

pH Sensitive Polymeric Binders for Energetic Materials

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The aim of this research has been to develop a new generation of eco-friendly binders, soluble at alkaline pH, which could allow facile recovery of explosive fillers without using organic solvents, while maintaining their chemical and physical characteristics. For this purpose, "smart" polymeric binders are to be designed based on acrylic acid and other acrylic monomers. In this view, theoretical and experimental studies have been performed in order to establish which synthesized polymer is adequate for the desired application.

Keywords: acrylic polymers, synthesis, pH sensitivity

In the context of harsher and increasingly complex international and European environmental legislation, numerous states are more and more aware of the necessity of developing reliable and efficient methods for the demilitarization and disposal of ammunition. It is already acknowledged that ammunition demilitarization [1] is a complex, dangerous and expensive process. The removal of energetic materials (especially secondary explosives) is one of the most difficult steps in this process. Conventional methods are based on solvent solubilisation or water jet removal of explosives from the ammunition shell [2].

Following this process, the energetic material (EM) is extracted and then it can be neutralised or recovered, recycled and reused. Neutralisation of energetic materials usually involves open burning or open detonation, which are limited or no longer accepted in many European countries. Another option is incineration in special designed facilities with subsequent air purification systems.

Nowadays, the decrease of the EM producers' number at global level has made the recovery process more feasible. But using organic solvents is always expensive and hazardous while water-based methods can be applied to a small range of explosive formulations and give large amounts of contaminated waste water to be purified.

Another challenge of the EM recovery process is to maintain intact their physical and chemical properties. In modern explosive compositions, the crystalline solid explosive substances are embedded in a polymeric matrix (binder). One of the disadvantages of these modern explosive compositions is the low solubility of the typical binders [3-5], for which the recovery of explosives at the end of ammunition's life cycle is considered to be an expensive and dangerous process.

Usually, in explosive compositions there are used crystalline explosives with broad particle sizes (bi-modal or tri-modal mixtures) coated in a polymeric binder/adhesive. Further, during classical solvent-based recovery processes, the morphology of the explosive crystals changes.

In this context, the object of the study was to develop a new generation of eco-friendly binders, which could allow facile recovery of the explosive filler, without using organic solvents, while maintaining its chemical and physical

properties. For this purpose, *smart* polymeric binders have been designed. These new polymers possess excellent adhesive properties, are insoluble in water at normal temperature and pH conditions, but should readily dissolve when one or both of these parameters are affected. Especially polymers becoming soluble at basic pH (10-11) are interesting from the point of view of explosives processing, because acidic solutions/impurities ratio usually affects the stability of nitro-derivatives.

Copolymers of acrylic acid and alkyl acrylates were identified as potential candidates for this new class of polymers. In fact, the acidic units could provide ionic groups in the presence of a basic reagent increasing the solubility of the polymer, while alkyl acrylate groups make the polymer insoluble in water and provide the desired mechanical properties.

Since now, the synthesis of this kind of acrylic polymeric adhesives - soluble in weak basic aqueous solutions has never been reported previously in the open literature.

Polymers derived from acrylic acid and methacrylic acid are most commonly used in adhesive synthesis [6]. These polymers are used either alone or copolymerized with a variety of other polymers, e.g. polyethylene or vinyl acetate, particularly for laminating processes and the production of pressure sensitive materials (PSAs - *pressure-sensitive adhesives* [7], with applications in automotive, aerospace and electronics industries [8], bio-electrodes [9] and as smart adhesives for transdermal drug delivery systems [10]). In all these cases, the polymer is preformed in a manufacturing process and is applied either as a solution in an organic solvent or as an aqueous dispersion [11].

Usually, mixtures of acrylic acid and its esters are used to obtain adhesives. These esters are short chain derivatives (e.g. methyl or butyl methacrylate) or derive from much higher molecular weight alcohols (e.g. tetrahydrofurfuryl or 2-ethylhexyl). The adhesive contains a free radical initiator, which is usually an organic peroxide, and a free radical stabilizer. These are included with the acrylate materials in a viscous gel, commonly described as *the adhesive*. The polymerisation reaction is initiated by butyraldehyde and aniline, which is a powerful reducer that causes the free radical initiator to decompose. Copper octanoate accelerates the polymerisation reaction [12].

