Flocculant Based on Acrylamide and Acrylic Acid Grafted on Sodium Alginate by Electron Beam Irradiation

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The paper presents the obtaining, characterization and testing of a new type of polyelectrolyte based on acrylamide (2.63 mol/L), acrylic acid (1.73 mol/L) and sodium alginate ($4.63x10^{-3}$ and $9.26x10^{-3}$ mol/L), for flocculation purposes. Two types of monomeric solutions were irradiated in electron beam at room temperature and in atmospheric conditions with doses between 0.5 and 2 kGy using ALID 7 linear electron accelerator of 5.5 MeV. The potassium persulfate ($9.25x10^{-4}$ mol/L) was used as reaction initiator in both types of solutions. The flocculants thus obtained were characterized using various physical and chemical methods in order to determine conversion coefficient, residual monomer content, intrinsic viscosity, grafting ratio and grafting efficiency. The flocculation efficiency was evaluated in 0.1 and 0.2 wt % blue kaolin suspension at room temperature using a standard Jar test apparatus.

Keywords: electron beam irradiation, flocculants, acrylamide, sodium alginate

Coagulation and flocculation still play a dominant role in many water and waste water treatment schemes [1], that require both inorganic and organic flocculants [2]. Among the organic type, polymeric flocculants (synthetic as well as natural) are preferred because of their low dosage, easy handling, production of large cohesive flocs and biodegradability potential. The use of flocculants having biodegradable potential in waste water and industrial effluent treatments, are justified by the actual concern for environmental degradation [2, 3]. Radiation processing offers a clean and additive-free method for the preparation of value-added novel materials based on renewable, non-toxic and biodegradable natural polymers and natural polymer waste. Past research has shown that, depending on the irradiation conditions, natural polysaccharides (alginate, chitin, chitosan, carrageeneans, carboxyl methyl cellulose, etc.) can be used. This paved the way for the development of many successful applications, some of which have been commercialized for use in agriculture, healthcare and environmental protection [4-6]. Natural polysaccharides function as bridging flocculants. It has been established that by grafting polyacrylamide branches on polysaccharides, the dangling grafted chains have easy approachability to the contaminants [2]. The goal of the paper is to present the obtaining, characterization and testing of a new type of polyelectrolyte obtained by electron beam irradiation, for flocculation purposes. The polyelectrolyte, based on acrylamide, acrylic acid and sodium alginate, was characterized from the chemical and physical point of view. Flocculation efficiency was also evaluated in 0.1 and 0.2 wt % blue kaolin suspension.

Experimental part

Materials

Acrylamide (AMD) (min 99 % purity, molar mass 71.08 g/mol, density 1.13 g/cm^3, solubility in water 2.04 kg/L at 25^{o}C), acrylic acid (AA) (min 99 % purity, molar mass 72.06 g/mol, density 1.051 g/cm^3, solubility in water: miscible, viscosity 1.3 cP at 20 ^{o}C), sodium alginate (Alg) (molecular weight 216.121 g/mol, density 1.601 g/cm^3, solubility in water; no more than 2% on the dried basis), potassium persulfate (I) (min 99 % purity, molar mass 270.322 g/mol, density 2.477 g/cm^3, solubility in water 5.29 g/100 mL at 20^{o}C) were obtained from LACHEMA, Germany, and used directly, without purification.

Sample preparation

For the polyelectrolytes obtaining, two types of monomeric solutions were used as fallows: *Sol I* (AMD-AA/Alg I) containing sodium alginate $4.63x10^{-3}$ mol/L, acrylamide 2.63 mol/L, acrylic acid 1.73 mol/L and *Sol II* (AMD-AA/Alg II) containing sodium alginate $9.26x10^{-3}$ mol /L, acrylamide 2.63 mol/L, acrylic acid 1.73 mol/L. In both of them, $9.25x10^{-4}$ mol/L of potassium persulfate was added as reaction initiator.

