Nanocomposite starch graft copolymers with carbon nanotubes – synthesis and flocculation efficiency*)

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Abstract: Nanocomposite flocculants based on polyacrylamide-grafted starch copolymers with carbon nanotubes (PAM-St-CNT) were prepared using natural polymer – potato starch (St), acrylamide (AM) as monomer and CNTs by *in situ* polymerization process. The effect of monomer to starch molar ratio, dose of flocculants and content of CNTs in composition on flocculation efficiency were investigated. All materials were characterized by FT-IR (Fourier transform infrared spectroscopy), TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry) methods. An aqueous suspension of kaolin was used for the flocculation studies. The flocculation effectiveness was evaluated on the basis of reduction of suspension absorption and the sludge volume. It was found that synthesized nanocomposites PAM-St-CNT exhibit satisfactory flocculating properties.

Keywords: flocculants, starch graft copolymers, polyacrylamide, carbon nanotubes, starch nanocomposites.

Nanokompozytowe kopolimery szczepione skrobi z nanorurkami węglowymi – synteza i efektywność flokulacyjna

Streszczenie: Z zastosowaniem naturalnego polimeru – skrobi ziemniaczanej (St) – akryloamidu (AM) jako monomeru i nanorurek węglowych (CNTs) w procesie polimeryzacji *in situ* wytworzono nanokompozytowe poliakryloamidowe kopolimery szczepione skrobi z nanorurkami węglowymi (PAM-St-CNT) do wykorzystania w charakterze flokulantów. Badano zależność wydajności flokulacji od stosunku molowego monomeru do skrobi oraz dodatku flokulantów i zawartości CNTs w materiale. Otrzymane układy scharakteryzowano metodami spektroskopii w podczerwieni z transformacją Fouriera (FT-IR), analizy termograwimetrycznej (TGA) i różnicowej kalorymetrii skaningowej (DSC). Do testów flokulacyjnych zastosowano wodną zawiesinę kaolinu. Skuteczność flokulacji oceniono na podstawie zmian absorpcji zawiesiny modelowej i objętości osadu poflokulacyjnego. Stwierdzono, że zsyntetyzowane nanokompozyty PAM-St-CNT wykazują zadowalające właściwości flokulacyjne.

Słowa kluczowe: flokulanty, kopolimery szczepione skrobi, poliakryloamid, nanorurki węglowe, nanokompozyty skrobiowe.

Copolymerization allows the creation of materials that combine the desired properties of several compounds in one polymer chain. A very effective method of combining the properties of compounds is graft copolymerization. The amount, type and chain length of the grafted polymer depend on the manner of reaction and the nature of the reagents used. Grafted copolymerization for polysaccharides is of particular importance. This method allows to adjust the final properties of the product in accordance to current needs.

Copolymers of starch with acrylamide are obtained by grafting polyacrylamide onto starch. Easily available polysaccharide (starch) is a kind of scaffold to which polyacrylamide chains are added [1]. This is radical polymerization in an aqueous environment and can be carried out in various ways. From the literature we know about several methods of acrylate and starch synthesis: using high energy radiation [2], microwave radiation [3, 4], a combination of chemical initiator and microwave radiation [1], by reactive extrusion [5], or the most commonly used chemical initiation [6–11]. Polyacrylamide graft starch copolymers due to their structure have some properties of both polymers. They are soluble in water thanks to the hydrophilic groups on the chain (-OH and -CONH$_2$). As the molecular weight increases, they become insoluble but their water absorption increases [8, 12]. The polysaccharide chain is relatively not resistant

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to high temperatures. However, grafting increases the number of carbon-carbon bonds that are more resistant to high temperature and oxidation than ether bonds. As a result, the higher number of grafted chains, the better heat resistance [6, 10].

It has been reported that starch acrylamide copolymers can be used as a flocculating substance [12–19]. It should be emphasized that polyacrylamide is a safe substance, unlike monomer – acrylamide. In addition, Wen and colleagues report isolating bacteria capable to biodegradate polyacrylamide without releasing the toxic monomer [20].