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Yana Peykova et al. [13] have studied the influence of the incorporation of an additional co-monomer, namely, hydroxyethyl acrylate, methyl methacrylate and acrylic acid, on the adhesion of statistical, uncrosslinked buthyl acrylate-methyl acrylate copolymer. The adhesion performance of uncrosslinked and crosslinked butyl acrylate-methyl acrylate copolymers was compared. It was observed that the crosslinked polymers showed the best adhesion. Macais et al. [14] have studied the adhesion performances of MMA/2-EHA(2-ethylhexyl acrylate) obtained by continuous and semicontinuous emulsion polymerisation. Shull et. al. [15] have studied some triblock copolymers that have poly(methyl methacrylate) at ends and in the middle poly(butyl methacrylate). In another study, R. Jovanovic et al. [16] have studied how the method chosen influences the adhesion properties. The thermal degradation of butyl acrylate/acrylic acid copolymers was studied by Z. Czech et al. [17]. In this study were obtained several polymers containing various amounts of butyl acrylate and acrylic acid. After characterization, the results showed that carbon dioxide and 1-butene were the main gaseous pyrolysis products of the acrylic polymers studied, and the main thermal degradation products were 1-butanol, butyl acrylate and butyl methacrylate.

Experimental part

Materials and methods

In order to obtain the desired polymeric binder, the following monomers were employed: butyl acrylate (BuAc, FLUKA, 98%), 2-ethylhexyl acrylate (2EHA) – industrial grade, ethyl acrylate (EtAc, ALDRICH) and acrylic acid (AAc, FLUKA, 99%). Azobisisobutyronitrile (AIBN) recrystallized from methanol served as initiator. All the solvents used were analytical reagents. 2EHA was passed through a column with basic alumina to remove the inhibitor. The other monomers, AAc, BuAc and EtAc, were purified by vacuum distillation. For the preparation of the alkaline solutions, a solution of NaOH (Lachema) diluted in distilled water was used.

In order to obtain the polymer/sand composite, the synthesized polymer was dissolved in N,N-Dimethyl-formamide (DMF, Merck).

During the study, the following analytical grade solvents were used: toluene, methanol, absolute ethanol, hexane, propylene glycol, acetone, petroleum ether, ethyl acetate, ethylene glycol, dimethylsulfoxide (DMSO), DMF and chloroform.

Mixtures of monomers were prepared in different molar ratios (table 1). The reagents (table 1) were added in glass round-bottom reactor flasks of 25 mL resulting 4 mL monomers mixture. It was also added the initiator, the solvent (16 mL) and a magnetic bar. The initiator is added in a ratio of ca. 1% versus monomers (w:v). The flasks are sealed with septa tops and adhesive tape. To eliminate the oxygen from the flasks they were bubbled with nitrogen for 15 min. After bubbling, the flasks were introduced in an oil bath at 65°C and allowed the reaction to take place under stirring for 24h.

After 24h, the flasks were removed from the oil bath. The obtained polymers were precipitated in petroleum ether in polyethylene test tubes to avoid sticking on the walls. The precipitation was made slowly drop by drop and under stirring. The polymers which were very viscous were diluted in ethyl acetate and precipitated afterwards. When the solvent was not easy to remove, the granular polymers were filtered. After precipitation, the polymers were dried under vacuum.

Characterisation

To characterise the polymers obtained, infrared spectroscopy (FT-IR) and Differential Scanning Calorimetry (DSC) analyses were performed.

FT-IR spectra were registered with a Bruker VERTEX 70 spectrometer with ATR device, using 32 scans at a resolution of 4 cm⁻¹ and the characteristic frequencies of the molecules of each polymer were determined.

The glass transition temperature (T_g) of the synthesized polymers was determined by measurements with NETZSCH 204 F1 Phoenix apparatus, under nitrogen steam at a heating rate of 10 °C/min. Samples weighing ca. 10 mg were heated/cooled between -80 and 150°C, T_g being determined from the kink point during the second heating cycle.

Molar ratio	EtAc, mL	AAc, mL	AIBN, g
7:3	3.2	0.8	0.038
5:5	2.5	1.5	0.039
3:7	1.7	2.3	0.004
	BuAc, mL	AAc, mL	AIBN, g
7:3	3.3	0.7	0.036
5:5	2.7	1.3	0.037
3:7	1.9	2.1	0.038
	2EHA, mL	AAc, mL	AIBN, g
7:3	3.5	0.5	0.036
5:5	3	1	0.037
3:7	2.25	1.75	0.038