Experimental installations and flocculants synthesis

The irradiation of *Sol I* and *Sol II* was performed using the ALID 7 linear electron accelerator of travelling-wave type built in the National Institute for Laser, Plasma and Radiation Physics, with the following characteristics: 5.5 MeV electron beam (EB) energy, 130 mA peak current, 3.75 ìs pulse duration, 134 W maximum output power at 50 Hz pulse repetition frequency. The EB effects are related with the precise control of absorbed dose (D) and absorbed dose rate (D*) [7-9]. In experiments the electron beam dose rate was fixed at 2 kGy/min in order to accumulate doses between 0.5 kGy and 2 kGy. The absorbed dose was determined using the graphite calorimeter. In order to assure equal doses at the entry and at the exit of the irradiated sample, the electron beam penetration depth in the sample was calculated as being 20 mm [9]. 15 mL from each monomeric solution (Sol I and Sol II) have been distributed for irradiation in polyvinylchloride (PVC) containers of 3 cm diameter [10]. Details concerning chemical composition and irradiation dose are presented in table 1.

Purification of the grafted polymers

Purification of the grafted polymers was realized in order to remove the homopolymer [9, 11] and to separate the unreacted monomers from the grafted polymers. Different concentrations of polymerized mixtures from each sample

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Table 1
THE POLYELECTROLYTES CHEMICAL COMPOSITION AND SYNTHESIS DETAILS

Samples codes	Solutions codes	Amount of chemicals (mol/L)				Irradiation dose (kGy)
		AMD	AA	Alg	PP	
AMD-AA/Alg I/0.5	Sol I	2.63	1.73	$4.63x10^{-3}$	$9.25x10^{-4}$	0.5
AMD-AA/Alg I/0.75						0.75
AMD-AA/Alg I/1.0						1.0
AMD-AA/Alg I/1.25						1.25
AMD-AA/Alg I/1.5						1.5
AMD-AA/Alg I/1.75						1.75
AMD-AA/Alg I/2.0						2.0
AMD-AA/Alg II/0.5	Sol II	2.63	1.73	$9.26x10^{-3}$	$9.25x10^{-4}$	0.5
AMD-AA/Alg II/0.75						0.75
AMD-AA/Alg II/1.0						1.0
AMD-AA/Alg II/1.25						1.25
AMD-AA/Alg II/1.5						1.5
AMD-AA/Alg II/1.75						1.75
AMD-AA/Alg II/2.0						2.0

were completely diluted in water, then added dropwise into a large excess of methanol (250 ml) in order to remove the homopolymer. The precipitated polymer was ûltered off and washed with methanol for 10 times [9, 11]. Afterwards, it was precipitated by adding 250 mL of acetone in order to separate the unreacted monomer (acrylamide) from the grafted polymer and finally it was dried in a hot air oven at 60°C for 6 h. The grafting ratio (GR, %) and grafting efficiency (GE, %) were calculated using the following relations [9, 12-14]:

$$GR(\%) = \frac{wt._{GP} - wt._{Alg}}{wt._{Alg}} \times 100 \quad (1)$$

$$GE(\%) = \frac{wt._{GP} - wt._{Alg}}{wt._{M}} \times 100 \quad (2)$$

where $wt._{GP}$, $wt._{Alg}$, $wt._{M}$, are weights of the grafted polymer, sodium alginate and monomers (acrylamide and acrylic acid).

Physico-chemical characteristics

For determining the conversion coefficient of monomers (C_C) and the residual monomer concentration (M_r), 2 grams from each polymer types were placed in 200 ml distilled water for 24 hours, than stirred for 1 h at 400 rpm for a very well mixing. C_C and M_r were determined by titrimetric method in which bromine reacts with the double bond of residual monomer. After complete dissolution in water, the polymers were treated excessively with a bromide-bromate solution and the bromine excess was determined by means of the iodatometry method in presence of sodium thiosulfate solution (1 M) [9, 15-17]. The intrinsic viscosity ($h_{intr.}$) was determined using the falling ball Hoppler viscometer of BH-2 type [9, 17]. The measured parameter is the ball falling time in the cylindrical tube inclined with 10 degree against the vertical plane and filled with the liquid to be analyzed. The ball falling time through the polymeric solution was measured in five different concentrations. The working temperature was 30°C and sodium nitrate 1N ($NaNO_3$) was used as solvent.

