

Starch-graft copolymers of N-vinylformamide and acrylamide modified with montmorillonite manufactured by reactive extrusion

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ABSTRACT

Graft copolymers of potato starch with acrylamide, acrylamide and acrylic acid or N-vinylformamide in the presence of 1–16 wt % montmorillonite were manufactured via reactive extrusion. XRD and TEM measurements exhibited intercalated structure of clay dispersion (d001 distance up to 2.3 nm). The influence of graft polymer(s) system and montmorillonite content on thermal properties, water sorption as well as polyvalent metal cation (Cd²⁺ and Fe³⁺) sorption of obtained starch graft copolymers has been determined.

KEYWORDS Acrylamide, Montmorillonite, N-vinylformamide, Reactive extrusion, Starch-graft copolymer

INTRODUCTION

Nanocomposite materials based on biodegradable polymers and layered aluminosilicates have attracted significant interest in the last decade. Biodegradable polymers, especially based on renewable resources such as starch, have drawn considerable attention.

Starch graft hydrophilic acrylic copolymers as new cost-effective materials can be used for various environmental and industrial applications. In literature starch grafted copolymers with acrylamide (AAm) are widely described as finding numerous applications: in waste water treatment (floculants)^{1,2} or polyvalent metal cation sorbents^{3,4}, biodegradable superabsorbent for hygienic, agricultural and cosmetics purposes⁵⁻⁷, in paper industry⁸, textile industry⁹, petrochemical and mineral recovery.¹⁰

Besides AAm, N-vinylformamide (NVF) is being more often used for (co)polymerization reactions as it is considered to be more environmentally safe. Mostafa et al. described pregelled starch graft copolymerization with NVF (starch/monomer weight ratio 100:12.5-200) by conventional batch process using redox initiating system (bromate/cyclohexanone).¹¹ The materials obtained at 40°C (120 min, pH 6, 50 wt % NVF) exhibited 90 – 310% degree of swelling and 9.5 – 47.5% solubility in water.

We have recently performed graft copolymerization of NVF onto potato starch initiated with 2,2'-azobis(2-methylpropionamide) dihydrogen chloride (AAPH) or 2,2'-azobisisobutyronitrile via reactive extrusion.¹² The products (starch/monomer/water weight ratio 100:40:34, 60-80°C) exhibited solubility in water in a range of 18–43 wt %, real graft copolymer content 50–75% and molecular mass of the grafted branches 180 000–280 000 g/mol,¹⁶ i.e. 2–3 times lower than polyacrylamide grafted on starch.^{13,14}

Some papers on starch graft copolymerization of acrylic hydrophilic monomers in a presence of montmorillonite (MMT) by batch methods are also reported.^{15,16} The product exhibited superabsorbing properties.

Nakason et al. have recently described graft copolymerization of AAm on cassava starch (initiator: potassium persulfate, crosslinker: methylenebisacrylamide - MBA) realized in especially designed stainless steel reactor vessel equipped with internal geometry bars and adjusted agitator with high torque motor.¹⁵ Water content in the reaction systems was 53 wt % (per sum of starch and monomer) and equal weight ratio of AAm and starch. Montmorillonite, kaolin or nanosilica (10 wt %) have been introduced into reactor after copolymerization reaction and water absorbency evaluated after nanocomposite saponification. The best results of swellability reached 730 g/g in a case of MMT modified copolymer (606 g/g for neat starch-g-AAm copolymer).

Turkish research group synthesised in a glass reactor starch/AA graft copolymer (the components weight ratio was 1.5:1, using cerium (IV) salt initiator and MBA as a crosslinker) with 1–10 wt % MMT content.¹⁶ The saponified copolymer products exhibited water sorption up to 1000 g/g (material with 1wt % of MMT, whereas without MMT: 780 g/g). Such graft copolymers have been used for Cu²⁺ and Pb²⁺ removal from aqueous solutions and could be easily regenerated after use.¹⁷

As it was mentioned, processing of starch-based graft copolymers is typically done in batch processes, which consume large amounts of water. Starch-g-PAAm has been successfully manufactured using a co-rotating twin screw extruder but its maximum water absorption capacity is relatively low as compared to starch copolymers obtained by batch techniques.^{13,14}

The aim of this paper was to perform starch-graft copolymerization with NVF, AAm and AAm/AA monomer pair with various MMT content via reactive extrusion and characterization of the obtained (unsaponified) composite products.

EXPERIMENTAL

Materials

Monomers: NVF (technical grade, BASF), AAm (99%, Sigma-Aldrich), AA (98%, Fluka Chemika) were used without any pre-treatment. Initiators: AAPH (97%, Sigma-Aldrich) and APS (pure for analysis, POCh, Gliwice, Poland) were used as delivered. MBA (99%, Sigma-Aldrich) was applied as a crosslinker.

Sodium montmorillonite (technical grade, ZGM Zebiec S.A., Poland) was purified via centrifugation (MLW K23D, 3000 rpm, 10 min). Montmorillonite aqueous slurry (9 wt %) as well as potato starch (Nowamyl S.A., Nowogard, Poland) were applied after controlling the moisture content.