Table 1
MONOMER AND INITIATOR
QUANTITIES USED DURING
EXPERIMENTS

Molar ratio	Conversion 2EHA/AAc [%]	Conversion EtAc/AAc [%]	Conversion BuAc/AAc [%]
7:3	28.5	94.1	85.4
5:5	70	85.3	87.7
3:7	81.3	87.9	85.8

Table 2
2EHA/AAc, BuAc/AAc AND
EtAc/AAc CONVERSIONS

Water absorption test

The aim of this paper was to find a polymer capable of dissolving in an alkaline solution, while being insoluble in water. Ammunition can be stored in locations with high humidity, transported on a rainy weather or at some point immersed in water, so the polymer must be waterproof. Several milligrams of synthesized polymers and 200 mL of distilled water were introduced in beakers with lid and kept for 24h at room temperature. After 24h, the polymers were filtered, weighed and the absorption percentage was calculated.

Solubility test

The binders synthesized during this study are supposed to be soluble in an organic solvent in order to be able to be used to coat explosive crystals. For this purpose, first they have to be solubilised, then the lacquer obtained to be mixed with the solid particles and further the solvent to be evaporated.

20 mg of synthesized polymers and 5 mL of solvent were introduced in graduated glass tubes. The tubes were sealed with septa tops and adhesive tape and left 24 h at room temperature (20°C). After 24 h, the polymer dissolution was observed.

Solubility test - alkaline solution

The central aim of this work was to obtain a binder which is soluble in an alkaline aqueous solution without modifying the physical and chemical properties of the explosive filler. The classical binders exhibit very good mechanical, physical and chemical properties, but during the recovery process of explosives at the end life of ammunitions, their properties change.

4 mg of NaOH and 200 mL distilled water were introduced in a beaker. The alkaline solution obtained had the concentration 1M and a measured pH of 14. From this, alkaline solutions of pH 13, 12 and 11 were made.

20 mg of polymers were introduced in 15 mL graduated glass tubes. The tubes were filled with alkaline solution and were sealed with septa tops and then were kept for 24 h at room temperature (20°C), 30 and 50 °C. After 24 h the polymer dissolution was observed.

Results and discussions

Polymer synthesis

Following the procedures described above, there were synthesized 2EHA/AAc, BuAc/AAc and EtAc/AAc copolymers in different molar ratios: 3:7, 7:3 and 5:5. The conversions obtained are given in table 2.

It was observed that the conversion increases with the amount of acrylic acid.

In the case of 2EHA/AAc, it was observed that after 24h the polymer with 7:3 molar ratio was viscous and did not precipitate; the polymer with 5:5 molar ratio did precipitate and the polymer with 3:7 molar ratio was cloudy, viscous and did not precipitate.

From table 2 it can be observed that the best conversion of EtAc/AAc copolymer was obtained for a 7:3 molar ratio. After 24 h, the EtAc/AAc copolymer with 3:7 molar ratio did precipitate; the polymer with 5:5 molar ratio precipitated (less than 3:7 EtAc/AAc) and the polymer with 7:3 molar ratio did not precipitate, was viscous and cloudy.

For the BuAc/AAc copolymer, it can be observed that very good conversion rates were obtained (over 80%).

FT-IR analysis

Following FT-IR analysis, the characteristic bands of each polymer were observed. There were also observed the increase/decrease of characteristic peaks versus concentration. In figure 1 are shown the FT-IR spectra for the synthesized copolymers.

In figure 1a, one may notice both peaks, characteristic for 2EHA and AAc groups. For the 2EHA/AAc copolymer with 3:7 molar ratio, the characteristic peak can be observed at 1732 cm⁻¹ of C=O group from 2EHA, and at 1710 cm⁻¹ - the characteristic peak of -COOH group from

