“SMART” POLYMERIC BINDERS FOR ENERGETIC MATERIALS

***ANDREEA* VOICU**[1]
MIRCEA TEODORESCU[2]
TRAIAN ROTARIU
TUDOR VIOREL TIGANESCU

1. INTRODUCTION

Nowadays states are more and more aware of the necessity of a reliable and efficient demilitarization of ammunition. Ammunition demilitarisation [1] is a complex and expensive process. In 1997 „Environment Protection Agency” formulated very clear under what conditions explosives, military and civilian, can be used, stored, transported and destroyed. Today, new methods are being developed, based on water jet removal of explosives from the ammunition shell (the used water must be decontaminated) [2]. Following this process the energetic material (EM) is extracted. The EM can be destroyed or recovered, recycled and reused. One of the challenges of the recovery process of EM is to maintain intact their physical and chemical properties.

In the 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 usual binders [3], for which the recovery of explosives at the end of ammunitions’ life cycle is considered to be an expensive and dangerous process.

Usually in the explosives mixtures there are used different particle size classes. During the recovery process, the purity and the morphology of the explosives change. For this reason researchers have been trying to develop a new type of binder which could fulfil the new requirements. Polymers derived from acrylic acids and methacrylic acids are most commonly used for the synthesis of

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[1] Military Technical Academy, 39-49 G. Cosbuc Blv., 050141, Bucharest, Romania

[2] University Politehnica of Bucharest, 313 Splaiul Independentei Blv., sector 6, Bucharest, Romania

adhesives. These polymers are used either alone or copolymerized with a variety of other polymers, eg polyethylene or vinyl acetate, particularly for laminating processes and the production of pressure sensitive materials (PSAs – *pressure-sensitive adhesives* [4], with applications in automotive, aerospace and electronics industries[5], bio-electrodes[6] and like smart adhesives for trans-dermal drug delivery systems[7]). In all these cases, the polymer is performed in a manufacturing process and is applied either as a solution in an organic solvent or as an aqueous dispersion [8].

Usually to obtain an adhesive it is used a mixture of acrylic acids and the esters of these acids. These esters are sometimes quite simples, short chain derivatives (eg. methyl or butyl methacrylate) or may be derived from much higher molecular weight alcohols (eg 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 reducing agent and which causes the free radical initiator to decompose. Cooper octoanoate accelerates the polymerisation reaction [9].

Yana Peykova et al. had 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 acrilate copolymers was compared. It was observed that the crosslinked polymers showed the best adhesion [10]. Macais et al. [11] have studied the adhesion performances of MMA/2-EHA (2-ethylhexyl acrylate) obtained by continuous and semicontinuous emulsion polymerisation, Shull et. Al. [12] have studied some triblock copolymers that have at ends poly(methyl methacrylate) and in the middle poly(bthyl methacrylate). In an another study, R. Jovanovic et al.[13] 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. 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[14].

2. EXPERIMENTAL

2.1. Materials

To obtain the desired binder were used the next monomers: butyl acrylate (BuAc, FLUKA, 98%), 2-ethylhexyl acrylate (2EHA) - industrial, ethyl acrylate (EtAc, ALDRICH) and acylic acid (AAc, FLUKA, 99%).

As initiator was used azobisizobutyronitrile (AIBN), recrystallized from methanol and all the solvents used were for analysis (RA).

2-Ethylhexyl acrylate (2EHA) was passed through a column with basic aluminium to remove the inhibitor. The other monomers, acrylic acid, butyl acrylate and ethyl acrylate, were purified by vacuum distillation.

For the alkaline solution was used distilled water and NaOH (Lachema).

2.2. Methodes

Were made several mixtures of monomers of different molar ratios: 2-ethylhexyl Acrylate / Acrylic acid, molar ratio: 3:7; 7:3; 5:5; solvent ethyl acetate.

The quantities needed for the experiment were put in glass made, round-bottomed reactor flasks of 25 mL, for 4 mL monomers mixture. It was also added the initiator, the solvent (16 mL) and a magnetic bar. The initiator is added 1% of monomers mixture. The flasks are sealed with septa tops and adhesive tape. To eliminate the oxygen from the flasks they were bubbled with nitrogen for 15 minutes. During the bubbling with nitrogen the flasks were introduced in Berzelius glasses containing water with ice to prevent the polymerisation reaction. After bubbling, the flasks were introduced in a oil bath at 65˚C (with stirring) for 24h.