Fourier Transform Infrared Spectroscopy (FTIR)

The polyelectrolyte chemical structure was investigated using a spectrophotometer Perkin Elmer-Spectrum 100 instrument equipped with ATR diamond crystal plate. Spectra were acquired in ATR mode and each spectrum consisted of 20 scans per sample, in the wavenumbers range between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}. The registered FTIR spectra were processed by applying normalization and ATR correction available on the Spectrum v.6.3.2 software.

Flocculation studies

The flocculation studies were carried out on blue kaolin suspension (0.1 wt % and 0.2 wt %) at room temperature of 20°C to 25°C using the standard Jar test apparatus of Velp FC 6S type having 6 stirrer blades. In each beaker, 500 mL of kaolin suspension was taken and placed on the flocculator. Under a slow stirring condition, the polymer solution in concentrations of 1 ppm to 10 ppm was added by means of a pipette in order to determine the polymer concentration influence. The experiments were carried out at 90 rpm for 15 min. Clear supernatant was drawn from the top layer (up to depth 1-2 cm) and its transmittance was measured at 620 nm using the Cary Bio-100 UV-Vis spectrophotometer.

Results and discussions

Grafting ratio and grafting efficiency

The two types of polyelectrolytes, called from now forward type I and type II, were obtained by electron beam irradiation in atmospheric conditions at room temperature of 25°C, from the monomeric solutions having the compositions described below (*Sol I* and *Sol II*). Keeping the dose rate at 2 kGy/min and varying the irradiation dose between 0.5 kGy and 2 kGy, were obtained polymers having various grades of grafting. The acrylamide and acrylic acid grafted on the sodium alginate backbone were evaluated through the grafting ratio (GR) and grafting efficiency (GE) expressed in % and the results are presented in figures 1 and 2.

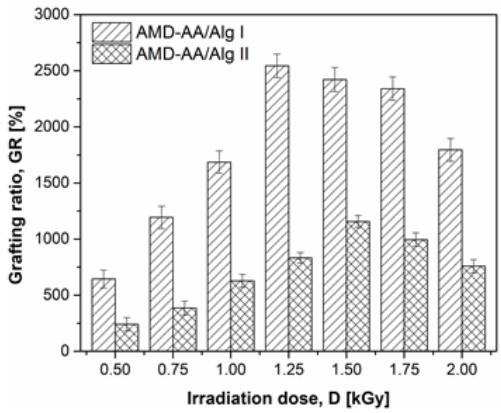

Fig 1. The grafting ratio (GR) versus the electron beam irradiation dose for AMD-AA/Alg I and AMD-AA/Alg II polymer types

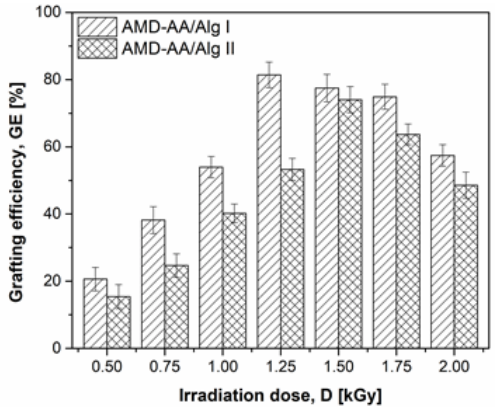

Fig 2. The grafting efficiency (GE) versus the electron beam irradiation dose for AMD-AA/Alg I and AMD-AA/Alg II polymer types

In figures 1 and 2 it can be seen that both GR and GE have increases with increasing of the irradiation dose, obtaining the maximum values of 2500% (GR) and 80% (GE) at the irradiation dose of 1.25 kGy for polymers of type I (AMD-AA/Alg I) and of 1100 % (GR) and 78 % (GE) at 1.5 kGy for polymers of type II (AMD-AA/Alg II), respectively. As the irradiation dose increased, both GR and GE decreased. But, while GR was very sensitive on both polymer type and irradiation dose, GE was less sensitive to the polymer type. Low values of GE obtained at the irradiation doses up to 1.25 kGy and 1.5 kGy respectively, are directly connected with the presence of high amounts of homopolymer in the system [9, 11, 16].