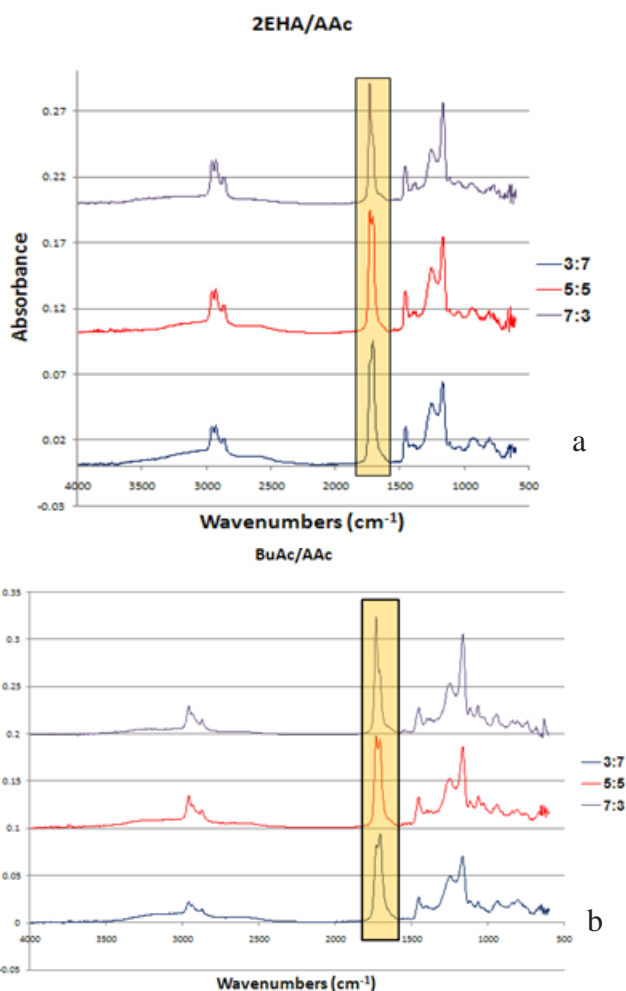


Fig. 1. Comparative FT-IR spectra of: a) 2EHA/AAc; b) BuAc/AAc

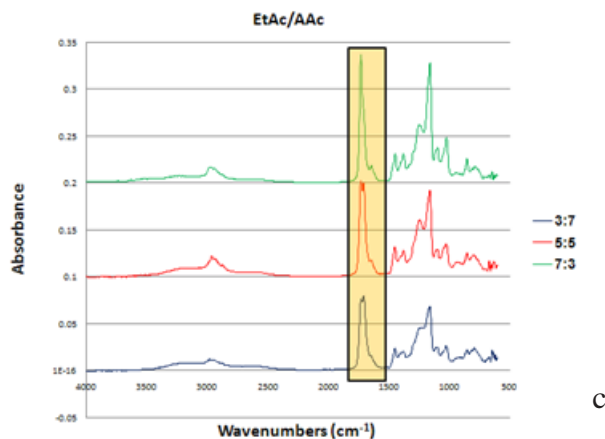


Fig. 1. Comparative FT-IR spectra of: c) EtAc/AAC

AAC. From the FT-IR spectrum, it can be seen that the characteristic C=O group of 2EHA is lower than the -COOH peak from AAC, which confirms the initial molar ratio of the comonomers used to obtain 2EHA/AAC 3:7 copolymer. For the 2EHA/AAC copolymer with 5:5 molar ratio, it can be seen that the characteristic peak of C=O from 2EHA is at 1732 cm^{-1} , and the -COOH from AAC is at 1728 cm^{-1} . The characteristic peak of C=O group from 2EHA is almost equal to the characteristic peak of -COOH group of AAC, which confirms the initial molar ratio of the monomers used for obtaining the 2EHA/AAC 5:5 copolymer. In case of the 2EHA/AAC copolymer with 7:3 molar ratio, it is observed a characteristic peak C=O of 2EHA at 1732 cm^{-1} and at 1716 cm^{-1} the COOH characteristic peak from AAC. The FT-IR spectrum shows that the C=O characteristic peak from 2EHA is higher than the COOH characteristic peak from AAC, which confirms the initial molar ratio of the comonomers used for obtaining 2EHA/AAC 7:3 copolymer.

In figure 1b, both peaks, characteristic to BuAc and to AAC, can be seen. For the BuAc/AAC copolymer with 3:7 molar ratio, the characteristic peak can be observed around 1732 cm^{-1} for C=O group of BuAc, and at 1708 cm^{-1} for -COOH from AAC. From the FT-IR spectrum, it can be seen that the characteristic group of AAC is higher than the characteristic peak from BuAc, which confirms the initial molar ratio of the monomers used to obtain BuAc/AAC 3:7 copolymer. For the BuAc/AAC copolymer with 5:5 molar ratio, it can be seen that the C=O characteristic peak from BuAc is still at 1732 cm^{-1} , but the -COOH characteristic peak from AAC moves to 1728 cm^{-1} . From this spectrum, one may notice that the characteristic peaks of BuAc and AAC are almost equal, which confirms the

initial molar ratio of the comonomers used for obtaining the BuAc/AAC 5:5 copolymer. In the case of BuAc/AAC copolymer with 7:3 molar ratio, it is observed the characteristic peak of C=O from BuAc at 1732 cm^{-1} and at 1728 cm^{-1} it can be seen the characteristic peak of -COOH from AAC. It is obvious from the FT-IR spectrum that the characteristic peak of BuAc is higher than the characteristic peak of AAC, which confirms the initial molar ratio of the comonomers used for obtaining the BuAc/AAC 7:3 copolymer.