Starch gelatinization

Dry starch (drying: 6 h at 60°C) was premixed with distilled water (starch/water weight ratio 100:40) in a laboratory mixer (Henschel FML10, 2 dm³ capacity) for 15 min and then left for 24h in closed PE bag. Subsequently, wet starch was plasticized using single-screw extruder (W-20, Metalchem, Poland) at increasing temperature profile: 60/75/80/80/80/80/80°C. Treating the starch extrudate with liquid nitrogen was followed by grinding it in a hammer mill (Trymet, Poland). The final starch/water weight ratio in the obtained starch material was 100:33.5 (partial water evaporation during plasticization step occurred) – as determined using thermobalance (WPS 110S, Radwag, Poland).

Graft copolymerization

Starch graft copolymerization was performed using freshly prepared batch of thermoplastic starch. The starch/water weight ratio was kept constant 100:40. AAPH and APS have been used at concentration of 0.1 wt % (per dry starch); concentration of MBA was 0.25 wt % (per dry starch).

Starch graft copolymers with NVF, AAm or AAm/AA systems as well as materials prepared in the presence of MMT (NVF/MMT, AAm/MMT, AAm/AA/MMT) were manufactured using reactive extrusion performed in corotating twin-screw extruder (Mapre, Belgium) with D=30 mm and L/D=32. MMT was fed into extruder in a form of aqueous dispersion containing monomer(s).

The amount of water introduced into extrusion system with components (i.e. starch, monomer(s), initiator, crosslinking agent and MMT) was adjusted in a range of 40-100 wt parts/100 parts of dry starch. The weight ratios of monomers and MMT as well as extrusion parameters are given in Table 1. The extruded starch material was kept for 24h at ambient conditions, then pre-grounded, dried at 60°C for 24h and subsequently grounded in a knife mill.

Water sorption tests

The copolymer powder (0.5 g, sieved fraction: 0.25-0.5 mm) was added to 50 cm³ of distilled water and left under cover for 24 h at 20°C. Subsequently, sample was filtered under reduced pressure and weighted. The water sorption was calculated from the equation: $W = [(m_a - m_0)/m_0]$, where: W – water sorption (g/g), m_a – mass of filtered sample (g), m_0 – mass of dry sample (g).

Polyvalent metal cations sorption

The solutions containing Cd²⁺ or Fe³⁺ were prepared using technical grade metal sulphate salts. The concentration was 141mg Cd²⁺/dm³ and 50 mg Fe³⁺/dm³. The copolymer sample (0.5 g) was placed into Erlenmeyer flask and 100 cm³ of heavy metal containing solution was added. The mixture was stirred using laboratory shaker for 1h, and subsequently filtered under reduced pressure. The filtrate was tested to determine the concentration of remaining heavy metal ions. The Fe³⁺ content was determined using UV-Vis spectrophotometer (Spekol 11, Carl Zeiss) in an extinction mode, at the wavelength of 480 nm. The Cd²⁺ content was tested using atomic emission spectroscopy with inductively coupled plasma ICP-OES (Optima 5300 DV, Perkin-Elmer). The results are presented in mg of sorbed cations per 1g of sorbent.

Instrumental methods

X-ray diffraction tests were performed using X-ray diffractometer X'Pert PRO (Cu K α , 1.5-10 2 Θ) with High Score Phillips software.

Thermal properties were determined using differential scanning calorimeter (Q-100, TA Instruments) - hermetic aluminum pans were used, samples of ca. 10 mg were scanned in a temperature range of -90 to 300°C with a heating rate 10°C/min.

Surface observations were performed using laser scanning microscope (LSM, VK9700, Keyence) with a magnification of 4000 times. The nanocomposites specimens were performed with high resolution Transmission Electron Microscope HRTEM, Tecnai F30 from FEI. The specimens were sliced in with Leica Ultramicrotome EM UC7, the thickness was 50nm.

RESULTS AND DISCUSSION

Starch-grafted copolymerization in reactive extrusion process

Manufacturing of starch-graft copolymers modified with MMT using *in situ* continuous method such as reactive extrusion has not been reported in research literature. The reasons could be: (i) low effectiveness of MMT dispergation during extrusion processing (because of short residence time and/or necessity of MMT pre-treatment into aqueous dispersion), (ii) difficulties with controlled feeding of viscous MMT dispersion into extruder, (iii) limited range of MMT content dosage in relation to starch because of rather low amount of the solid matter in aqueous MMT dispersion (usually 5 – 8 wt %) and too high amount of water introduced into the extrusion system, (iv) products exhibit relatively low water sorbency, (v) lower molecular weight products (solution viscosities) after (co)polymerization of AAm in a presence of MMT.¹⁸

Very recently we have described graft copolymerization of NVF on potato starch, initiated with 2,2'-azobis(2-methylpropionamidine) dihydrogen chloride or 2,2'-azobis(isobutyronitrile) performed by reactive extrusion with NVF/starch/water 40:100:34 weight ratio. FTIR spectrum evidenced formation of starch-graft copolymers (50-75 wt %) beside of NVF homopolymer.¹² Now starch-graft copolymers of AAm, AAm/AA or NVF as well as copolymers synthesized in the presence of MMT have been manufactured (Table 1) in reactive extrusion process.