Physico-chemical characteristics

For the grafted polymers obtained as above, were determined the conversion coefficient (CC), residual monomer concentration (M_r) and intrinsic viscosity ($h_{intr.}$). In table 2 it can be seen that for both types of polymers, AMD-AA/ALg I and AMD-AA/ALg II, high conversion coefficients (up to 97% approximately) are correlated with low residual monomers contents (under 0.02%) as the radiation dose increased.

In radiation processing, the probability of a higher molecular contact is increased by the irradiation dose increasing, resulting in the propagation of active chain and continuously C_C increase [9, 18, 19]. For both C_C and M_{rez} it cannot be observed notable differences between the samples having different initial concentrations of sodium alginate irradiated at the same dose. The highest levels of CC and lowest levels M_{rez} were obtained and correlated at the irradiation dose of 1.75 kGy and 2 kGy. The only physical parameter affected by the irradiation dose increasing was η_{intr}. It increased up to 1.04 dL/g at the irradiation dose of 1 kGy, then decreases up to 0.58 dl/g for the polymer of type I. The polymers of type II did not show intrinsic viscosities over 1 dL/g at any irradiation dose. The effect of sodium alginate concentration and irradiation dose on the grafting reaction was investigated and then correlated with the FTIR analysis.

Fourier Transform Infrared Spectroscopy (FTIR)

In order to evaluate the binding of acrylamide and acrylic acid on the sodium alginate backbone, the infrared spectra of the grafted polymers was performed. Infigures 3-6 are presented the spectra of AMD-AA/ALg I/ and AMD-AA/ALg

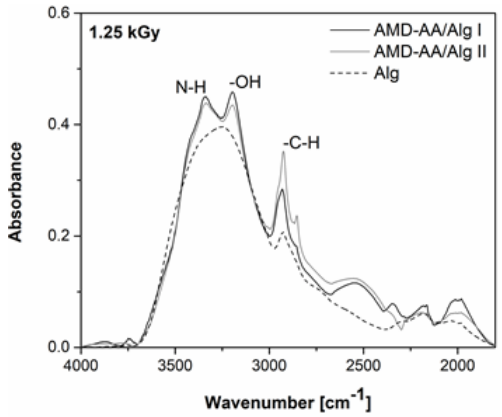

Fig. 3. The FTIR spectra of AMD-AA/Alg I and AMD-AA/Alg II obtained at 1.25 kGy between 4000-2000 cm^{-1}

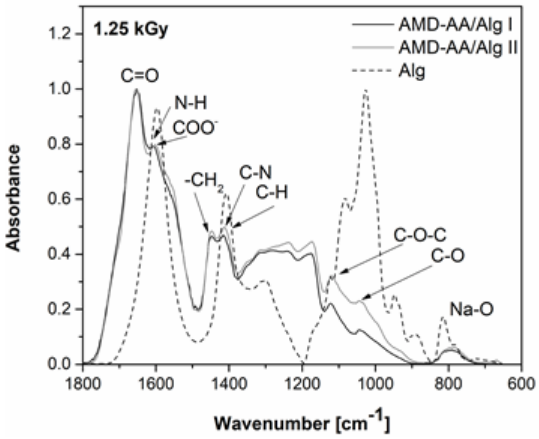

Fig. 4. The FTIR spectra of AMD-AA/Alg I and AMD-AA/Alg II obtained at 1.25 kGy between 1800-650 cm^{-1}

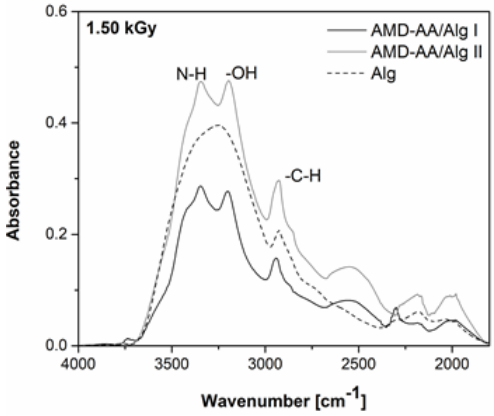

Fig. 5. The FTIR spectra of AMD-AA/Alg I and AMD-AA/Alg II obtained at 1.50 kGy between 4000-2000 cm^{-1}