In figure 1c, both peaks, characteristic to EtAc and AAC, are emphasized. For the EtAc/AAC copolymer with 3:7 molar ratio, the characteristic peak of C=O from EtAc can be observed at 1730 cm^{-1} , and at 1706 cm^{-1} it can be seen the characteristic peak of -COOH from AAC. From the FT-IR spectrum of this peak, it can be noticed that the characteristic peak of AAC is higher than the characteristic peak of EtAc, which confirms the initial molar ratio of the comonomers used to obtain EtAc/AAC 3:7 copolymer. In case of EtAc/AAC copolymer with 5:5 molar ratio, it can be seen that the peak of the characteristic C=O from EtAc remains at 1732 cm^{-1} , while the peak of -COOH from AAC moves to 1706 cm^{-1} . From the FT-IR spectrum, it is noticeable that the characteristic peaks of EtAc and AAC are almost equal, which confirms the initial molar ratio of the comonomers used for obtaining the EtAc/AAC 5:5 copolymer. In case of EtAc/AAC copolymer with 7:3 molar ratio, it is observed the characteristic peak of C=O from EtAc at 1730 cm^{-1} and that of -COOH from AAC at 1714 cm^{-1} . The characteristic peak for EtAc is higher than the characteristic peak of AAC, thus confirming the initial molar ratio of the comonomers used for obtaining the EtAc/AAC 7:3 copolymer.

DSC analysis

In figure 2 are given the thermograms of polymers synthesized and in table 3 the values obtained for Tg.

Thermograms of 2EHA/AAC copolymer are presented in figure 2a. It can be seen that Tg decreases in value, from 57.8°C to -25.9°C (table 3). This is due to the content of AAC in the polymer. As more AAC we mix, the Tg value of 2EHA/AAC copolymer increases, AAC homopolymer having Tg ca. 105°C . Also, if the amount of 2EHA increases, Tg of 2EHA/AAC copolymer decreases, 2EHA having a Tg around -50°C . The Tg variation shows copolymer formation.

Thermograms of BuAc/AAC copolymer are given in figure 2b. It can be seen that Tg decreases in value, from 109.1°C to -3.6°C (table 3). This is due to the content of