Dispersion of clay in the composite copolymers

To assess the degree of nanofiller dispersion X-ray measurements were performed. XRD patterns of AAm/AA(2:1) starch copolymers manufactured in the presence of 1, 2 or 4 wt % MMT are presented in Figure 1. Figure 2 presents XRD patterns of S-g-NVF copolymers with 1–16 wt % clay. For graft copolymers with low amount of MMT (up to 2 wt %) shifting 2Θ value from ca. 7.8° (Fig. 2) to lower values as well as broadening of the diffraction peaks are observed. These features are characteristic for intercalated or mixed: intercalated/exfoliated degree of clay dispersion. However, part of the nanofiller remains in a form of microparticles as less intense peak at 7.8° is still observed (Fig. 1 and 2).

Basing on the starch-graft copolymers diffractograms interlayer distance value in aluminosilicate has been calculated from Bragg's equation (Table 2). Generally, d spacing of MMT layers is higher for starch-grafted NVF (up to 2.31 nm for 1 wt % MMT) in comparison to starch/AAm/AA copolymers (up to ca. 1.95-1.99 nm for 1 wt % MMT). It may be the result of side transfer reactions during NVF polymerization resulting in formation of quaternary carbon atoms (by hydrogen abstraction from the formic group).¹⁹ As a consequence stronger interactions between starch-g-NVF copolymer and electronegatively charged MMT platelet surface occur giving higher interlayer distance in comparison with anionogenic starch/AAm/AA copolymers.

The surface of S-g-NVF/MMT composite particles has been observed by LSM technique. As shown in the micrograph of S-g-NVF/MMT2% composite copolymer (Figure 3) the potato starch granules were destroyed and the sample surface is rough and homogeneous. TEM technique allows to observe nanofiller dispersing and distribution. Figure 4 shows TEM micrograph of S-g-NVF/MMT2% magnified 100 thousand times. S-g-NVF copolymer formed a continuous phase, MMT existed as stacks formed by several platelets. The length of single intercalated multilayered particle was up to ~ 80 nm. TEM results correspond with XRD measurements and confirm relatively good MMT dispersion, i.e. intercalated structure of nanoparticles in composites with lower clay content.

Influence of monomer type and MMT content on DSC thermograms

Glass transition temperature (T_g) of native starch as well as graft copolymers can be determined from the first endothermic transition of DSC thermograms.^{21,22} Native potato starch showed only one endotherm: at 147°C (Table 3).

Figure 5 presents DSC thermograms of S-g-AAm/MMT (Fig. 5A) and S-g-AAm/AA(1:2)/MMT copolymers (Fig. 5B). The DSC results (Table 3) allow for following conclusions: (i) T_g values for S-g-AAm and the series of AAm-based composite copolymers containing 1–4 wt % of MMT exhibited similar values (137.2–139.2°C) independently of nanofiller content; these T_g values were about 8–10°C lower than T_g of native starch. It means that graft copolymerization of AAm on potato starch causes its slight plasticization, (ii) graft copolymerization of AAm/AA(2:1) mixture on starch in the presence of MMT influenced substantially the maximum position of the first broad endotherm: it was shifted upwards even up to 152.3°C for S-g-AAm/AA(2:1)/MMT4%, i.e. above T_g value of native potato starch (Table 3), (iii) starch grafted with AAm/AA(1:2) monomer pair exhibited lower T_g value (123.4°C) than for native starch, however, introduction of MMT to the starch graft-copolymerizing system shifted minimum of the first endothermic peak of the copolymers to higher temperature values: 138.0°C, 144.9°C and 158.6°C for 1, 2, and 4 wt % of MMT, respectively (Fig. 5B). On the other side graft copolymerization of NVF onto potato starch caused substantially deeper T_g value decrease for the neat starch/NVF products than in a case of starch/AAm copolymer; similarly substantially lower T_g values exhibited S-g-NVF/MMT composite copolymers (Figure 6, Table 3). Glass transition data for S-g-NVF/MMT copolymers containing up to 2 wt % MMT changed in a range 111–117°C and were ca. 24–26°C lower than those of respective S-g-AAm/MMT copolymers. It means that PNVF branches plasticize starch evidently better than PAAm chains (decreasing T_g value more than 30°C as related to T_g of native starch). It seems also that starch copolymers with the lowest content (1 wt %) and thus the highest degree of MMT dispersion exhibited lower T_g values than the respective neat S-g-AAm as well as S-g-NVF copolymers. However, additional DSC investigation is necessary to confirm this explicitly.

Considering environmental acceptability of NVF monomer and better starch plasticizing ability of PNVF branches than PAAm, the former should be preferred as comonomer for grafting on starch.