Carbon particles of various sizes, structures and surfaces are called carbon fillers. The most common carbon nanotubes (CNTs) are allotropic varieties of carbon structures in the form of pipes with a nanometer diameter and a length of up to 100 microns. Due to the length/diameter ratio, they can be considered as one-dimensional particles. Nanotubes have a large specific surface area and low density [21–23]. The results presented by Simate and others exhibit that CNTs have the ability to coagulate and subsequently flocculate particles dispersed in brewery wastewater. Anyhow, CNTs do not indicate such good coagulation and flocculation capacity as iron(III) chloride [24].

However, the systems formed from the combination of starch or/and polyacrylamide with CNTs [25–29] are usually obtained in an aqueous medium, assisting mixing, *e.g.* with sonication. CNTs have inherent insolubility in aqueous solvents. Therefore, recent studies have demonstrated great interest in preparing polymerization with the participation of CNTs in water environmental [30–34]. The order of adding ingredients to polymerization is important due to creation a dispersion of a filler in a polymer matrix [25].

In the study reported here, the nanocomposite starch grafted copolymers with carbon nanotubes were synthesized via radical polymerization of starch and acrylamide on carbon nanotubes in aqueous environment.

The products were characterized by FT-IR (Fourier transform infrared spectroscopy), TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry). The grafted chains of starch enhance functionality of the synthesized graft copolymer and the water solubility depends on content of CNTs in the composite. The products have been studied for their flocculation efficiency in model aqueous suspension of kaolin in the standard jar test.

EXPERIMENTAL PART

Materials

To receive polyacrylamide starch graft nanocomposite with carbon nanotubes, acrylamide (AM) (~99%, Merck, Germany) were used.

Potato starch (super standard quality) was obtained from Potato Industrial Enterprise "Nowamyl" S.A., Poland.

The CNTs from Belgium Nanocyl SA were applied.

Ammonium persulfate (ASP) – polymerization initiator (~99%) and acetone (analytical reagent grade) were purchased from Chempur, Poland.

Kaolin (Alfa, II Quality, Slovakia) has been used as inorganic pollutant in jar tests. All materials were used without further purification.

Synthesis of starch grafted polyacrylamide with carbon nanotubes composites

To receive starch grafted polyacrylamide with carbon nanotubes composites (PAM-St-CNT), CNT (1.0 wt % and 3.0 wt % based on the weight of acrylamide in starch graft copolymers) the monomer AM (molar concentration: 0.3 mol/dm^3, 0.5 mol/dm^3 and 0.7 mol/dm^3) and constant concentration of starch (0.1 mol/dm^3) were used. Polymerization initiator ASP was used in 1.0 wt % on the weight of AM. The grafting reaction was carried out in a four-neck reactor equipped with a stirrer, a thermometer electrode, a condenser and a nitrogen connection in water bath. The polymerization reaction always started with the starch gelatinization. The adequate mass of dried starch and 60 cm^3 of distilled water were added to the flask. The mixture was stirred (rotation speed of stirrer – 200 rpm) and heated at 82 °C for 30 min. After gelatinization of starch, the mixture was cooled to 30 °C and then sonicated suspension of CNTs in water was inserted to the reactor during stirring under nitrogen atmosphere for 30 min. CNTs were sonicated using an ultrasonic bath (for 10 to 30 minutes depending on the amount of CNTs in water). Typically, the proper solution of AM was dropped to uniform, gelatinized starch dispersion with CNTs. Immediately after, the initiator solution was gradually introduced into the reaction mixture. Finally, the whole reactor contents were heated slowly up to 42–46 °C and the polymerization was carried out for 3 h.

The obtained dispersions of PAM-St-CNT nanocomposites were precipitated in acetone and filtrated to ensure washing out any unreacted monomer. The acquired products were dried in the vacuum oven at 50 °C for 12–16 h to attain constant mass and characterized by TG, DSC and FT-IR methods. The water solution of the obtained postreaction mixture (100 ppm in 1 cm^3) was used in flocculation tests.