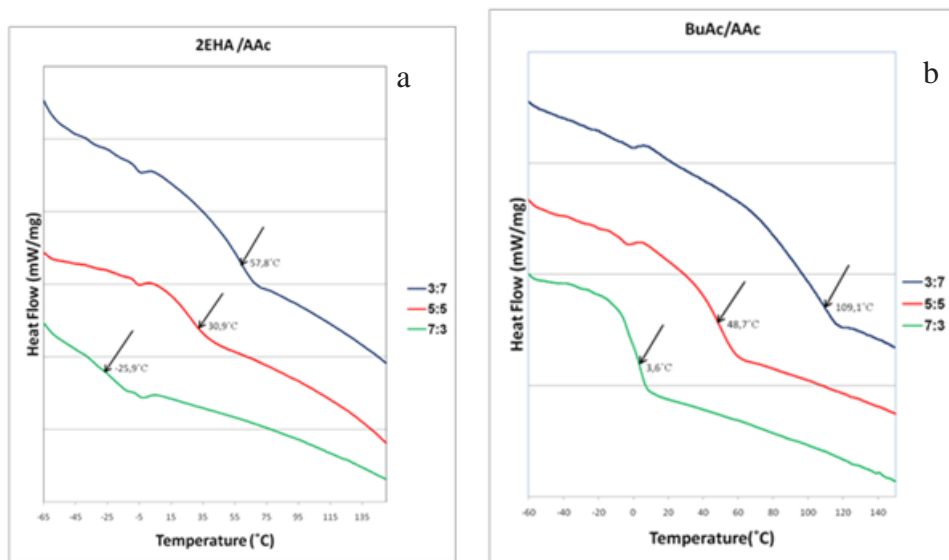


Fig. 2. DSC thermograms: a) 2EHA/AAC; b) BuAc/AAC

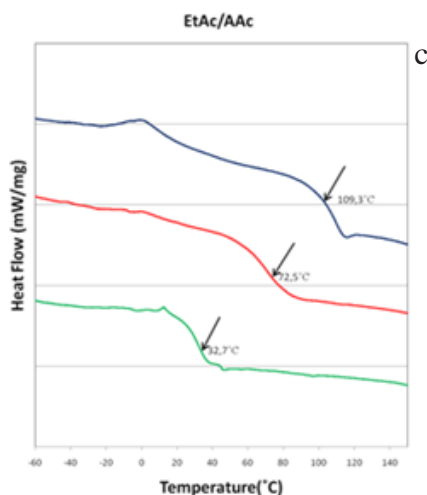


Fig. 2. DSC thermograms: c) EtAc/AAC

Molar ratio of the comonomers	Tg of 2EHA/AAC copolymers [°C]	Tg of EtAc/AAC copolymers [°C]	Tg of BuAc/AAC copolymers [°C]
7:3	-25.9	3.6	32.7
5:5	30.9	48.7	72.5
3:7	57.8	109.1	109.3

Table 3
Tg VALUES FOR 2EHA/AAC POLYMER

AAC in the copolymer. As more AAC is added, the Tg value of BuAc/AAC copolymer increases. More, if the amount of BuAc increases, Tg of BuAc/AAC copolymer decreases, BuAc having a glass transition temperature around -54°C. It is to note that in the case of large amounts of AAC, the value of Tg exceeds the Tg value of pure pAAC, although BuAc FT-IR spectra showed the presence of the copolymer. Probably, due to dehydration, intramolecular anhydride copolymer cycles form during DSC analysis, which yield higher Tg values than expected. Anhydride cycles stiffen chain and thus increase the Tg, which can reach 140 °C at a content of 100% cycles [18].

Thermograms of EtAc/AAC copolymer are illustrated in figure 2c. It can be observed that Tg decreases in value, from 109.3 °C to -32.7 °C (table 3). This is also due to the content of AAC in the polymer. Moreover, if the amount of EtAc increases, the Tg value of EtAc/AAC copolymer decreases, EtAc having a glass transition temperature around -24 °C. It is worth noting that in this case it is also likely to occur anhydride cycles formation, as shown by the higher Tg value for the copolymer 3:7 versus the value reported in the literature for pAAC.

Swelling test

To determine the water absorption degree of the synthesised polymers, 30-40 mg of polymer were immersed in 200 mL distilled water for 24h. After 24h, the polymers were weighted and the water absorption degree was calculated. The results are shown in table 4.

The results indicate that the water absorption percentage is rather low. It can be also observed that the percentage value decreases while increasing the BuAc, EtAc and 2EHA comonomers ratios in the copolymer.

Solubility test in various organic solvents

The copolymers obtained were introduced in different polar and non-polar solvents to determine whether they are soluble or not. The solvents used were: toluene,

methanol, absolute ethanol, hexane, propylene glycol, acetone, petroleum ether, ethyl acetate, ethylene glycol, DMSO, DMF and chloroform.

After having introduced 20 mg of polymers in 5 mL of solvent, they were allowed to react at room temperature during 24h. Tests were performed at least in triplicate. The results obtained are shown in table 5.

It can be observed that methanol, hexane, petroleum ether and chloroform did not dissolve any of the prepared polymers. Toluene dissolved only the 2EHA/AAC copolymer with 7:3 molar ratio. Absolute ethanol dissolved 2EHA/AAC and EtAc/AAC copolymers, and partially dissolved BuAc/AAC copolymer. Propylene glycol completely dissolved EtAc/AAC copolymers with 3:7 and 5:5 molar ratios, the other polymers being insoluble in this solvent.

Acetone dissolved 2EHA/AAC with 5:5 and 7:3 molar ratios, EtAc/AAC with 5:5 and 7:3 molar ratios and BuAc/AAC with 5:5 and 7:3 molar ratios. The following polymers were only partially dissolved in acetone: 2EHA/AAC with 3:7 molar ratio and EtAc/AAC with 3:7 molar ratio. BuAc/AAC copolymer with 3:7 molar ratio did not dissolve in acetone.

Ethyl acetate solubilised: 2EHA/AAC with 7:3 molar ratio; BuAc/AAC with 7:3 molar ratio; EtAc/AAC with 7:3 molar ratio. The other polymers were insoluble in ethyl acetate.

Ethylene glycol dissolved only EtAc/AAC copolymers with 3:7 and 5:5 molar ratios.

DMSO dissolved all the polymers, except for 2EHA/AAC with a 7:3 molar ratio.