Water sorption

The results of water sorption of starch graft copolymers are presented in Figure 7. Starch grafted with AAm exhibited slight decrease of water sorption (5.8–4.6 g/g) with increasing MMT amount (0–4 wt %) - Figure 7A. Similar tendency was observed for S-AAm/AA/MMT materials with lower AA amount. The highest values of water sorption were observed for S-AAm/AA with higher AA content (AAm/AA 1:2): 10.9 g/g. Starch copolymers grafted with NVF were substantially more sensitive to water at lower MMT

content - Figure 7B. A maximum of water sorbency with ca. 1-2 wt % of MMT was observed. The value of this parameter is ca. 4 times higher when compared to unfilled S-g-NVF copolymer, 16.2 g/g and 3.5 g/g, respectively. Lower water absorption (ca. 2.1 g/g) of (unsaponified) S-g-NVF copolymer (starch:NVF weight ratio 100:50) was found by Mostafa et al.¹¹

Introducing an additional nanoclay amount (8 and 16 wt %) caused a drastic decrease of water sorption (to ca. 3.0 g/g) – Fig. 7B. That could be explained by the different degree of MMT dispersion in the polymer matrices - intercalated/exfoliated for low filled materials and microcomposite structure for high filled copolymers.

Cation metal sorption

Large specific surface area, chemical and mechanical stability, layered structure as well as high cation exchange capacity have made MMT an excellent adsorbent material.²²⁻²⁴ In aqueous solutions interlayer swelling of montmorillonite structure occurs. Al and Si atoms exposed to the crystalline edges are partially hydrolyzed to silanol (SiOH) and aluminol (AlOH) groups. These unsaturated edge sites are much more reactive than the saturated basal sites. However, in MMT adsorption can occur both at the edge sites of the clay (inner-sphere metal complexes) and the internal sites of the clay (outer-sphere metal complexes).²² The effort to develop composite material based on polymers modified with MMT is observed.^{16,24} There are many research publications presenting studies on heavy metal cations adsorption on montmorillonites.

Recently numerous approaches have been studied for development of cheap and effective adsorbents containing natural polymers, among them starch based materials.^{17,25} It is well known that starch and its derivatives have capacity to associate by physical and chemical interactions with a wide variety of molecules. Hence, adsorption on starch/montmorillonite materials can be a low-cost process in water decontamination.

Starch graft copolymers modified with MMT have been preliminarily tested as polyvalent metal cation sorbents. The results of Cd²⁺ and Fe³⁺ sorption tests (at 20°C) are presented in Figure 8. The sorption of Cd²⁺ and Fe³⁺ on S-g-AAm/MMT copolymers was found 9–10 mg/g and 6-7.5mg/g, respectively (Figure 8A). Introduction of AA units into starch-AAm copolymer system led to decrease of sorption efficiency.

Similar tendency, i.e. drop of Fe^{3+} sorption with increasing content of AA units in starch graft copolymers with AAm (unfilled material) has been observed in our previous research.²⁶

The difference between Cd^{2+} and Fe^{3+} sorption efficiency of S-g-NVF/MMT composite copolymers were more significant. The sorption of Cd^{2+} and Fe^{3+} on S-g-NVF/MMT copolymers was found 14–16 mg/g and 4–6 mg/g, respectively (Figure 8B). Generally, for both types of starch graft copolymers based on AAm and NVF adsorption of cadmium cation is higher than Fe^{3+} . This can be explained by the differences between the metal ions characteristics, i.e.: relative atomic size; ability of metal ion to interact with the polymer, metal ion charge density and reactivity of the metal ion.¹¹ The preliminary adsorption tests correlate with the results on adsorption of Cd^{2+} and Fe^{3+} on montmorillonites/bentonites (cadmium cation sorption in a wide range: 7.3-32.7 mg/g and Fe^{3+} 12-28.9 mg/g), depending on the aluminosilicate clay type and experimental conditions) presented by other authors.^{22,24} Mostafa et al. have tested crosslinked S-g-NVF copolymers for removing Cu^{2+} , Cd^{2+} , Pb^{2+} and Hg^{2+} ions (100 ppm/g, pH 8, 20 min, 26°C).¹¹ The highest sorption ability has been measured for Hg^{2+} ; sorption efficiency dropped in the following order: $\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+}$.

Additionally, the adsorption efficiency of Cd^{2+} and Fe^{3+} on the investigated composite copolymers is practically uninfluenced by the clay content. These findings correlate to some extent with the results of Güçlü et al. obtained for S-g-AA/MMT hydrogels.¹⁷ An introduction of MMT into hydrogel copolymers based on grafted starch allowed for regeneration and reemployment of sorbents used for cation removal.¹⁷ Works on repeated sorption/desorption tests are under investigation.

CONCLUSIONS

Graft copolymers of potato starch with acrylamide, acrylic acid or N-vinylformamide in the presence of crosslinker and montmorillonite have been manufactured via reactive extrusion. The composite copolymers with low montmorillonite loading exhibited intercalated structure of clay dispersion in the copolymer matrix as has been evidenced by XRD and TEM measurements. Higher interlayer distance has been found for starch grafted with NVF (increase of d_{001} distance from 1.1 nm up to 2.3 nm for copolymer containing 1 wt % montmorillonite). DSC measurements show that grafted poly(N-vinylformamide) branches better plastify starch matrix than polyacrylamide. The decrease of

glass transition values for starch-g-N-vinylformamide copolymers (neat and modified with 1 and 2 wt % MMT) were at least 30°C when compared to T_g value of native potato starch.

