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Amine activators influence on grafting reaction between methacrylic acid and starch

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ABSTRACT

The aim of this work was synthesis of grafted copolymers of poly(methacrylic acid) and starch (PMAA-*graft*-starch) with high percentage of grafting, G (%). The effect of temperature (55–75 °C), concentration of methacrylic acid monomer (0.775–1.452 mol/dm^3), amount of initiator potassium persulfate (PPS) (0.00075–0.0025 mol), reaction time (30–270 min) and nature and amount (0.001–0.005 mol) of amine activator on percentage of grafting were investigated. The following amine activators were used: *N*,*N*-dimethylaminoethanol, *N*,*N*-diethylaminoethanol, triethylamine, propylamine, iso-butylamine, pentylamine, hexylamine, 4-(2-hidroxyethyl) morpholine and 1-(2-hidroxyethyl) piperazine. The graft copolymer was characterized by Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy. The highest G was 40.92%. Reaction conditions were as follows: 10.00 g of starch, monomer concentration was 0.775 mol/dm^3, temperature of 70 °C, the amount of PPS was 0.001 mol. The 4-(2-hidroxyethyl) morpholine was used as amine activator in amount of 0.001 mol.

1. Introduction

Starch is a natural carbohydrate. It is composed of linear polysaccharide molecules (amylose) and branched molecules (amylopectin). It is accumulated in plants. Starch is desirable as an environmentally friendly alternative material for making biodegradable plastics, because it is a natural polymer that can be degraded by microorganisms. It is inexpensive and obtained from renewable resources. Starch is also suitable for blending with other polymers (Abdel-Hatiz, 1997; Bernkop-Schnurch, Konig, Leitner, Krauland, & Brodnik, 2002; Bocchini, Battegazzore, & Frache, 2010; Shin, Narayan, Lee, & Lee, 2008; Shin, Jang, & Kim, 2011; Vaidya, Bhattacharya, & Zhang, 1995; Yang, Bhattacharya, & Vaidya, 1996; Zhou et al., 2009). Composites of starch and poly(methacrylic acid) are commonly used for medical applications for drugs delivering to specific locations in the body (Clausen, & Berknop-Schnurch, 2001; El-Hag Ali, & AlArifi, 2009; McConnell, Short, & Basit, 2008). Chemical modification of starch via grafting of vinyl monomers is one of the most effective methods to incorporate desirable properties into starch without sacrificing its biodegradable nature. Lee and Cho (1998) reported that methyl methacrylate (MMA) can be graft copolymerized onto corn starch by emulsion polymerization. Razi, Qudsieh, Yunus, Ahmad, and Rahman (2001) used potassium persulfate (PPS) as initiator for grafting MMA onto sago starch. Poly(acrylamide) can be grafted with starch (Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002; Singh, Tiwari, Pandey, & Singh, 2006; Willett, & Finkenstadt, 2003; Wu, Wei, Lin, & Lin, 2003). Polystyrene graft starch copolymers can be obtained by suspension polymerization (Kaewtatip, & Tanrattanakul, 2008), emulsion polymerization (Cho, & Lee, 2002), ^{60}Co radiation (Fanta, Burr, Doane, & Russell, 1977; Henderson, & Rudin, 1981; Kiatkamjornwong, Sonsuk, Wittayapichet, Prasassarakich, & Vejjanukroh, 1999) and also in presence of different initiators (Graaf, & Janssen, 2000; Janarthanan, Yunus, & Ahmad, 2003; Singh, & Sharma, 2007). Another chemical modification of starch is grafting starch with biodegradable polymers, such as poly(lactide) (Chen et al., 2005) and polycaprolactone (Hang, Yu, Ma, & Jin, 2005; Rutot, Degee, Narayan, & Dubois, 2000).

PMAA-*graft*-starch copolymers can be obtained by using different initiator systems such as potassium persulfate (Khalil, Mostafa, & Hebeish, 1993), ammonium peroxydisulfate (Abo-Shosha, & Ibrahim, 1992), manganese (IV)–acid system (Khalil, Mostafa, & Hebeish, 1990), hydrogen peroxide–ferrous ammonium sulfate (Vazquez, Goni, Gurruchaga, Valero, & Guzman, 1989), KMnO$_4$/citric acid (Mostafa, 1995), tetravalent cerium (Ce^{4+})

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(Athawale, & Rathi, 1997), potassium persulfate/sodium thiosulfate redox system (Beliakova, Aly, & Abdel-Mohdy, 2004), H_2O_2/Fe^{2+} initiator system (Li, Zhu, & Jin, 2010).