	Irradiation dose (kGy)						
	0.5	0.75	1.0	1.25	1.5	1.75	2.0
	Conversion coefficient, C_C (%)						
AMD-AA/Alg I	82.33	83.05	89.99	95.63	96.84	98.01	97.99
AMD-AA/Alg II	82.34	87.26	90.22	96.12	97.08	97.34	97.87
	Intrinsic viscosities $\eta_{intr.}$ (dl/g)						
AMD-AA/Alg I	0.90	0.92	1.04	1.03	1.01	0.64	0.58
AMD-AA/Alg II	0.51	0.72	0.77	0.92	0.91	0.70	0.61
	Residual monomers contents $M_{rez.}$ (%)						
AMD-AA/Alg I	0.114	0.109	0.068	0.027	0.020	0.014	0.014
AMD-AA/Alg II	0.112	0.082	0.063	0.024	0.019	0.017	0.014

Table 2
PHYSICAL AND CHEMICAL CHARACTERISTICS (C_C, $\varsigma_{intr.}$ $M_{rez.}$) OF THE POLYMERS

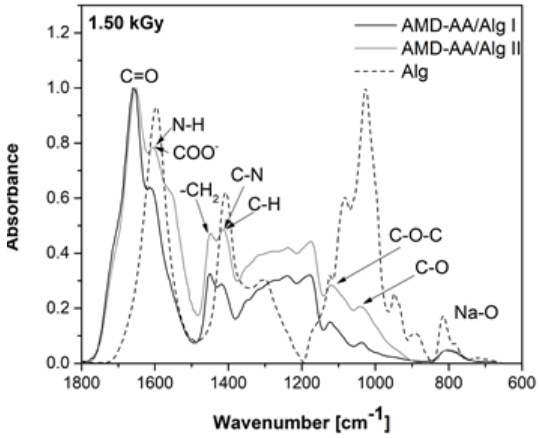

Fig. 6. The FTIR spectra of AMD-AA/Alg I and AMD-AA/Alg II obtained at 1.50 kGy between 1800-650 cm^{-1}

II/ samples irradiated at 1.25 and 1.5 kGy on two spectral intervals (4000-2000 cm^{-1} and 1800-650 cm^{-1}).

The band near 3100 cm^{-1} that correspond to the stretching vibration of -OH groups of sodium alginate [20-22] can be seen in both AMD-AA/ALg I and AMD-AA/ALg II spectra obtained at 1.25 kGy (fig. 3) and 1.5 kGy also (fig. 5). On this band, there are observed modifications in absorbance for samples obtained at the same irradiation dose as a function of sodium alginate concentration. Samples obtained at the irradiation dose of 1.5 kGy present significant differences in absorbance compared to those obtained at 1.25 kGy. The variation in intensity and the shifted appearance at 3192 cm^{-1}, indicates the partially participation of hydroxyl groups in chemical reaction [21]. A decreasing of intensity in the case of AMD-AA/ALg II samples indicates that, by doubling the sodium alginate concentration in the irradiated samples, the grafting reaction was affected [22]. The sharp bands around 1620 cm^{-1} are attributed to the asymmetric COO- stretching (figs. 4 and 6). The bands around 1417 cm^{-1} (figs. 4 and 6) correspond to the C-H deformation with secondary alcohols [22]. Finally, the bands around 1120 cm^{-1}, 1093 cm^{-1} and 1031 cm^{-1} are due to the asymmetric C-O-C stretching, C-O stretching in CH-OH structure and symmetric C-O stretching in C-O-C structure, respectively (figs. 4 and 6) [22].