Water sorption of the composite unsaponified copolymers was the highest in a case of materials based on N-vinylformamide modified with 1–2 wt % MMT (up to 16.0 g/g for S-g-NVF/MMT2%). For series of starch copolymers based on AAm/AA monomers that parameter decreased with MMT increase; maximum ca. 10.8 g/g was found for neat S-g-AAm/AA 1:2 copolymer. Polyvalent metal cation sorption on the composite copolymers was higher for Cd^{2+} than for Fe^{+3} . Especially distinct differences were found for starch based copolymers of NVF (~15mg/g for Cd^{2+} and 4–6 mg/g for Fe^{3+}). Practically no influence of MMT content in the copolymers on the cation sorption was observed.

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AUTHORSHIP

Szymon Kugler – copolymerization and physicochemical characterization of starch products, paper editing;

Tadeusz Spychaj – main concept, paper revising;

Katarzyna Wilpiszewska – microscopic characterization of starch products, paper editing;

Krzysztof Gorący – DSC characterization of starch products, paper editing;

Zofia Lendzion-Bieluń – metal cation sorption characterization, paper editing.

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Figures

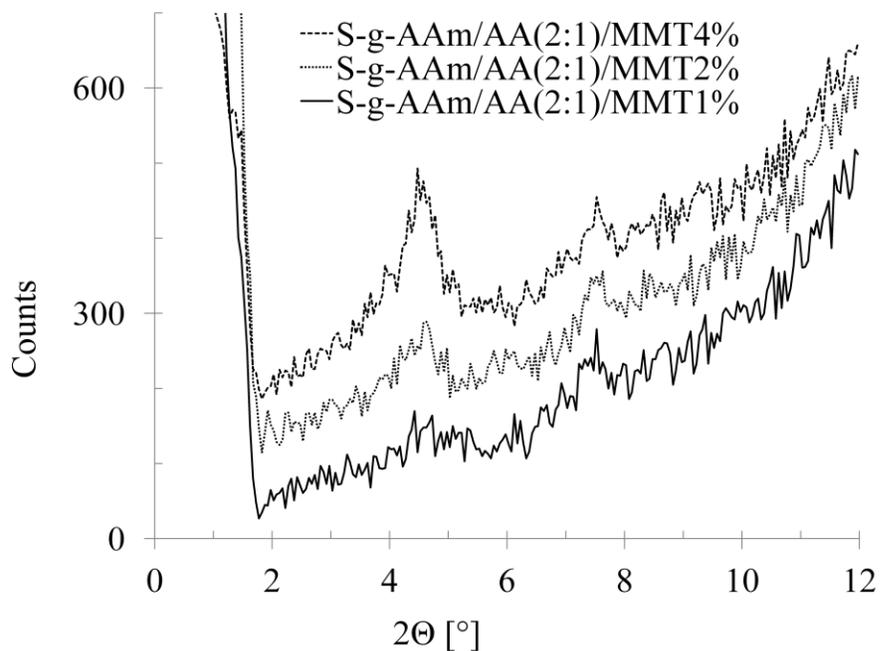


FIGURE 1 XRD patterns of S-g-AAm/AA(2:1) copolymers containing 1, 2 or 4 wt % MMT

