – J in Table 4. The influence of these parameters on DS and $[\eta]$ was followed experimentally. The reaction efficiency (RE) was also calculated as follows:

$$RE(\%) = \frac{\text{Amount of bounded } (-\text{CH}_2\text{COONa})}{\text{Initial amount of } (-\text{CH}_2\text{COONa})} \cdot 100$$

Influence of carboxymethylation time

The duration of carboxymethylation was varied by performing the reaction for 50, 100, 150 and 200 min. It

Table 4. The reaction parameters used in the carboxymethylation of starch and the reaction efficiency (RE)

Experiment No.	Starch type ^{a)}	Solvent	t, min	T, °C	n(NaOH): n(MCA): n(AGU)	Starch: liquor, ₃ g/cm	RE, %	
A	1 2 3 4 5	NS	Ethanol	25	58	1.26:0.69:1	1:3	58
				50				72
				100				80
				150				70
				200				85
B	1 2 3 4 5	NS	Ethanol	40	58	1.26:0.69:1	1:3	41
				58				72
				63				74
				68				70
				80				80
C	1 2 3	SA	Ethanol	40	58	1.26:0.69:1	1:3	51
				58				90
				68				94
D	1 2 3	OS	Ethanol	40	58	1.26:0.69:1	1:3	41
				58				58
				68				72
E	1 2 3 4 5	NS	Ethanol	100	58	0.70:0.69:1 1.26:0.69:1 2:0.69:1 3:0.69:1 4.47:0.69:1	1:3	19
								80
								87
								70
								39
F	1 2 3	OS	Ethanol	100	58	1.26:0.69:1 3:0.69:1 4.47:0.69:1	1:3	58
								67
								75
G	1 2 3	NS	Ethanol	100	58	4.47:0.69:1 4.47:2:1 4.47:3:1	1:3	39
								34
								33
H	1 2 3	NS	Ethanol	100	58	1.26:0.69:1	1:3	80
							1:5.5	32
							1:8	38
I	1 2 3 4	NS	Ethanol 75 vol.% Ethanol 50 vol.% Ethanol Water	100	58	1.26:0.69:1	1:8	38
								46
								27
								23
J	1 2 3	NS	Water	100	58	1.26:0.69:1	1:8	23
		OS						22
		SA						29

^{a)}In all experiments 20 g of starch were used

may be seen from the results presented in Table 4, that $[\eta]$ and DS increase with reaction time achieving an almost constant value after 50 min. An acceptable explanation for the data scattering at the longer reaction times could not be found. All the other reactions of carboxymethylation were carried out for 50 or 100 min. The reaction efficiency (see Table 4) changed in a similar way as the DS in this set of experiments.

Influence of the temperature of carboxymethylation

The dependence of DS and $[\eta]$ values on the reaction temperature for the samples obtained by carboxymethylating native starch (CMNS) and starch enriched with amylose (CMSA) are shown in Fig. 6. and for samples obtained by carboxymethylating oxidized starch (CMOS) only in Table 4. The values of

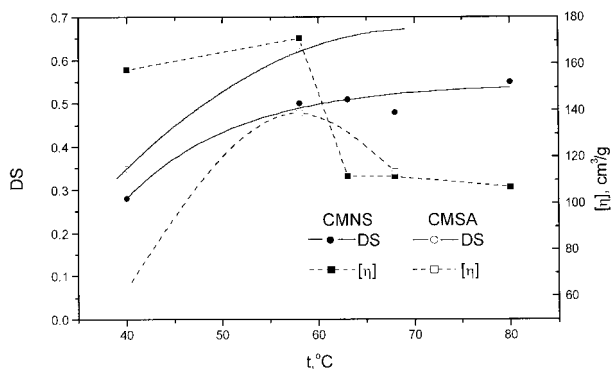


Figure 6. Dependence of $[\eta]$ and DS on the reaction temperature for CMNS and CMSA samples. Other reaction conditions as shown in Table 4.

the DS of CMNS increase with reaction temperature, achieving an asymptotic value at 80°C. The values of the DS of the CMSA samples are higher than for the CMNS and CMOS samples but show a similar trend with reaction temperature as the DS of CMNS. The lowest values of the DS were obtained for CMOS (see Table 4); the values increased with temperature in the whole investigated range of reaction temperatures.

For the investigated samples, the values of $[\eta]$ change in a different manner with reaction temperature than the values of the DS. This dependence is approximately the same for CMNS and CMSA, but is quite different for CMOS. The values of $[\eta]$ for the first two samples decrease abruptly at a reaction temperature of about 58°C. The values of $[\eta]$ for CMOS increase with temperature. It is interesting to note that the value of $[\eta]$ for all three samples is the same at the reaction temperature of 68°C. The abrupt decrease in $[\eta]$ might indicate some conformational change of the CMNS and CMSA macromolecules or their degradation, but no evidence for this is yet available.

Further investigations of starch carboxymethylation were carried out at 58°C since the highest DS values were obtained at this temperature for all the investigated samples under the stated experimental conditions.