The bands at 3360 cm^{-1} and 1320 cm^{-1} are usually attributed to the stretching vibration of N-H [22] and we found them slightly shifted at 3335 cm^{-1} and 1321 cm^{-1}, respectively. Same situation was met in the case of band corresponding to the C=O stretching (around 1651 cm^{-1} instead of 1670 cm^{-1}). The bands corresponding to the N-H deformation for primary amine, CH_2 in-plane scissoring, C-N stretching for primary amide, C-H deformation and NH2 in-plane rocking were found at 1621 cm^{-1}, 1448 cm^{-1}, 1417-1415 cm^{-1}, 1349 cm^{-1} and 1122 cm^{-1}, respectively.

Flocculation studies

Grafted polymers characterized as above were used in flocculation studies that were carried out on blue kaolin suspension at room temperature of 25°C. Were studied the influence of kaolin concentration (0.1 wt % and 0.2 wt %), polymer concentration (from 0.5 ppm to 5 ppm) and rotation speed (from 60 rpm to 90 rpm) on flocculation efficacy in terms of transmittance against distilled water.

For the first experiments set, in the Jar test glass bakers filled with 500 mL kaolin suspension of 0.1 wt % and 0.2 wt %, were added polyelectrolytes of AMD-AA/ALg I and AMD-AA/ALg II types (obtained at 1.25 and 1.5 kGy) in different concentrations between 0.5 ppm and 5 ppm. Samples were stirred first at 60 rpm for 15 min , then left to rest for another 15 min before sampling for analysis from the top layer clear supernatant. The results are presented in figures 7 and 8.

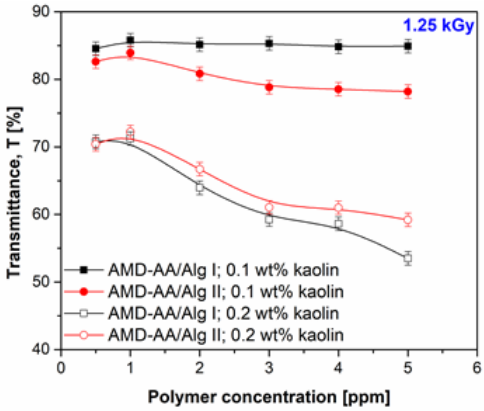

Fig. 7. The influence of the polymers (AMD-AA/Alg I and AMD-AA/Alg II) obtained at 1.25 kGy on the kaolin concentration (rotation speed: 60 rmp)

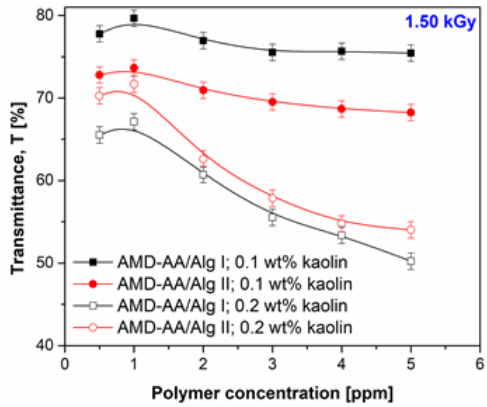

Fig 8. The influence of the polymers (AMD-AA/Alg I and AMD-AA/Alg II) obtained at 1.50 kGy on the kaolin concentration (rotation speed: 60 rmp)

In the experiments that were made on kaolin suspension of 0.1 wt %, the polymers of AMD-AA/Alg I type obtained at 1.25 kGy have lead to a transmittances over 85% (fig. 7) while the polymers of both types obtained at 1.5 kGy, have lead to a transmittances under 80% but not less than 70% (fig. 8). It can be observed that the increasing of the polymer concentration leads to a slowly decreases of the transmittance, excepting the case of the AMD-AA/Alg I type obtained at 1.25 kGy.

In the experiments that were made on kaolin suspension of 0.2 wt %, irrespective of the irradiation dose (1.25 kGy or 1.5 kGy) and polymer type or concentration, the transmittances were under 70%. We can even see the abrupt decrease of the transmittance with the polymer concentration, in the case of the polymers obtained at the irradiation dose of 1.5 kGy (fig. 8).