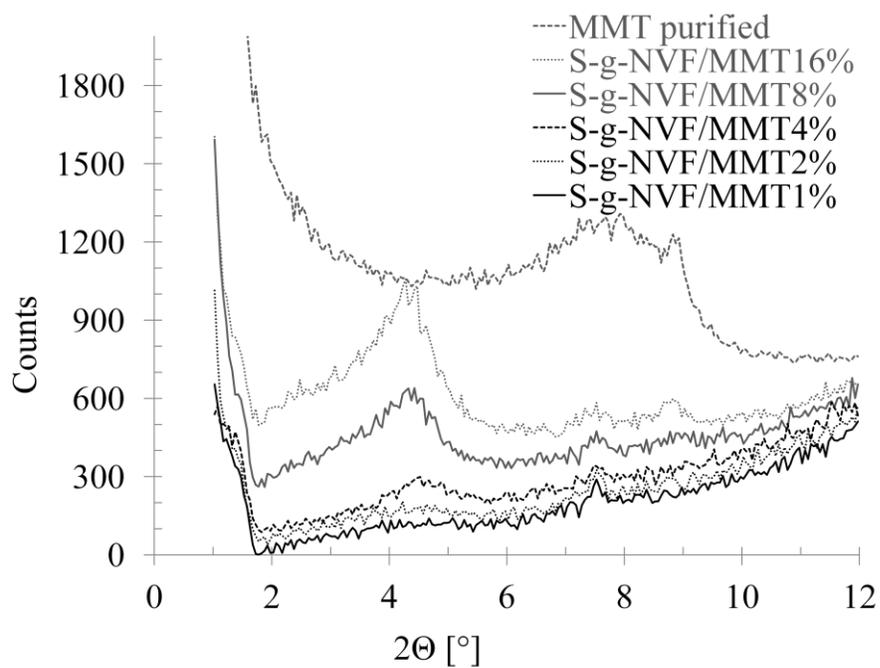


FIGURE 2 XRD patterns of MMT and S-g-NVF copolymers containing 1–16 wt % MMT

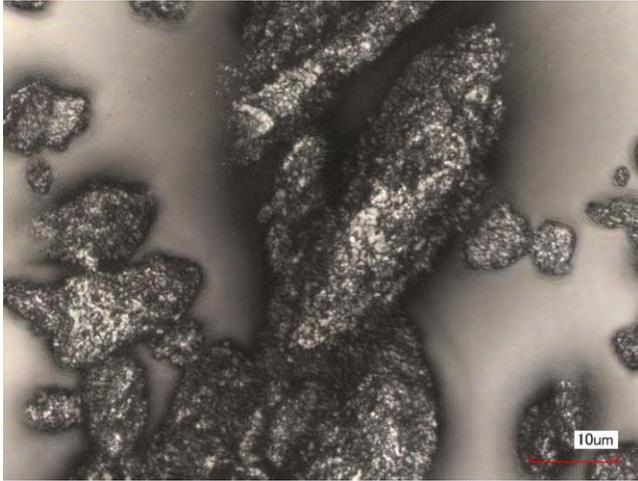


FIGURE 3 LSM micrograph of S-g-NVF/MMT2% composite copolymer

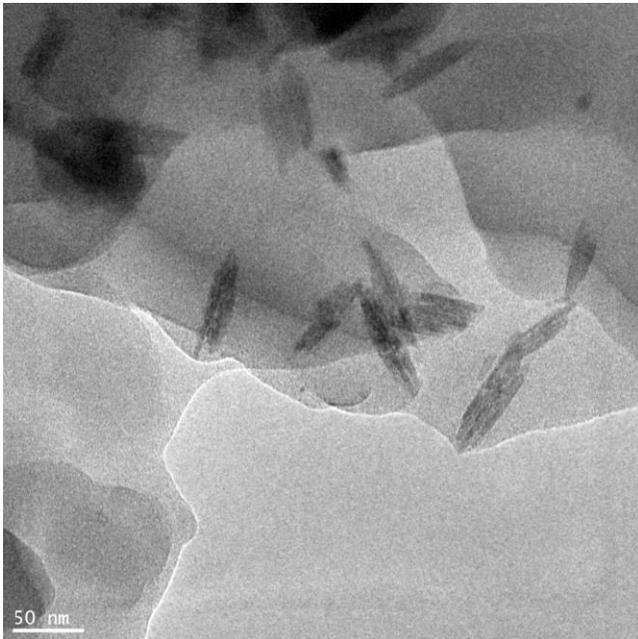


FIGURE 4 TEM microphotograph of S-g-NVF/MMT2% composite copolymer

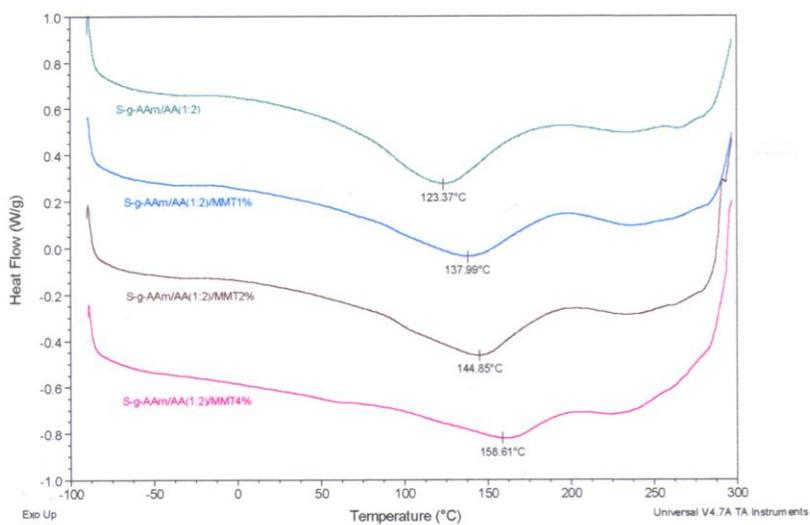
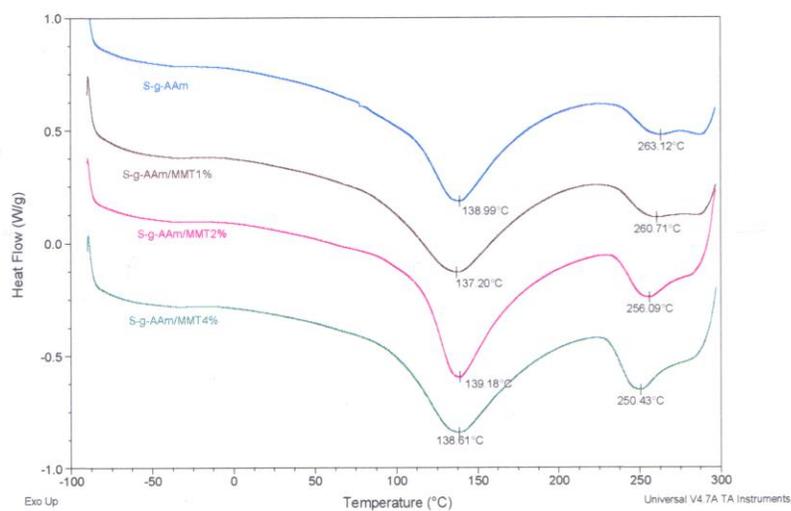