Flocculation tests

To prepare a model kaolin suspension 5 g of fine particle material was mixed with 1 dm^3 of distilled water in a glass beaker at 500 rpm for 2 min. Required amount of the tested PAM-St-CNTs nanocomposites (the doses of flocculants were 1, 3, 5 and 10 cm^3) was added into the beaker while stirring with reduced rotational speed of the stirrer to 50 rpm and continued for 10 minutes. The entire suspension was then immediately transferred to a calibrated Imhoff funnel and allowed to settle down.

Methods of testing

Characterization of starch graft nanocomposites

– The FT-IR spectra of dried powdered samples of PAM-St-CNT nanocomposite and starch (for comparison) were obtained using Nexus FTIR spectrometer (Thermo Nicolet Corp., USA) with Golden Gate (ATR) attachment and OMNIC computer program.

– TGA of synthesized PAM-St-CNTs were performed using thermal analyzer, TGA Q5000 TA Instruments, with the heating rate of 10 °C/min to 900 °C.

– Q100 DSC (TA Instruments Inc., USA) was used for the composite materials characterization (10 °C/min, from 0 to 250 °C). Samples were weighed (~5 mg) on the aluminum pans and hermetically sealed before analyses.

– The spectrophotometer, SP-830 Plus Metertech was used to monitor the flocculation process. The absorbance of the aqueous phase was measured every 10 minutes for 2 hours at the wavelength 470 nm. Additionally, the volume of the settled deposit was noted. Flocculation abilities of nanocomposites were compared to untreated kaolin suspension.

RESULTS AND DISCUSSION

A series of PAM-St-CNT nanocomposites with different AM content (0.3–0.7 mol/dm^3) and 1 or 3 wt % CNT in the system were successfully synthesized. The concentration of potato starch was always 0.1 mol/dm^3.

Figure 1 shows the FT-IR spectra of native potato starch (St), polyacrylamide-graft-starch copolymer (PAM-St) and nanocomposite polyacrylamide-graft-starch with CNTs (PAM-St-CNT). A characteristic FT-IR spectrum was obtained for starch with a wide band in the wavelength range 3650–3000 cm^{-1} (the presence of OH groups – stretching vibrations) and with a much narrower band at 2900 cm^{-1} (stretching vibrations of the C-H and symmetrical CH$_2$ groups). In addition, we can see sharp three peaks close together 1160, 1080 and 1015 cm^{-1} a typical for starch FT-IR spectra (C-O-C stretching vibrations) [7, 35]. The PAM-St copolymer spectra contain, beside characteristic starch peaks, additional bands representative for the CONH$_2$ groups resulting from acrylamide (3400, 1650 and 1600 cm^{-1} coming up from N-H, C = O and N-H stretching vibrations, respectively) [36]. CNT spectra are not included in Fig. 1 due to their almost straight nature. Existence of the characteristic absorption peaks of PAM-St-CNT, such as N-H at 3400 cm^{-1}, C-H at 2900 cm^{-1}, C=O at 1650 cm^{-1}, -CH-CO- at 1450 cm^{-1}, OH and C-O stretching vibration of neighboring carboxyl groups at 1250–1175 cm^{-1} in the FT-IR spectrum indicates formation of a CNT polymer nanocomposite [30, 31, 37].

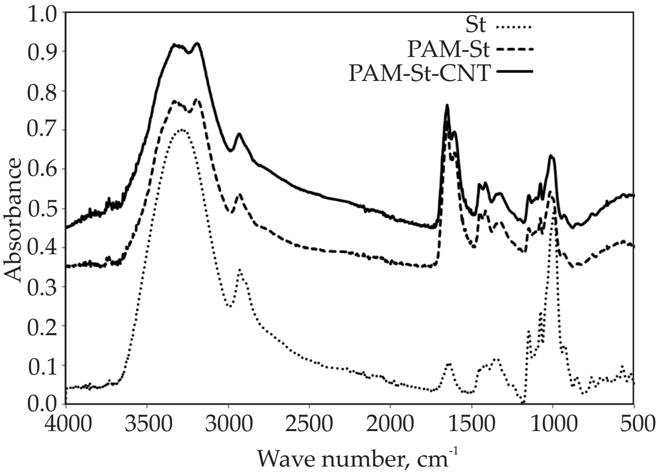

Fig. 1. FT-IR spectra of potato starch (St), polyacry-lamide-graft-starch copolymer (PAM-St) and nanocomposite polyacrylamide-graft-starch with CNTs (PAM-St-CNT)