In this manuscript, copolymers of methacrylic acid and starch were obtained in aqueous medium using PPS as an initiator and different amines as activators. Currently, there is no existing literature data about amine polymerization activators influence on obtaining grafted PMAA-*graft*-starch copolymer, although the influence of amine activators had been studied in other systems. It is possible to perform polymerization reaction of itaconic acid in aqueous solution, at lower temperatures and shorter times, when amine alcohol is added (Velickovic et al., 2008). Tertiary amines have been known as good activators in polymerization of methyl methacrylate with peroxide initiator (Elvira, Levenfeld, Vazquez, & San Roman, 1996) and tertiary aromatic amines were good activators in photo polymerization reaction (Encinas, & Lissi, 1993).

The PMAA-*graft*-starch copolymer can be used in various applications. In the field of targeted drug delivery it can pose an advantage over IPN hydrogels, because of the covalent nature of links in PMAA-*graft*-starch, while keeping the efficiency and precision of a standard hydrogel system, and unhindered pH sensitivity. This copolymer can also be a material for basic dye adsorption, as it was recently reported (Anirudhan & Tharun, 2012) that another pollysacharide based polymer, PMAA-*graft*-cellulose, shows very promising results in adsorption of a model basic dye methylene blue. These two lines of investigation are currently in progress in our laboratory.

2. Experimental

2.1. Materials

Starch (Centrohem, Serbia) was dried for 3 days under vacuum at 50 °C. Methacrylic acid (Fluka), PPS (Aldrich Chemicals), ethanol (Zorka Pharma) and amines–*N*,*N*-dimethylethanolamine, *N*,*N*-diethylethanolamine, triethylamine, propylamine, iso-butylamine, pentylamine, hexylamine, 1-(2-hidroxyethyl) piperazine and 4-(2-hidroxyethyl) morpholine (all Fluka), were used as obtained.

2.2. Preparation of PMAA-graft-starch copolymer

In three necked flask equipped with Liebig condenser and thermometer, starch (10.00 g) and distilled water (80–150 ml) were added. Concentration of methacrylic acid was between 0.775 and 1.452 mol/dm^3. The reaction mixture was stirred for 30 min in order to homogenize it and to reach reaction temperature. After homogenization, the initiator was dissolved in 10.0 ml of distilled water, and amine activators (between 0.001 and 0.005 mol) were added to the mixture. Reaction temperatures were between 55 and 75 °C. The amount of initiator varied between 0.00075 and 0.0025 mol. Besides monitoring of the influence of temperature, the amount of initiator, amine activators and monomer concentration etc., the influence of reaction time was monitored, too. The reaction times varied between 30 and 270 min.

After completion of reaction, the reaction mixture was put in a vessel with water for 24 h at room temperature in order to remove unpolymerized monomer of methacrylic acid and ungrafted poly(methacrylic acid). After 24 h, the reaction mixture was filtered and new amount of water added. This procedure repeated 3–4 times, or until decrease pH values occurred. To make sure that ungrafted poly(methacrylic acid) was removed, ethanol was added and reaction mixture was gently heated and stirred for 1 h. After this, the reaction mixture was centrifuged at 2000 rpm/min for 30 min. Obtained polymer was dried on 50 °C to constant weight. This polymer was PMAA-*graft*-starch copolymer.

To determine amount of grafted poly(methacrylic acid) in PMAA-*graft*-starch, copolymers were hydrolyzed, using 100 ml of 1 M HCl for every 5 g of copolymer. Hydrolysis temperature was 200 °C and reaction time was 1 h. Poly(methacrylic acid) that remains in solid state was removed by filtration and rinsed with distilled water. One portion of poly(methacrylic acid) was hydrolyzed and remained in solution with hydrolysis starch. Hydrolysis PMAA was precipitated with ethylacetate in ice bath. Precipitated PMAA had the form of fibers. This poly(methacrylic acid) was separated by filtration, rinsed with distilled water and added to PMAA which remained in solid state. All PMAA was dried under vacuum at 50 °C to constant weight. FTIR spectroscopy confirmed that product of hydrolysis was poly(methacrylic acid).

All syntheses were done three times and the results that are shown represent their mean values.