FIGURE 5 DSC thermograms of copolymers: A) S-g-AAm/MT, B) S-g-AAm/AA (1:2)

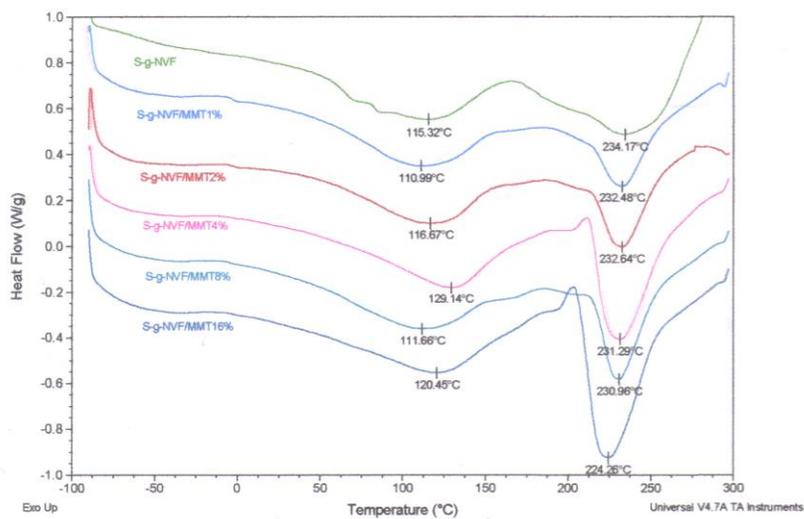


FIGURE 6 DSC thermograms of S-g-NVF/MMT composite copolymers

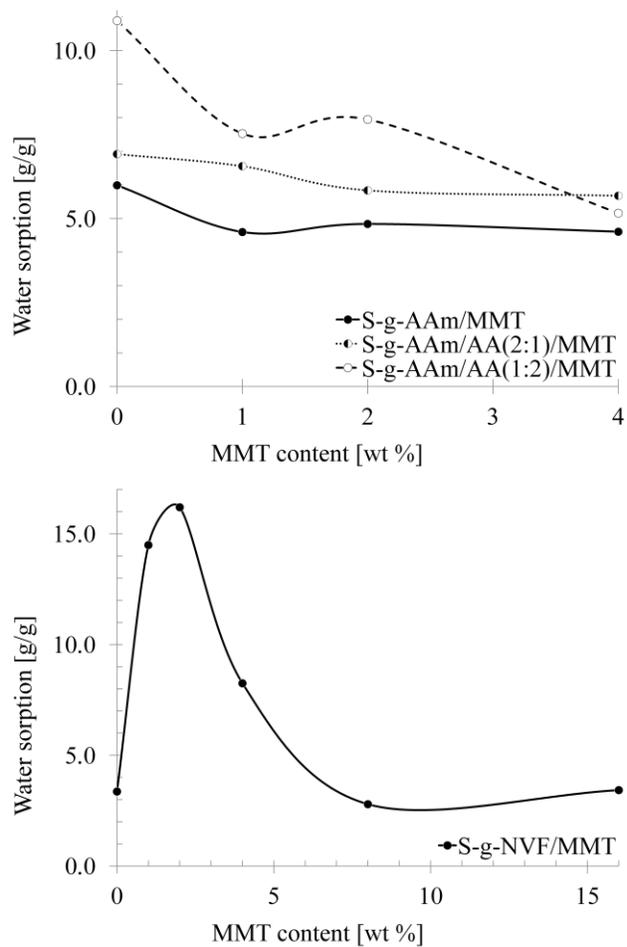


FIGURE 7 Water sorption of starch graft copolymers modified with MMT: A) S-g-AAm and S-g-AAm/AA, B) S-g-NVF