After 24h the flasks were removed from the oil bath. The obtained polymers were precipitated in petroleum ether in polyethylene glasses to avoid sticking on the walls. The precipitation was made slowly drop by drop and with stirring. The polymers which were very viscous were diluted in ethyl acetate and after they were precipitated. In the case that the solvent was not easily removed, the polymers presenting the form of small granules, they were filtered. After precipitation the polymers were dried in a vacuum desiccator.

2.3. Characterisation

To characterise the polymers obtained it was used Infrared Spectroscopy (IR spectroscopy) and Differential Scanning Calorimetry (DSC).

At IR analysis it was observed the characteristic frequencies of the molecules of each polymer. FT-IR spectra were registered with Bruker VERTEX 70 spectrometer with ATR device, using 32 scans at a resolution of 4cm^{-1}. The glass transition temperature Tg of the synthesized polymers was determined by differential scanning calorimetry (DSC) measurements with NETZSCH 204 F1 Phoenix apparatus, under nitrogen steam at a heating rate of 10˚C/min. Samples, weighing approximately 10 mg, were heated/cooled between -80C and 150˚C, Tg being determined from the kink point during the second heating cycle.

Water absorption test

In beakers with lid were added a few milligrams of synthesized polymers and 200 mL of distilled water for 24h at room temperature. After 24h the polymers were weighted and the absorption percentage was calculated.

Solubility test – solvents

The used solvents were: toluene, methanol, absolute ethanol, hexane, propylene glycol, acetone, petroleum ether, ethyl acetate, ethylene glycol, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and chloroform.

In graduated glass tubes were introduced a few milligrams of synthesized polymers and 5 mL of solvent. The tubes were sealed with septa tops and adhesive tape and left 24 h at room temperature (20˚C). After 24 h was observed if the polymers dissolved.

Solubility test – alkaline solution

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

In graduated glass tubes of 15 mL were introduced a few milligrams of polymers. They were filled with alkaline solution and were sealed with septa tops. They were kept 24 h at room temperature, at 30 ˚C and at 50 ˚C.

2.4. Results and conclusion

2.4.1. Polymer synthesis

There were synthesized polymers of different molar ratios: 2-ethylhexyl acrylate/acrylic acid (2EHA/AAc), butyl acrylate/acrylic acid (BuAc/AAc) and ethyl acrylate/acrylic acid (AtAc/AAc) with molar ratios: 3:7; 7:3 and 5:5. In table 1 are presented the conversions obtained.

Table 1.
2EHA/AAc convertions

Molar ratio	**2EHA/AAc, %**
7:3	28.5
5:5	70
3:7	81.3

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

From table 1 it can be observed that the best conversion was obtained for the polymer EtAc/AAc with molar ratio 7:3. After 24 h the polymer EtAc/AAc with the molar ratio 3:7 did precipitate; the polymer with the molar ratio 5:5 did precipitate (less than EtAc/AAc 3:7) and the polymer with molar ratio 7:3 did not precipitate, was viscous and cloudy.

2.4.2. IR analysis

Following IR analysis the characteristic bands of each polymer were observed. It can also be observed the increase/decrease of characteristic peaks depending on the concentration.

FTIR spectra were recorded on a Bruker Vertex 70, by ATR measurements. Below are shown the IR spectra for synthesised polymers:

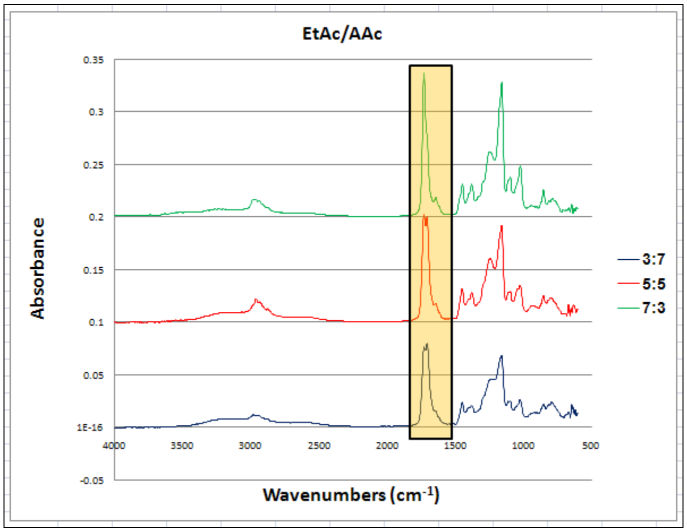

Fig.1. EtAc/AAc spectrograms

In the picture above you can see both peaks, characteristic to ethyl acrylate and in the same time the characterstics of acrylic acid groups.