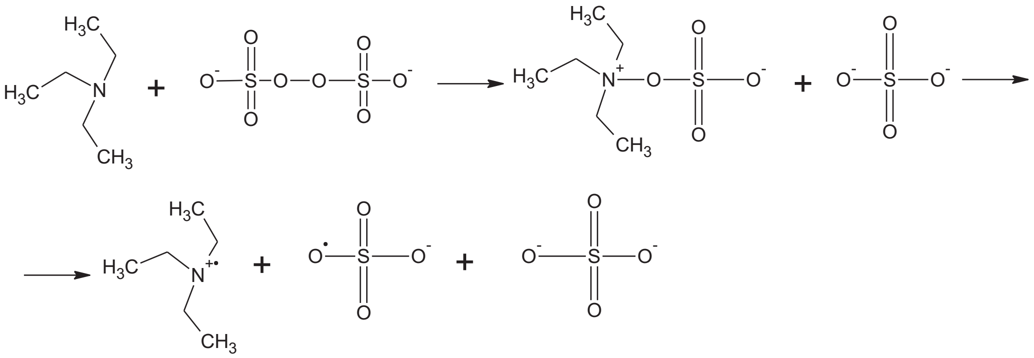
2.3. Characterization of PMAA-graft-starch copolymer

Percentage of poly(methacrylic acid) in PMAA-*graft*-starch copolymer was calculated by following formula:

$$G(\%) = \frac{\text{weight of grafted PMAA}}{\text{weight of PMAA-g-starch}} \times 100$$

In order to detect the presence of PMAA in grafted copolymer, Fourier Transform Infrared Spectroscopy (MB-100 Bomem FTIR spectrophotometer) was used. FTIR spectrum was recorded from KBr discs.

Scanning Electron Microscopy (SEM) was used to investigate surface morphology of PMAA-*graft*-starch copolymers. Samples were mounted on copper and metalized with gold–palladium at Polaron SC 502 sputter coater and recorded Scanning Electron Microscopy (Jeol JSM 6610 LV) with filament operating at 20 keV to determine the presence of PMAA on starch granules.



Scheme 1. Initiation mechanism of PPS with triethylamine.

3. Results and discussion

3.1. Graft copolymerization mechanism

Initiation mechanism of potassium persulfate with amine (in this case triethylamine) is shown on Scheme 1. In initiation reaction only anionic radical participates. Obtained anion and cationic radical are neutralized and they do not start polymerization. The anionic radical starts polymerization of methacrylic acid monomer or leads to formation of the free radicals on the starch.

The next step in the reaction mechanism is:

$$\text{St—OH} + \text{R}* \rightarrow \text{St—O}* + \text{RH}$$

$$\text{St—O}* + \text{M} \rightarrow \text{St—OM}*$$

$$\text{St—OM}* + n\text{M} \rightarrow \text{PMAA-}\textit{graft}\text{-starch copolymer}$$

where St is starch, M is the methacrylic acid and R* is radical anion.

In this system there is a reaction of homopolymerization of methacrylic acid:

$$\text{R}* + \text{M} \rightarrow \text{R—M}*$$

$$\text{R—M}* + x\text{M} \rightarrow \text{homopolymer of PMAA}$$

3.2. Optimization of grafting conditions

In this experiment, in order to obtain PMAA-*graft*-starch copolymers with highest percentage of grafting the influence of temperature, monomer concentration, reaction time, amount of initiator, amount and nature of amine activator were followed.

3.2.1. Influence of temperature and monomer concentration

Influence of temperature and monomer concentration (methacrylic acid) on percentage of grafting is shown in Table 1. The reaction time was 150 min, amount of PPS was 0.0015 mol and amount of starch was 10.00 g.

From Table 1 it is obvious that percentage of grafting increases with temperature. *G* (%) decreases, as expected, when monomer concentration decrease. Exception of this rule was the reaction at 75 °C with monomer concentration of 0.775 mol/dm^3, where the percentage of grafting is lower than in the reaction at 70 °C. Reason for this anomaly was that polymerization of poly(methacrylic acid) on 75 °C was very fast and poly(methacrylic acid) could not be grafted on starch in higher concentration. A large part of poly(methacrylic acid) stayed in form of homopolymer, which could not be grafted on starch. Table 1 showed that some reaction occurred instantly. Because of high monomer concentration and high temperature, polymerization of methacrylic acid occurred instantly (immediately after the addition of initiator). In the reaction system there was rapid increase of viscosity, so the stirring was blocked and synthesis stopped. In these syntheses, percentage of grafting was not determined. From Table 1 it is obvious that with temperature increasing, number of reaction that occurred instantly increases and monomer concentration that required for successfully grafting decreases. In some reactions (Failure) concentration of methacrylic acid was too low (at a given temperature), so that there was no polymerization of methacrylic acid at given temperature and there was no grafting. In this reaction *G* (%) was 0%. With temperature increase, number of failed reactions decreases. To obtain copolymers with higher percentage of grafting, it was necessary to exactly determine the optimal reaction temperature and monomer concentration.