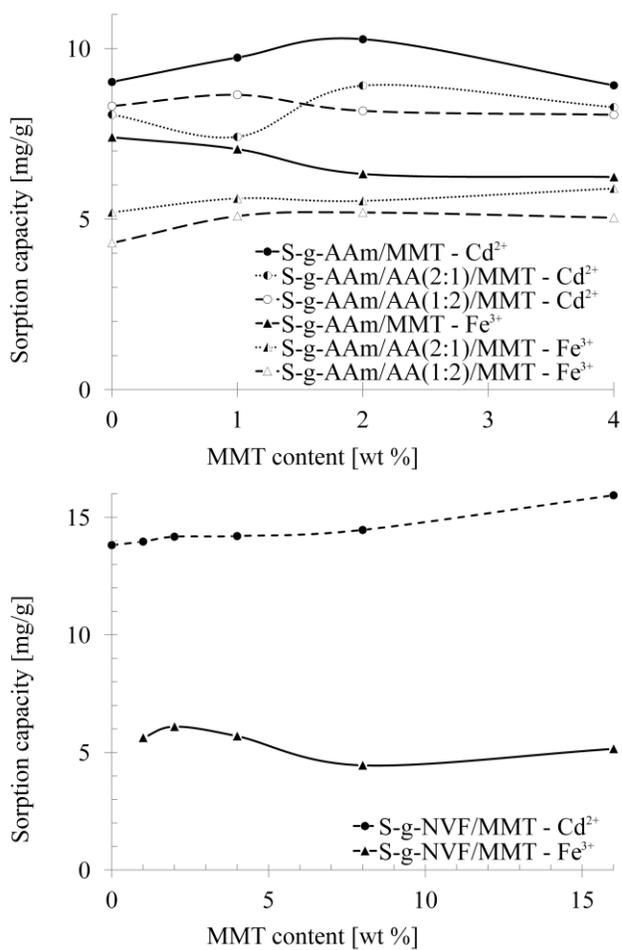


FIGURE 8 Cd²⁺ and Fe³⁺ ion sorption tests on starch graft copolymers modified with MMT: A) S-g-AAm and S-g-AAm/AA, B) S-g-NVF

Tables

TABLE 1 Starch graft copolymers: substrates applied in reactive extrusion

Sample acronym	Substrates [wt parts]						Extrusion parameters	
	Starch	AAm	AA	NVF	MMT	Water	Temperature profile [°C]	Screw speed [rpm]
S-g-AAm/MMT1%	100	50	0	0	1	84	60-90	100
S-g-AAm/MMT2%	100	50	0	0	2	84	60-90	100
S-g-AAm/MMT4%	100	50	0	0	4	84	60-90	100
S-g-AAm/AA(2:1)/MMT1%	100	33.3	16.7	0	1	84	60-100	125
S-g-AAm/AA(2:1)/MMT2%	100	33.3	16.7	0	2	84	60-100	125
S-g-AAm/AA(2:1)/MMT4%	100	33.3	16.7	0	4	84	60-100	125
S-g-AAm/AA(1:2)/MMT1%	100	16.7	33.3	0	1	84	60-110	100
S-g-AAm/AA(1:2)/MMT2%	100	16.7	33.3	0	2	84	60-110	100
S-g-AAm/AA(1:2)/MMT4%	100	16.7	33.3	0	4	84	60-110	100
S-g-NVF/MMT1%	100	0	0	50	1	44	60-90	100
S-g-NVF/MMT2%	100	0	0	50	2	54	60-90	100
S-g-NVF/MMT4%	100	0	0	50	4	55	60-90	130
S-g-NVF/MMT8%	100	0	0	50	8	44	60-90	130
S-g-NVF/MMT16%	100	0	0	50	16	40	60-100	160

TABLE 2 d spacing values of MMT in the starch composites

Sample acronym	d spacing [nm]
S-g-AAm/AA(2:1)/MMT1%	1.95
S-g-AAm/AA(2:1)/MMT2%	1.98
S-g-AAm/AA(2:1)/MMT4%	1.95
S-g-AAm/AA(1:2)/MMT1%	1.99
S-g-AAm/AA(1:2)/MMT2%	1.90
S-g-AAm/AA(1:2)/MMT4%	1.91
S-g-NVF/MMT1%	2.31
S-g-NVF/MMT2%	2.19
S-g-NVF/MMT4%	1.99
S-g-NVF/MMT8%	2.03
S-g-NVF/MMT16%	2.04
MMT	1.14

TABLE 3 DSC results for starch graft copolymers and starch composites containing MMT

Sample acronym	First endotherm [°C]
S-g-AAm	139.0
S-g-AAm/MMT1%	137.2
S-g-AAm/MMT2%	139.2
S-g-AAm/MMT4%	138.6
S-g-AAm/AA(2:1)	n.d. ^a
S-g-AAm/AA(2:1)/MMT1%	141.7
S-g-AAm/AA(2:1)/MMT2%	137.8
S-g-AAm/AA(2:1)/MMT4%	152.3
S-g-AAm/AA(1:2)	123.4
S-g-AAm/AA(1:2)/MMT1%	138.0
S-g-AAm/AA(1:2)/MMT2%	144.9
S-g-AAm/AA(1:2)/MMT4%	158.6
S-g-NVF	115.3
S-g-NVF/MMT1%	111.0
S-g-NVF/MMT2%	116.7
S-g-NVF/MMT4%	129.1
S-g-NVF/MMT8%	111.7
S-g-NVF/MMT16%	120.5
TPS	147.4

^aNot developed.