DMF was the solvent in which all the polymers dissolved.

Solubility test in alkaline solution

For this test, 30-40 mg of polymers were immersed in test tubes of 15 mL filled with alkaline solution. The tubes with polymer and alkaline solution were sealed and maintained for 24h at room temperatures, at 30°C and at 50°C. The results obtained are presented in table 6.

Analysing the results presented in table 6, it can be observed that at pH 14, at room temperature, all six polymers dissolved.

At pH 13, at room temperature, except for 2EHA/AAC copolymer with 7:3 molar ratio, all the polymers dissolved. It can also be observed that at room temperature the synthesized polymers did not dissolve in the alkaline solutions with pH 12 and pH 11. 2EHA/AAC copolymer with 7:3 molar ratio did not dissolve in the alkaline solution with pH 13. At 30°C, in the alkaline solution with pH 12 four polymers were dissolved: EtAc/AAC molar ratio 7:3; BuAc/AAC molar ratio 3:7; BuAc/AAC molar ratio 5:5; BuAc/AAC molar ratio 7:3.

It is important to observe that EtAc/AAC polymer with 3:7 molar ratio dissolved in the alkaline solution with pH 11 at 30°C.

Table 4
WATER UPTAKE FOR THE COPOLYMERS OBTAINED AFTER 24h OF SWELLING

Copolymer	Molar ratio of the comonomers	Initial weight [mg]	Final weight after 24h [mg]	Water absorption [%]
2EHA/AAc	3:7	14.0	16.0	14.28
	5:5	6.4	7.1	10.93
	7:3	9.9	10.2	3.03
BuAc/AAc	3:7	30.5	40.4	32.45
	5:5	36.5	47.1	29.04
	7:3	37.4	39.5	5.61
EtAc/AAc	3:7	8.3	10.1	21.68
	5:5	10.0	12.0	20
	7:3	12.3	16.7	11.38

Table 5
POLYMERS SOLUBILITY AFTER 24h

Solvent	2EHA/AAc			EtAc/AAc			BuAc/AAc		
	3:7	5:5	7:3	3:7	5:5	7:3	3:7	5:5	7:3
Toluene	-	-	+	-	-	-	-	-	-
Methanol	-	-	-	-	-	-	-	-	-
Absolute ethanol	+	+	+	+	+	+	+/-	+/-	+/-
Hexane	-	-	-	-	-	-	-	-	-
Propylene glycol	-	-	-	+	+	-	-	-	-
Acetone	+/-	+	+	+/-	+	+	-	+	+
Petroleum ether	-	-	-	-	-	-	-	-	-
Ethyl acetate	-	-	+	-	-	+	-	-	+
Ethylene glycol	-	-	-	+	+	-	-	-	-
DMSO	+	+	-	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+	+
Chloroform	-	-	-	-	-	-	-	-	-

*(-) polymers not dissolved; (+) polymers dissolved; (+/-) polymers partially dissolved

Solvent	2EHA/AAc			EtAc/AAc			BuAc/AAc		
	3:7	5:5	7:3	3:7	5:5	7:3	3:7	5:5	7:3
pH 14, 20 °C	+	+	+	+	+	+	+	+	+
pH 13, 20 °C	+	+	-	+	+	+	+	+	+
pH 12, 20 °C	-	-	-	-	-	-	-	-	-
pH 11, 20 °C	-	-	-	-	-	-	-	-	-
pH 13, 30 °C	+	+	-	+	+	+	+	+	+
pH 12, 30 °C	-	-	-	-	-	+	+	+	+
pH 11, 30 °C	-	-	-	+	-	-	-	-	-
pH 13, 50 °C	+	+	-	+	+	+	+	+	+
pH 12, 50 °C	+	+	-	+	+	+	+	+	+
pH 11, 50 °C	+	-	-	+	-	-	+	-	-

Table 6
POLYMERS
SOLUBILITY
AFTER 24h

*(-) polymer not dissolved; (+) polymer dissolved

Table 7
WEIGHT PERCENTAGE COMPOSITION

	m, g	wt. %
EtAc/AAc	0.306	5.02
Sand	5.794	94.98

In the alkaline solution with pH 12, at 50°C, all the polymers, except 2EHA/AAc with 7:3molar ratio, dissolved.

At 50°C, for the alkaline solution with pH 11, three polymers dissolved: 2EHA/AAc molar ratio 3:7, EtAc/AAc molar ratio 3:7 and BuAc/AAc molar ratio 3:7.