Table 1
Influence of temperature and monomer concentration on *G* (%).

Temperature (°C)	Concentration of methacrylic acid (mol/dm^3)			
	1.452	1.162	0.968	0.775
55	7.17%	Failure	Failure	Failure
60	10.98%	9.97%	Failure	Failure
65	Instantly	16.74%	14.63%	Failure
70	Instantly	Instantly	17.63%	16.02%
75	Instantly	Instantly	Instantly	12.94%

Table 2
Influence of the reaction time on percentage of grafting.

Reaction time (min)	Percentage of grafting (*G*%)
30	11.39
90	13.16
150	16.02
210	15.97
270	13.18

3.2.2. Influence of reaction time

For further investigation, the synthesis where *G* = 16.02% was chosen, although this was not the synthesis with the highest percentage of grafting. In this reaction, reaction time was 150 min, PPS amount was 0.0015 mol, amount of starch was 10.00 g, temperature was 70 °C and monomer concentration was 0.775 mol/dm^3. Reason for this was in easier reaction conditions, such as low viscosity and easier sustaining of reaction temperature. Influence of the reaction time on *G* (%) is shown in Table 2.

Based on results shown in Table 2, it is clear that *G*% is highest at 150 min. With the short reaction time (30 min), methacrylic acid could not polymerize completely and amount of grafted poly(methacrylic acid) was smaller than maximum. With increasing of reaction time methacrylic acid polymerized in larger amount and percentage of grafting was maximum (the reaction times was 150 and 210 min). With further reaction time increase, *G* (%) decreases, because the monomer and initiator concentration decrease as well as reduction in the number of sites available for grafting.

3.2.3. Influence of initiator amount

In this investigation, the influence of initiator amount (PPS) on percentage of grafting was investigated. Results are shown in Fig. 1. The reaction conditions were: amount of starch was 10.00 g, temperature was 70 °C, concentration of methacrylic acid was 0.775 mol/dm^3 and reaction time was 150 min.

From Fig. 1 it is obvious that percentage of grafting increases 2.5 time (from 8.57 to 22.94%) with PPS amount increasing from 0.0007 to 0.001 mol. With further PPS amount increase, *G* (%) decreases and *G* (%) values were approximately the same (between 14.54

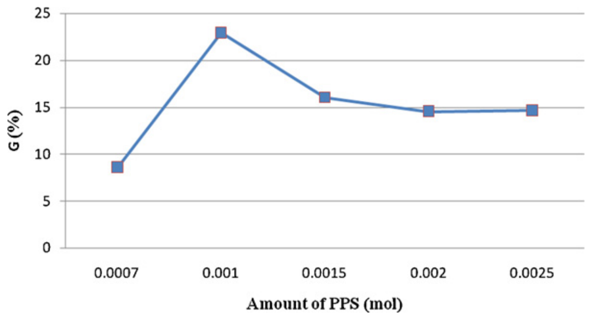


Fig. 1. Influence of amount of PPS on *G* (%).

Table 3
Influence of amine activators on *G* (%).

Amine activator	p*K* value	Percentage of grafting (*G*%)
Propylamine	10.60	16.93
Iso-butylamine	10.68	20.56
Pentylamine	10.63	14.89
Hexylamine	10.56	9.52
N,*N*-dimethylethanolamine	10.30	21.12
N,*N*-diethylethanolamine	9.87	24.69
Triethylamine	10.75	16.66
1-(2-Hidroxyethyl) piperazine	9.27	15.63
4-(2-Hidroxyethyl) morpholine	6.95	40.92

and 16.02%). The increase in *G* (%) may be due to an increase in starch macroradicals, since an increase in concentration facilitates more of PPS free radicals to attack the saccharide unit of starch. This would generate more starch macroradicals and more active sites to react with MAA. By further increasing the amount of PPS (>0.001 mol), the concentration of $-OSO_3^*$ radicals would increase resulting in a decrease of % *G*. This phenomenon may be due to the efficiency of PPS to participate in the termination reaction of the growing grafted chain as well as homopolymerization of methacrylic acid, which competes with the grafting reaction for the available monomer. Based on these results, the highest percentage of grafting was 22.94% when PPS amount was 0.001 mol.