Figure 2 shows the TGA curves of PAM and PAM-St (Fig. 2a) and nanocomposite starch-grafted-polyacrylamide with 3 wt % CNT and different amount of AM; 3 mol/dm^3 – 3PAM-St-CNT3, 5 mol/dm^3 – 5PAM-St-CNT3, 7 mol/dm^3 – 7PAM-St-CNT3 – (Fig. 2b). The TGA curves of PAM-St essentially indicated three distinct zones of mass loss. The initial mass loss is at 30–150 °C. This is due to trace of moisture present. The second mass loss zone at 220–330 °C is due to degradation of the starch backbone, and third one at 340–600 °C, due to the grafted PAM chains. Pure PAM has additional mass loss zone at

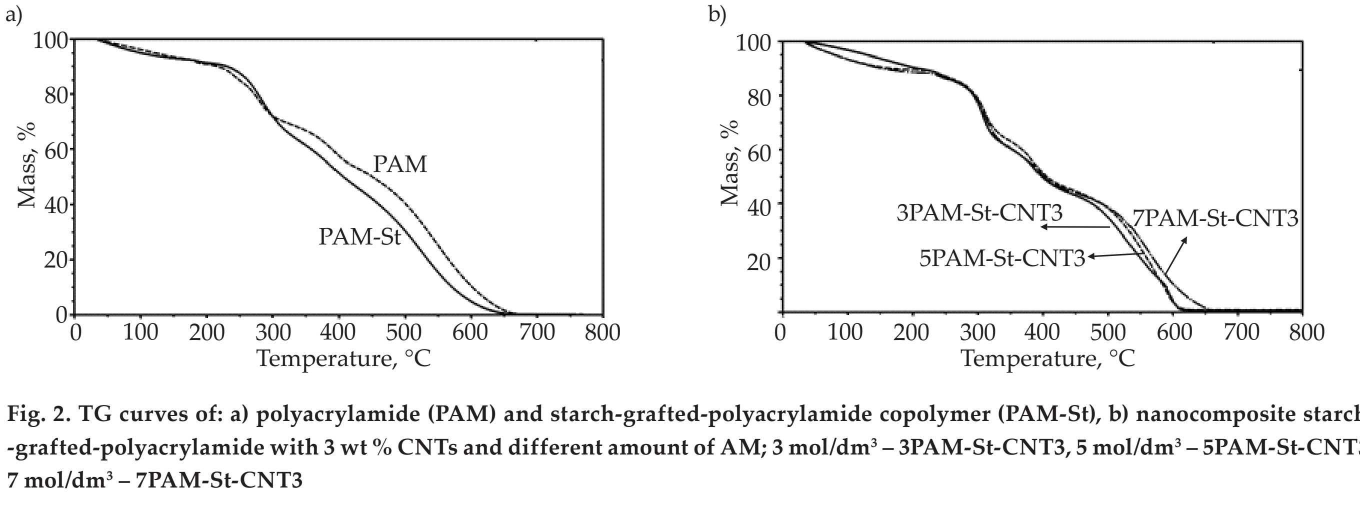

Fig. 2. TG curves of: a) polyacrylamide (PAM) and starch-grafted-polyacrylamide copolymer (PAM-St), b) nanocomposite starch-grafted-polyacrylamide with 3 wt % CNTs and different amount of AM; 3 mol/dm^3 – 3PAM-St-CNT3, 5 mol/dm^3 – 5PAM-St-CNT3, 7 mol/dm^3 – 7PAM-St-CNT3