Polymer/sand composite

In order to observe the behaviour of the selected polymer EtAc/AAc with 3:7 molar ratio when used as binder matrix for a filler material, as a first stage towards developing the binder for energetic materials, we used an inert filler, respectively sand.

0.306 g of EtAc/AAc were dissolved in 5 mL of DMF and then 5.794 g of sieved sand (0.1 - 0.2 mm fraction) were added (table 7).

The paste thus obtained was left 1h to dry partially, at room temperature, under slow mixing, and then it was granulated by passing through a 1-mm sieve. The granules obtained were dried up to constant weight in an oven at 60 °C in order to completely evaporate the solvent.

2-g portions of granular composite material were pressed at 1400 bar using a hydraulic press and a 10-mm diameter steel mould, in cylindrical shaped pellets (fig. 3).

The cylindrical pellets were introduced in 100 mL alkaline solution with pH 11 at room temperature (20°C). After 24 h, the complete disintegration of the cylinders was

observed (fig. 4). The alkaline solution became viscous indicating that the polymer was dissolved.

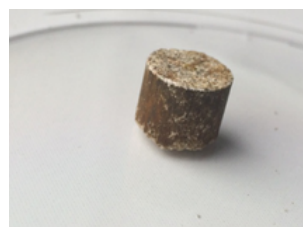


Fig. 3. Polymer/sand composite pellets

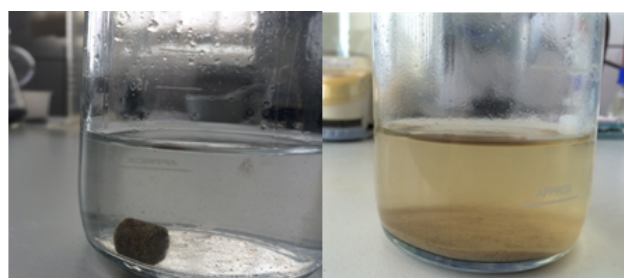


Fig. 4. Polymer/sand composite disintegration



Fig. 5. Sand recovered after composite pellet disintegration

The solution resulted was filtrated and the sand was recovered having the same granulometric properties (fig. 5).

Conclusions

Copolymers of acrylic acid and alkyl acrylates in different ratios were synthesized and characterized by FT-IR and DSC. The spectra analysis confirmed the presence of the specific absorptions for each monomer and the initial molar ratios of the comonomers used for obtaining each polymer.

The DSC thermograms indicated how the values of T_g vary versus the content in homopolymer components. Furthermore, it was noticed that T_g 's value increases with the increasing molar ratio of AAc binder. For BuAc/AAc and EtAc/AAc copolymers, it has been observed that T_g for the copolymers with 3:7 molar ratios exceeds the T_g for pure AAc, although FT-IR spectra show the presence of BuAc and EtAc units in the copolymers. This is probably due to dehydration with formation of intra-molecular anhydride copolymer cycles during DSC analysis, which led to higher T_g values than expected.

Further, it was intended for the polymers to be insoluble in water at neutral pH and soluble in weak alkaline solutions. The water uptake, the solubility in various organic solvents and also in alkaline solutions were determined. The water absorption tests showed that the percentage of absorbed water is rather low. As expected, it can be seen that the percentage of absorbed water increases with the increasing percentage of AAc units. Solubility tests in various organic solvents indicated that the solvent in which all nine synthesized polymers dissolve is DMF. The test regarding the solubility in an alkaline solution indicated that the EtAc/AAc copolymer with 3:7 molar ratio dissolved in an alkaline solution with pH 11 at 30°C. Also, at 50°C, other two polymers dissolve: 2EHA/AAc with 3:7 molar ratio and BuAc/AAc with 3:7 molar ratio.

In order to see the behaviour of the EtAc/AAc copolymer with 3:7 molar ratio selected for further tests as binder for a filler material, the polymer was mixed with sand. It was observed that the composite pellets obtained were completely disintegrated in alkaline solution (pH 11) and the sand was recovered in the original granular size range.

Thus, nine copolymers based on acrylic acid and other three comonomers: 2-ethylhexyl acrylate, butyl acrylate

and ethyl acrylate were synthesized, using various molar ratios. The EtAc/AAc copolymer with 3:7 molar ratio was found to be soluble in an alkaline solution with pH 11 at 30°C, while two other copolymers, 2EHA/AAc with 3:7 molar ratio and BuAc/AAc with 3:7 molar ratio, were found to be soluble in a pH 11 alkaline solution at 50 °C.

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