3.2.4. Influence of amines

Influence of amount and nature of amine activators on percentage of grafting was also investigated. For this investigation, the reaction with highest percentage of grafting (22.94%) was used. The aim was to obtain copolymers with maximum values of *G* (%). The reaction conditions were: starch was added in amount of 10.00 g, methacrylic acid concentration was 0.775 mol/dm^3, PPS amount was 0.001 mol, reaction temperature was 70 °C and reaction time was 150 min. Amine activator was added immediately after initiator (PPS). Following amine activators were used: *N*,*N*-dimethylethanolamine, *N*,*N*-diethylethanolamine, triethylamine, propylamine, iso-butylamine, pentylamine, hexylamine, 1-(2-hidroxyethyl) piperazine and 4-(2-hidroxyethyl) morpholine. Amount of added amine activator was 0.001 mol (activator initiator ratio was 1:1). Influence of these amine activators on *G* (%) is shown in Table 3.

Based on results shown in Table 3, it is obvious that amines showed dual impact. They act as activators and as inhibitors of polymerization reaction. The activator effect was seen in two cases: first when *N*,*N*-diethylethanolamine was used as activator and second when 4-(2-hidroxyethyl) morpholine was used. Increasing in *G* (%) was slightly below 2% in first case and in second case this increasing was very large (18%). In all other cases, amines showed inhibitory effect. Reason for this influence should be sought in their acidity, comparing the p*K* values of similar amines. p*K* values of these amines are shown in Table 3.

Based on p*K* values of amines, it can be said that they are all weak acids. Comparing the p*K* values of primary amines, it is obvious that these values are very similar. Differences in percentage of grafting originated only from alkyl chain length. Percentage of grafting decreases with increasing of alkyl chain length. Deviation occurred with iso-butylamine, where *G* (%) value was higher than *G* (%) value with propylamine. Here, the strong influence of steric effect on percentage of grafting was seen. When *G* (%) values for *N*,*N*-dimethylethanolamine, *N*,*N*-diethylethanolamine and triethylamine were compared, it could be seen that with decreasing of p*K* values increases percentage of grafting. Among these three amines, the strongest acid was *N*,*N*-diethylethanolamine and it showed the highest *G* (%) value, while the weakest acid was triethylamine and it showed the smallest *G* (%) value. When considered *G* (%) values for 1-(2-hidroxyethyl) piperazine and 4-(2-hidroxyethyl) morpholine, it can be seen that percentage of grafting differs more than 2.5 times. Reason for this difference can be found by comparing their p*K* values. Morpholine derivative is a stronger acid than piperazine derivative and their p*K* values differ for 2.3 units. The morpholine derivative was the strongest acid of all amines and it percentage of grafting was the highest (*G* = 40.92%). Based on this research, it can be concluded that the acidic activators with lowest p*K* values were suitable for grafting reaction of poly(methacryllic acid) on starch.

Influence of amount of amine activators were investigated with the aim to obtain copolymers with highest *G* (%). Syntheses were

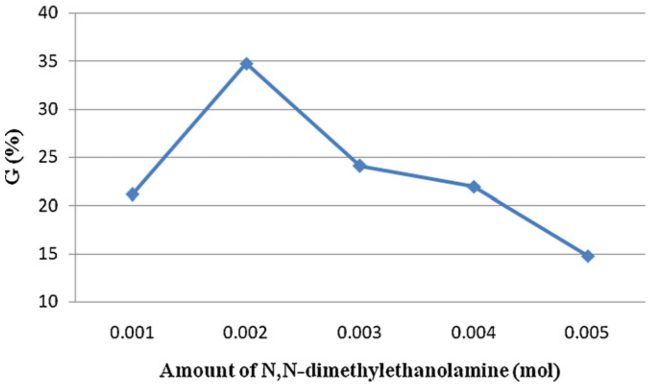


Fig. 2. Influence of amount of *N*,*N*-dimethylethanolamine on *G* (%).