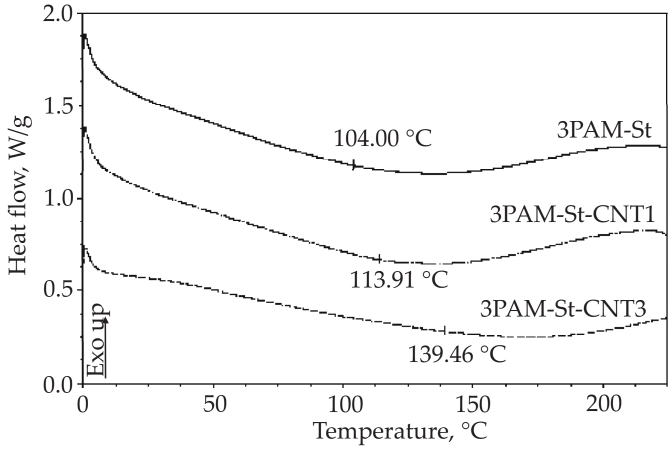

Fig. 3. DSC thermograms of starch-grafted-polyacrylamide (3PAM-St) and starch-grafted-polyacrylamide nanocomposite PAM-St-CNT with different amount of CNTs; 1 wt % CNTs – 3PAM-St-CNT1 and 3 wt % CNTs – 3PAM-St-CNT3 at constant concentration of AM – 0.3 mol/dm³

340–460 °C – the losing of functional groups (Fig. 2a) [1, 31]. The thermal stability of the PAM-St is worse than PAM, that results from poor thermal stability of starch.

The TGA curves of PAM-St-CNTs composites have similar to PAM four mass loss zones but definitely more visible (Fig. 2b). A major decomposition at a temperature range from 220–480 °C (two zones) corresponding to PAM layer on the surface of CNTs [31].

The TGA PAM-St-CNT thermograms show that with the increase of PAM nanocomposite content, its thermal stability caused by PAM-CNT linkage increases (see Fig. 2b).

The DSC heat flow thermographs of starch polyacrylamide copolymer – 3PAM-St and starch-grafted-polyacrylamide nanocomposite PAM-St-CNT with different amount of CNT: 1 wt % CNT – 3PAM-St-CNT1 and 3 wt % CNT – 3PAM-St-CNT3 at constant concentration of AM – 0.3 mol/dm³ are shown in the Fig. 3. Heat flow thermographs show that the presence of CNT in the PAM-St nanocomposite (characteristic transition temperature 104 °C) causes shift of exothermic peaks maxima to the higher temperature of 113.9 °C for 3PAM-St-CNT1 and to the temperature of 139.5 °C for 3PAM-St-CNT3. DSC measurements of obtained materials complete TGA results and confirm the increase in thermal resistance for nanocomposites compared to systems that do not contain CNT.

The flocculation study in model kaolin suspension as dependence of absorbance as the function of time for different nanocomposite doses was graphically illustrated in Figs. 4 and 5. Additionally, Table 1 shows the sludge volume changes dependent on material type and dose in jar test. The flocculation activity was investigated at various doses of flocculants (1, 3, 5 and 10 cm³ which corresponds with concentration of nanocomposite in test equal 1, 3, 5 and 10 ppm, respectively).

Figure 4 shows the results of jar test for nanocomposite obtained from AM at concentration of 0.3 mol/dm³ with 1 wt % CNT – 3PAM-St-CNT1 (Fig. 4a) and 3 wt % CNT – 3PAM-St-CNT3 – (Fig. 4b). The nanocomposite flocculants with 1 wt % CNT indicated flocculation ability at all doses used (Fig. 4a). Finally, the reduction in suspension turbidity was in the range 0.1–0.12 for all doses. In this case, the flocculation efficiency was satisfactory, however, it did not depend on the concentration in the tested range (1–10 ppm).

Figure 4b presents results that are definitely more interesting in scientific terms. A "flocculating window" was specified for a nanocomposite containing 3 wt % CNT, which is in the range 3–5 ppm. The best results in the absorbance reduction of kaolin suspension were obtained for 5 ppm concentration of nanocomposite flocculants: from 0.46 for untreated suspension to 0.11 after 10 minutes jar test and 0.06 for after 70 minutes (Fig. 4b). Flocculants doses of 1 and 10 cm³ were ineffective. Dose equal to 1 cm³ was too low, which in effect did not allow the formation of sufficient bridges between the kaolin and nanocomposite. Dose equal to 10 cm³ was too high, increase in absorbance relative to the absorbance of the model suspension arised from the colour of carbon nanotubes (0.7 after 10 minutes and 0.36 for after 70 minutes).