Influence of NaOH

Native and oxidized starch were used to investigate the influence of the amount of NaOH on the carboxymethylation reaction. The values of the DS and $[\eta]$ of carboxymethylated samples of native starch are shown as a function of the molar ratio of NaOH to AGU of the starch samples, $n(\text{NaOH})/n(\text{AGU})$, in Fig. 7. For the carboxymethylated samples of oxidized starch they are presented only in Table 4.

It may be seen from Fig. 7 that during the carboxymethylation of native starch the dependence of the DS and $[\eta]$ on the $n(\text{NaOH})/n(\text{AGU})$ ratio in the reaction mixture is presented by a curve which goes through a maximum. A similar change of the DS during the carboxymethylation of native starch was obtained by

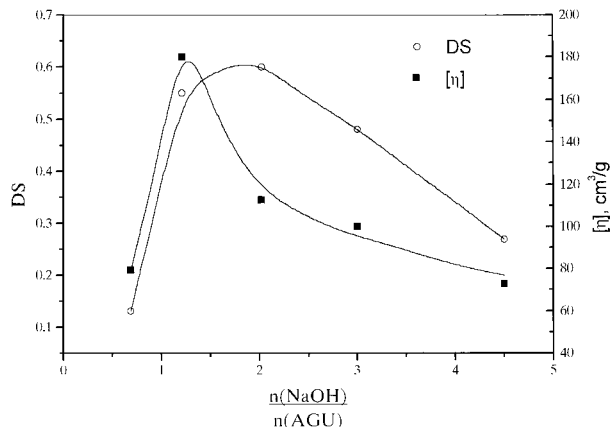


Figure 7. Dependence of $[\eta]$ and DS on the $n(\text{NaOH})/n(\text{AGU})$ ratio for CMNS samples at 58°C. Other reaction conditions as shown in Table 4.

Khalil et al. [24]. They explained the obtained result by assuming that the side reaction between NaOH and sodium monochloracetate (eq.3) occurred more intensively with increasing NaOH content in the reaction mixture, decreasing in that way the concentration of sodium monochloracetate in the reaction mixture. Consequently, lower values of the DS of the synthesized samples were obtained. It may also be seen from Fig. 7 that the highest value for the DS was obtained for an $n(\text{NaOH})/n(\text{AGU})$ ratio of 2, and for the highest value of $[\eta]$ this ratio was 1.2. These results indicate that during carboxymethylation of native starch with increasing $n(\text{NaOH})/n(\text{AGU})$ ratio, a significant degradation of the amylose and amylopectin macromolecules occurs, and even intramolecular crosslinking might occur causing a decrease of the $[\eta]$ values. The values of the DS for oxidized starch increase with increasing $n(\text{NaOH})/n(\text{AGU})$ ratio, while the $[\eta]$ values decrease (see Table 4). The DS values increase more slowly than for native starch (Fig. 7) and do not go through a maximum. This might be caused by the partial neutralisation of the added NaOH by acidic groups in the oxidised sample. The difference in the dependency of $[\eta]$ on the $n(\text{NaOH})/n(\text{AGU})$ ratio obtained during the carboxymethylation of oxidized compared to native starch is most probably due to the fact that the primary structure of oxidized starch has already been destroyed and that the depolymerization reaction occurs much more rapidly from the very beginning of carboxymethylation.

The reaction efficiency for the carboxymethylation of NS (see Table 4) also goes through a maximum and the explanation for decreasing values at the higher $n(\text{NaOH})/n(\text{AGU})$ ratio is the same as for the DS behaviour.

Influence of MCA

Native starch was used for the investigation of the influence of the MCA content in the reaction mixture on the DS and $[\eta]$ values of synthesized CMS samples. In

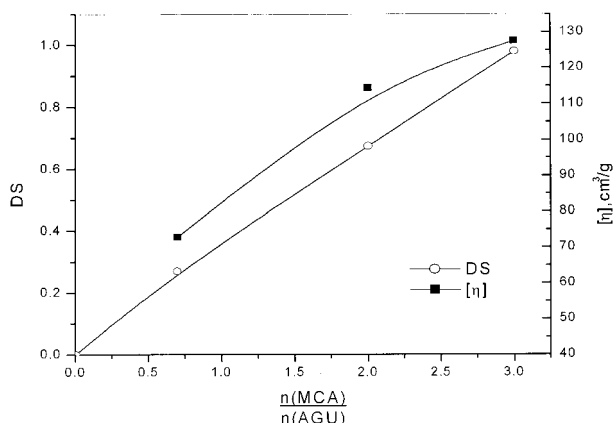


Figure 8. Dependence of $[\eta]$ and DS on the $n(\text{MCA})/n(\text{AGU})$ ratio for CMNS samples at 58°C. Other reaction conditions as shown in Table 4.

these experiments the molar ratio of MCA to AGU, $n(\text{MCA})/n(\text{AGU})$, was varied from 0.5 to 3.0. The obtained results are shown in Fig. 8. The values of the DS and $[\eta]$ of CMNS increase almost linearly with the MCA content in the reaction mixture. The results from Fig. 8 also show that the DS values of carboxymethylated native starch increase more rapidly than the $[\eta]$ values. The reaction efficiency for this set of experiments (see Table 4) is relatively low which is probably also due to the high concentration of NaOH, favoring the side reaction (eq.3).