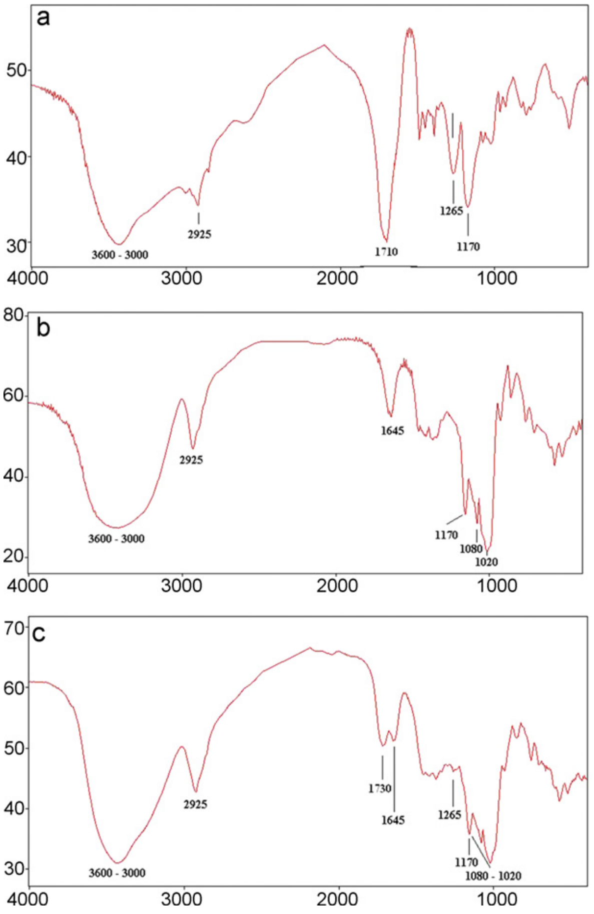


Fig. 3. FTIR spectra of poly(methacrylic acid) (a), starch (b) and PMAA-*graft*-starch copolymer (c), with *G* (%) = 21.12.

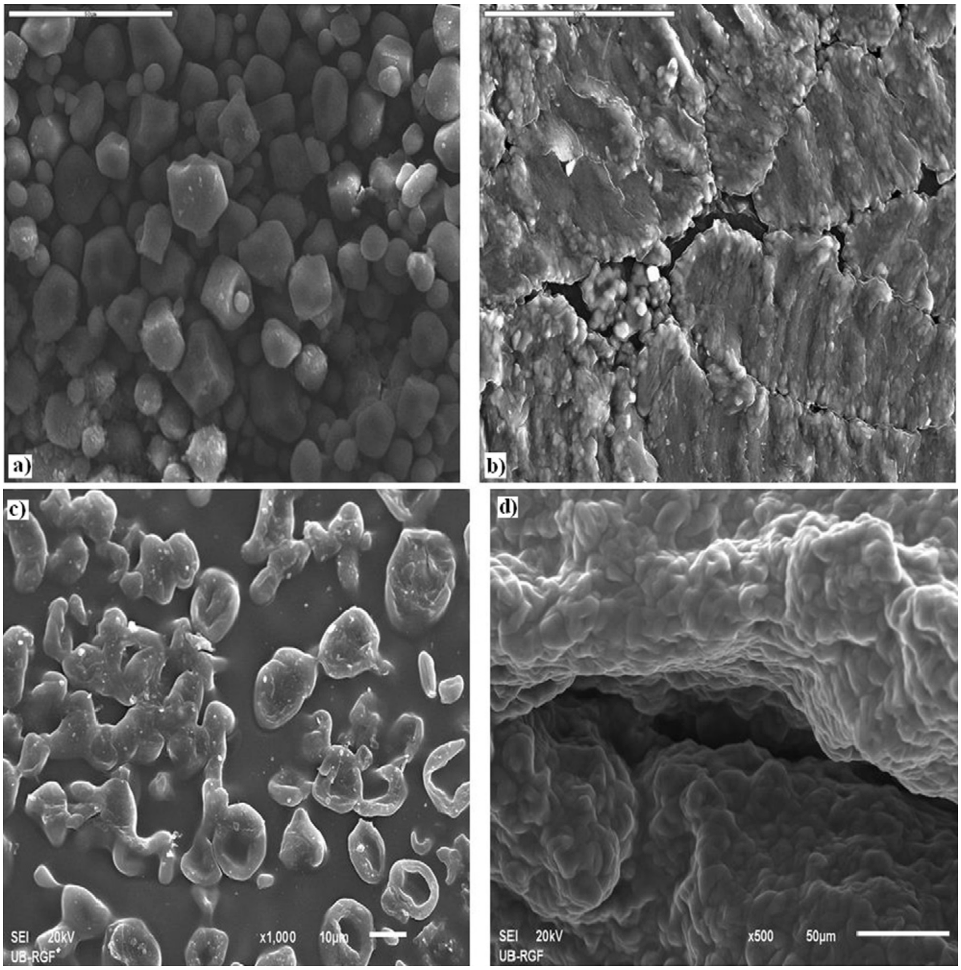


Fig. 4. SEM micrographs of starch (a), poly(methacrylic acid) (b) and PMAA-*graft*-starch copolymers (c) and (d), with different *G* (%), (c) *G* (%) = 22.94, (d) *G* (%) = 34.72.

done with all amines. The amount of amine was increased to 0.002 mol (initiator activator ratio was 1:2). The reference value for percentage of grafting in reaction without activator was 22.94%. Results of this experiment are presented in Table 4.