Figure 5 shows the absorbance changes in flocculation test nanocomposite starch-grafted-polyacrylamide with

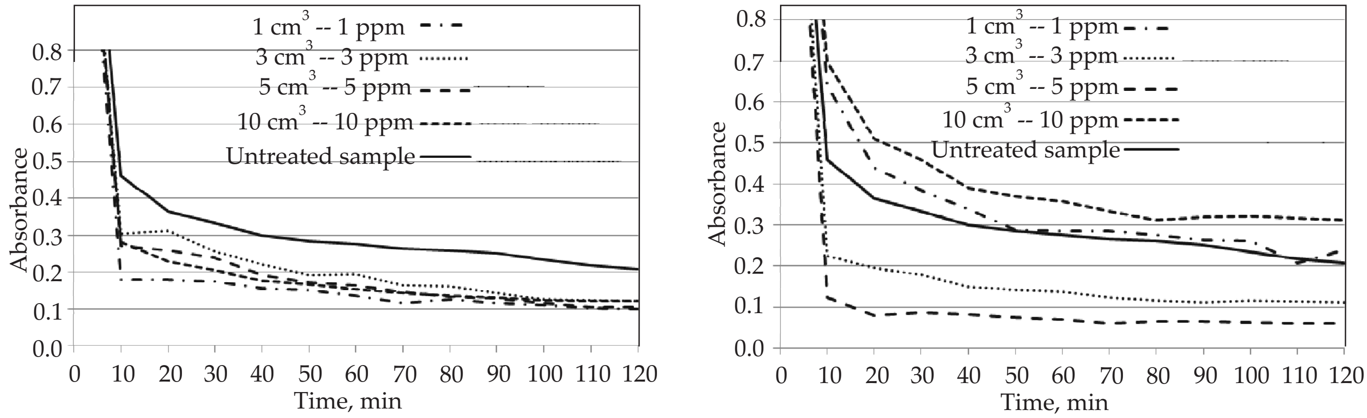

Fig. 4. Absorbance for kaolin aqueous suspension as a function of time for different doses nanocomposite starch-grafted-polyacrylamide (3PAM-St-CNT) of AM – 0.3 mol/dm³ and: a) 1 wt % CNTs – 3PAM-St-CNT1, b) 3 wt % CNTs – 3PAM-St-CNT3

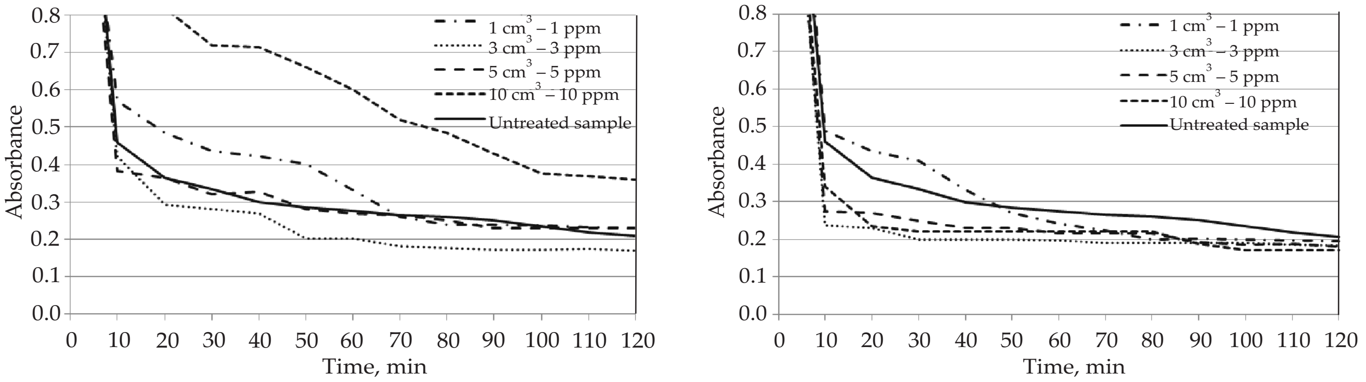

Fig. 5. Absorbance for kaolin aqueous suspension as a function of time for different doses nanocomposite starch-grafted-polyacrylamide with amount of 1 wt % CNTs and AM: a) 0.5 mol/dm^3 – 5PAM-St-CNT1, b) 0.7 mol/dm^3 – 7PAM-St-CNT1