Influence of reactant concentration

The results obtained by investigating the influence of reactant concentration on the values of the DS and $[\eta]$ of the synthesized CMNS are shown in Fig. 9. The amount of reactants during these experiments of the carboxymethylation of native starch was constant, but the concentration of the reactants was decreased by increasing the amount of solvent – ethanol. As may be seen in Fig. 9, the largest degree of substitution of native starch was obtained when there was 3.0 cm³ of

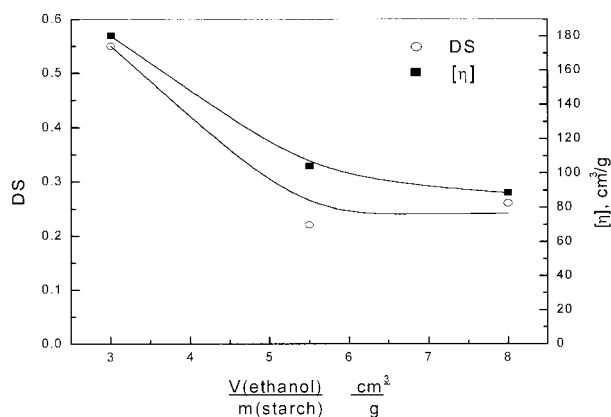


Figure 9. Dependence of $[\eta]$ and DS on the $V(\text{ethanol})/m(\text{starch})$ ratio for CMNS samples at 58°C. Other reaction conditions as shown in Table 4.

ethanol per 1.0 g of starch. There was an attempt to investigate even higher concentrations of starch, but the reaction mixture became one sticky mass after some time and stirring was impossible. It is interesting to note that the decrease of the DS with increasing amount of solvent is not linear, it becomes less steep at higher dilutions. This might mean that the dilution effect is partly compensated by a higher selectivity with respect to the desired reaction.

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IZVOD

MODIFIKOVANJE SVOJSTAVA SKROBA

(Naučni rad)

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Nativni skrob i WX – skrob, koji je obogaćen amilopektinom, mešani su sa plastifikatorima i termomehanički tretirani u dvopužnom mikseru u cilju dobijanja termoplastičnog skroba (TPS). Kao plastifikatori korišćeni su etilenglikol, propantriol (glicerin) ili poli(etilenglikol) čija je molarna masa bila manja od 1000 g/mol. Prevođenje u TPS je bilo uspešno samo kad su kao plastifikatori korišćeni glicerin ili etilenglikol, pri čemu je temperatura termomehaničkog tretmana zavisila od korišćenog plastifikatora i skroba. Dobijeni TPS je zatim umešan u dvopužnom mikseru sa poli(etilen–co–akrilnom kiselinom) (EAA), poli(etilen–co–vinil acetatom) (EVA) ili acetatom celuloze (CA) da bi se poboljšala njegova svojstva. Sadržaj ovih polimera u blendama je bio 5 i 10 mas. %. Ispitan je uticaj tako malih količina termoplastičnog polimera (TPP) na mehanička svojstva i otpornost na vodu termoplastičnog skroba. Uzorci za ispitivanje mehaničkih svojstava su pre merenja kondicionirani na 45, 67 i 85 % relativne vlažnosti RH. Dinamičko–mehanička ispitivanja TPS–a i njegovih blendi su izvršena pomoću mehaničkog spektrometra. Uzorci su bili podvrgnuti dinamičkom uvijanju pri konstantnoj frekvenciji u opsegu temperatura od 30 do 170°C. Na sniženje vrednosti temperature ostaklivanja mnogo je više uticala relativna vlažnost nego vrsta korišćenog TPP. Ispitivanja mehaničkih svojstava na istezanje su isto pokazala da RH ima mnogo veći uticaj od korišćenih TPP prisutnih u ispitivanim količinama. Bubrenje TPS–a i ispitivanih blendi je određeno gravimetrijski. Dobijeno je da su TPS/EAA blende najotpornije na vodu. Svojstva nativnog skroba su modifikovana karboksimetilovanjem pod heterogenim uslovima. Ispitan je uticaj sastava reakcione smeše, vremena i temperature reakcije.

Ključne reči: termoplastični skrob • smeša sa poli(etilen–co–akrilnom kiselinom) • poli(etilen–co–vinil acetat) • acetat celuloze • dinamičko–mehanička svojstva • svojstva na istezanje • bubrenje • karboksimetilovanje skroba •

Key words: thermoplastic starch • blends with poly(ethylene–co–acrylic acid) • poly(ethylene–co–vinyl acetate) or cellulose acetate (CA) • dynamic–mechanical properties • tensile properties • swelling • carboxymethylation of starch