Based on results shown in Table 4 it can be seen that when amount of amines increases, percentage of grafting increases for all amines, except for the 1-(2-hidroxyethyl) piperazine and 4-(2-hidroxyethyl) morpholine. 1-(2-hidroxyethyl) piperazine was inhibitor of this reaction independent of the amount added. When 4-(2-hidroxyethyl) morpholine is considered, it can be seen that morpholine derivative acts as reaction inhibitor, while in amount of 0.001 mol morpholine derivative was the best activator, with *G* (%) = 40.92. With all other amines *G* value increases. Beside the *N*,*N*-diethylethanolamine, propylamine and *N*,*N*-dimethylethanolamine become reaction activators. For all other amines, the percentage of grafting increasing is not enough to show activating effect on grafting reaction.

Table 4
Influence of amine activators on *G* (%). Amount of activator was 0.002 mol.

Amine activator	Percentage of grafting (*G*%)
Propylamine	26.99
Iso-butylamine	22.65
Pentylamine	20.69
Hexylamine	18.50
N,*N*-dimethylethanolamine	34.72
N,*N*-diethylethanolamine	24.81
Triethylamine	21.58
1-(2-Hidroxyethyl) piperazine	11.84
4-(2-Hidroxyethyl) morpholine	17.09

From Table 4 it can be seen that the highest increase in the percentage of grafting occurs in the case of *N*,*N*-dimethylethanolamine. This increase was 13.60%. Based on this result, influence of further increase of the *N*,*N*-dimethylethanolamine amount on the percentage of grafting was investigated. Graphical representation of this dependence is shown in Fig. 2. In Fig. 2 is shown the previous results where amount of *N*,*N*-dimethylethalolamine was 0.001 and 0.002 mol.

Based on results from Fig. 2 it is obvious that with further increase of *N*,*N*-dimethylethanolamine amount there was no increase in grafting percentage. When the amount of *N*,*N*-dimethylethanolamine increases from 0.001 to 0.002 mol, percentage of grafting increases to 34.72%. With further increase, the percentage of grafting decreases. *N*,*N*-dimethylethanolamine showed activating effect compared to the referent synthesis without activator (*G* = 22.94%) only in cases when it was added in amounts of 0.002 and 0.003 mol. When amounts of this amine were smaller or greater than the above, *N*,*N*-dimethylethanolamine acted as an inhibitor of grafting reaction between poly(methacrylic acid) and starch.

Based on all the experiments, the highest percentage of grafting was 40.92%. The reaction conditions were: amount of starch was 10.00 g, methacrylic acid concentration was 0.775 mol/dm^3, reaction temperature was 70 °C, reaction time was 150 min, amount of initiator (PPS) was 0.001 mol and 4-(2-hidroxyethyl) morpholine was used as an activator in amount of 0.001 mol.

3.3. Characterization of PMAA-graft-starch copolymer

3.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

PMAA-*graft*-starch copolymers were characterized by FTIR spectroscopy. Fig. 3 shows FTIR spectra of poly(methacrylic acid) (a), starch (b) and PMAA-*graft*-starch copolymer (c) with percentage of grafting of 21.12%.

FTIR spectra in Fig. 3(a) and (b) show characteristic peaks of poli(methacrylic acid) and starch. The characteristic peaks for poly(methacrylic acid) are: 2925 cm^{-1}, originates from stretching C—H vibrations; peak on 1710 cm^{-1} originates from C═O vibrations of carboxyl group; peak on 1265 cm^{-1} originates from C—C—O and C—O vibrations and peak on 1170 cm^{-1} originates from C—O stretching vibrations. Peaks characteristic for starch are the C—O stretching vibrations at 1170–1020 cm^{-1}, 2925 cm^{-1} are the stretching C—H vibrations from CH_2 group, while the broad 3600–3000 cm^{-1} region stems from O—H stretching vibrations. There is one more peak at 1640–1650 cm^{-1} that is characteristic for starch. Pal, Mal, and Singh (2005) believe that this peak originates from the first overtone OH bending, and Lee, Kweon, Koh, and Lim (2004) believe that this peak originates from the stretching COC vibrations.