Table 1. The sludge volumes changes during flocculation tests for kaolin aqueous suspension dependent on material type, dose flocculants and time

Time, min	20					100				
Flocculant concentration, ppm	0	1	3	5	10	0	1	3	5	10
Type of copolymer	Sludge volume, cm^3, after time									
3PAM-St-CNT1	12	35	22	19	18	15	17	18	16	17
3PAM-St-CNT3	12	24	24	22	18	15	18	19	21	15
5PAM-St-CNT1	12	24	25	19	15	15	18	18	16	15
7PAM-St-CNT1	12	22	24	22	23	15	17	17	16	17

amount of 1 wt % CNTs and concentration of 0.5 mol/dm^3 AM – 5PAM-St-CNT1 (Fig. 5a) and 0.7 mol/dm^3 AM – 7PAM-St-CNT1 (Fig. 5b). As can be seen in Fig. 5a, only a 3 cm^3 flocculants dose causes a slight improvement in the transparency of the suspension, results obtained at 5 cm^3 doses coincidence with untreated sample and the remaining doses cause deflocculation. In contrary to 5PAM-St-CNT1, nanocomposite 7PAM-St-CNT1, due to the high content of polyacrylamide in its composition, exhibit noticeable flocculating properties (Fig. 5b).

Table 1 shows the sludge volumes changes during jar tests depending on material type, flocculant dose and time. Nanocomposites with a content of 3 wt % CNTs (5PAM-St-CNT3, 7PAM-St-CNT3) were not considered because they did not dissolve in water. The volume of sludge for untreated kaolin suspension after 20 min test was 12 cm^3 and 15 cm^3 after 100 min. In all cases, after treating the suspension by the flocculant, the sediment volume was higher or equal than for the untreated sample.

The highest sludge volume was noted for 3PAM-St-CNT1 at 1 ppm concentration after 20 min running jar test. Additionally, this sample showed the largest reduction in sludge volume after 100 minutes – 18 cm^3 (from 35 cm^3 to 17 cm^3 – marked in Table 1). The best flocculation system-3PAM-St-CNT3, after 20 min of the test, showed a sludge volume 22–24 cm^3. The same results were measured for 7PAM-St-CNT1 nanokomposite. Taking into consideration similar results from sludge volume measurements for 3PAM-St-CNT3 and 7PAM-St-CNT1, the 3PAM-St-CNT3 has better flocculation efficiency because after 100 min of test, the sediments had higher volume (19 cm^3 for 3 ppm and 21 cm^3 for 5 ppm) compared to the sample 7PAM-St-CNT1 (17 and 16 cm^3, respectively). These results perfectly matches the outcomes of the absorbance change tests.

CONCLUSIONS

A simple procedure to prepare a CNTs suspension in water (currently the subject of a patent application) was applied for synthesis of starch grafted polyacrylamide with carbon nanotubes nanocomposites by radical polymerization. The obtained materials were characterized by FT-IR, TGA and DSC methods. The FT-IR spectrum indicated formation of a CNTs polymer nanocomposite. Additionally, the results from thermal analysis (TGA and DSC) confirmed formation of nanocomposites and higher thermal resistance of nanocomposites compared to pure PAM-St copolymer. Further, the flocculation efficiency of starch grafted nanocomposites were studied by jar tests in kaolin model suspension. It was found and proved that obtained nanocomposites show flocculation properties. It should be noted that the flocculating properties strongly depend on the composition of the nanocomposite, the polyacrylamide/CNTs amount ratio in the system and the dose of flocculant used. The nanocomposite with 0.3 mol/dm^3 and 3 wt % CNT – 3PAM-St-CNT3 demonstrated the best flocculation efficiency. The "flocculation window" for this sample was found for two concentration: 3 and 5 ppm.

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