For the second experiments set, the influence of the rotation speed of the stirrer blades (between 60 and 150 rpm) was investigated on the kaolin suspension of 0.1 wt % using the same polymers (having the best intrinsic viscosities, grafting degrees and grafting efficiencies) as in the previews experiments, in the concentrations of 0.5 ppm and 1 ppm. The results are presented in figures 9 and 10.

It can be seen that the increasing of the rotation speed of the stirrer blades over 90 rpm leads to the increasing of all transmittances over 80% (figs. 9 and 10), reaching even up to 95% in the case of AMD-AA/Alg II, obtained at 1.25 kGy used in the concentration of 1 ppm at a rotation speed of 150 ppm (fig. 10).

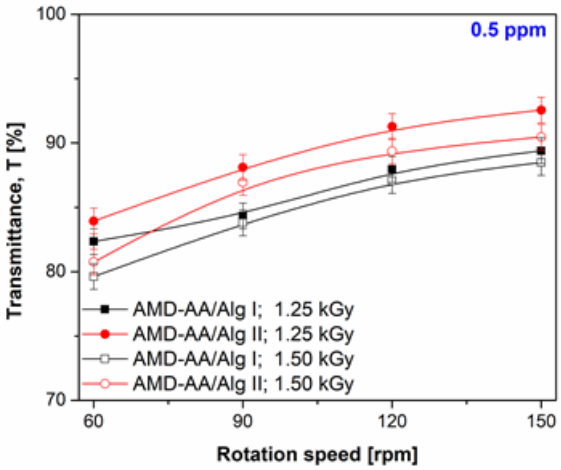

Fig 9. The influence of the rotation speed on the samples transmittance (polymer concentration: 0.5 ppm; kaolin concentration 0.1 wt%)

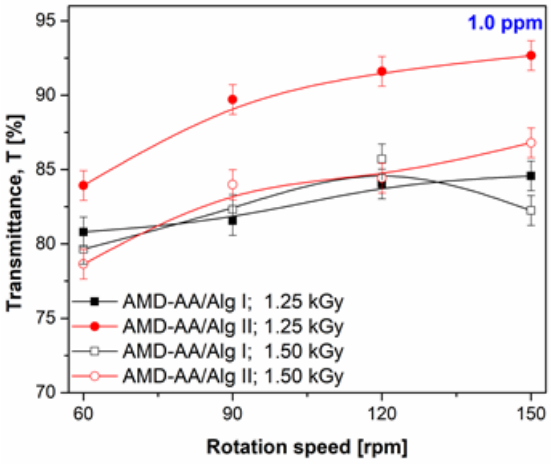

Fig 10. The influence of the rotation speed on the samples transmittance (polymer concentration: 1.0 ppm, kaolin concentration 0.1 wt%)

In figsures 7-10, it can be seen that both polymer types are effective in small concentrations (0.5 ppm and 1ppm) on both kaolin suspension of 0.1 wt % and 0.2 wt %. If the polymer concentration increased, only the polymers containing the smaller amount of sodium alginate (AMD-AA/Alg I) still remain effective when it was used on the kaolin suspension of 0.1% at the rotation speed of the stirrer blades of 60 rpm. If the polymer concentration was maintained at 1 ppm, only the polymers containing the bigger amount of sodium alginate (AMD-AA/Alg II) reached the transmittance over 90% at the rotation speed of the stirrer blades of 150 rpm.

Conclusions

A new type of polyelectrolyte based on acrylamide, acrylic acid and sodium alginate for flocculation purposes was obtained by electron beam irradiation. FTIR analysis showed the grafting of acrylamide and acrylic acid on sodium alginate backbone. The grafting efficiency of acrylamide and acrylic acid on sodium alginate increases with increasing of the absorbed dose and the maximum values were obtained around 1.25 kGy. Even if the addition of a double quantity of sodium alginate did not significantly modify the conversion coefficient and residual monomer concentration, the flocculation studies that were performed on blue kaolin suspension of 0.1 wt % and 0.2 wt % presented significant differences between the transmittances. The polymers concentration and rotation speed of the stirrer blades influence on the transmittance showed the effectiveness of both polymer types in proper conditions. Modest values of intrinsic viscosities were associated, in terms of transmittance, with flocculation efficiencies up to 90%.

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