Fig. 3(c) depicts the FTIR spectrum of PMAA-*graft*-starch copolymer with percentage of grafting of 21.12%. In this FTIR spectrum, all characteristic peaks from poly(methacrylic acid) and starch are present. The most important peaks are: the peak on 1645 cm^{-1} and region between 1170 and 1020 cm^{-1} that originates from starch and the peaks on 1730 cm^{-1} and 1265 cm^{-1} that originate from poly(methacrylic acid). Comparing the spectra 3 (a) and 3 (c) it can be seen that peak which originates from C═O vibrations of carboxyl group moves from 1710 to 1730 cm^{-1}. The appearance of a new characteristic absorption peak at 1730 cm^{-1} in the FTIR spectrum of the PMAA-*graft*-starch because of carbonyl stretching vibrations of carboxylic acid groups along with other bands with weak intensity indicates the formation of graft copolymer. There is no characteristic absorbance peak in region between 1770 and 1735 cm^{-1} because of ester moiety and no possibility of ester formation in the grafting reaction, which could be an effective evidence for the absence of formation of esters, and hence, formation of any esters is excluded.

3.3.2. Scanning Electron Microscopy (SEM)

PMAA-*graft*-starch copolymers were characterized by SEM microscopy. In Fig. 4, the SEM micrographs of starch (a), poly(methacrylic acid) (b) and PMAA-*graft*-starch copolymers (c) and (d) are shown. Fig. 4(a) shows particles of starch that are all almost spherically shaped. The particles size varies from 5 to 20 μm. SEM micrograph of poly(methacrylic acid) (Fig. 4(b)) shows that PMAA during polymerization creates plates (panels). These panels make dense structure, with smaller or larger cracks. The panels of poly(methacrylic acid) can reach dimension of 500 × 200 μm.

Fig. 4(c) and (d) shows SEM micrographs of PMAA-*graft*-starch copolymer with different *G* (%). Fig. 4(c) shows PMAA-*graft*-starch copolymer's surface micrograph with percentage of grafting of 22.94%. Fig. 4(d) shows the micrograph of copolymer intersection with percentage of grafting of 34.72%.

Based on micrographs shown in Fig. 4 it is obvious that PMAA was not only present on the sample's surface, but also in its interior. Fig. 4(c) shows that starch granules come out from plate structure of PMAA. In Fig. 4(d), which shows the intersection of the sample, it can be seen that large amount of poly(methacrylic acid) can be found in sample inside. PMAA completely covers starch granules, probably in thin layer, because starch granules are notice under PMAA. Based on these micrographs, it is obvious that there was a change in granular shape of starch, before and after polymerization.

Although SEM is not a method that confirms grafting, based on PMAA presence on surface and inner layers of copolymer and together with results of FTIR spectroscopy and products obtained after purification, it can be said that grafting occurred.

4. Conclusion

In this manuscript, the synthesis of poly(methacrylic acid) and starch copolymer was done. The maximum value for *G*% was 22.94%, without using initiation activator. Reaction conditions such as temperature, time, initiator amount and monomer concentration have shown an influence on grafting. The optimal reaction time was 150 min and the amount of initiator was 0.001 mol. It was found that with temperature and monomer concentration increase, the percentage of grafting increases. The addition of amines, only propylamine, *N*,*N*-dimethylethanolamine, *N*,*N*-diethylethaolamine and 4-(2-hidroxyethxl) morpholine showed activating effect. The best activator was 4-(2-hidroxyethyl) morpholine in amounts of 0.001 mol. Achieved percentage of grafting using this activator was 40.92%, which is almost two times more than *G* (%) achieved in reaction without activator. Based on p*K* values of used amines, it was found that percentage of grafting increases when the used amine was stronger acid. This claim can be confirmed on the example of 4-(2-hidroxyethyl) morpholine for which the p*K* was 6.95 and percentage of grafting was 40.92% in comparison with 1-(2-hidroxyethyl) piperazine whose p*K* was 9.27 and percentage of grafting was only 15.63%. The copolymers were characterized by FTIR spectroscopy and SEM microscopy. Grafting was confirmed by FTIR spectroscopy. The peak on 1710 cm^{-1} which originates from C═O vibration of poly(methacrylic acid) moved at 1730 cm^{-1} in PMAA-*graft*-starch copolymer. This shift was main proof for successful grafting reaction between starch and poly(methacrylic acid). Based on the way of copolymer purifying (water, ethanol purifying and hydrolysis), FTIR spectroscopy results and SEM micrographs, it was confirmed that bonding between polystyrene and starch occurred.

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