For the polymer EtAc / AAc with molar ratio of 3:7 the peak characteristic can be observed around 1730 cm^{-1} of C = O group EtAc, and around 1706 cm^{-1} it can be seen the characteristic peak of carboxyl group from acrylic acid. From the FTIR spectrum of this peak can be seen that the characteristic C = O group of acrylic acid is higher than the peak characteristic of EtAc carboxyl group, which confirms the initial molar ratio of the monomers used to obtain polymer EtAc / AAc and 3 7.

For the polymer EtAc / AAc with molar ratio of 5: 5 it can be seen that the peak of the characteristic C = O EtAc group stayed at 1732 cm^{-1}, but the characteristic peak of the carboxyl group of the acrylic acid to the amount of 1706

cm^{-1}. From this it can be seen that FTIR spectrum peak characteristic of C = O group of the acrylic acid is almost equal to the characteristic peak of the carboxylic group of EtAc, which confirmed the initial molar ratio of the monomers used for making the polymer EtAc / AAc and 5 : 5.

In the case of the polymer EtAc / AAc with molar ratio of 7: 3 is observed a characteristic peak C = O EtAc group around 1730 cm^{-1} and around 1714 cm^{-1} can be seen the characteristic peak of the carboxyl group of acrylic acid. From this it can be seen that FTIR spectrum peak characteristic of C = O group EtAc is higher than the peak of the characteristic of the carboxyl group of acrylic acid, which confirmed the initial molar ratio of the monomers used for making the polymer EtAc / AAc and 7 : 3.

2.4.3. DSC analysis

Phase transition temperature Tg of synthesised polymers was determined by differential scanning calorimetry measurements (DSC) with a NETZCH 204 F1 Phoenix device, under a stream of nitrogen at a heating rate of 10˚C / min. Samples weighting about 10 mg were heated/cooled between -80˚C şi 150˚C and the Tg was determined from the point of inflection obtained during the second heating cycle.

Below are shown the thermograms of polymers synthesized and glass transition temperature (Tg) values obtained.

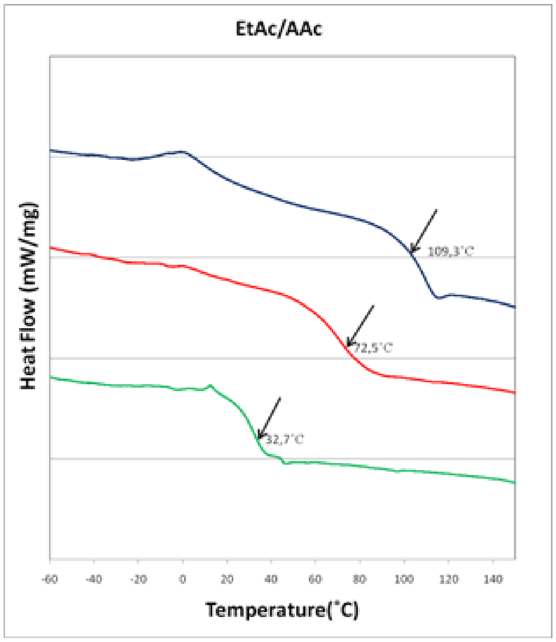

Fig. 2. EtAc/AAc thermograms

The figure above presents the thermograms of polymer EtAc / AAc. It can be seen that the glass transition temperature (Tg) decreases in value, from 109,3 °C to – 32,7 °C. This is due to the content of acrylic acid in the polymer. The more we mixed acrylic acid, the Tg value of the polymer EtAc / AAc increases, acrylic acid homopolymer having a glass transition temperature around 105 ° C. Also, if the amount of ethyl acrylate increases the value of Tg of the polymer EtAc / AAc decreases, EtAc having a glass transition temperature around -24. It’s worth noting that in this case likely to occur anhydride formation cycles, as shown by the higher Tg value for the copolymer 3-7 compared with the value reported in the literature for polyacrylic acid.

2.4.4. Water absorption test

The aim of this paper is to find a polymer capable of dissolving in an alkaline solution, but it must not dissolve in water. Ammunitions can be stored in locations with high humidity, transported on a rainy weather or a flood can appear, so the polymer must be waterproof.

To determine the water absorption degree of the synthesised polymers few milligrams of polymer was introduced in 200 mL distillate water for 24h. After 24h the polymers were weighted and the water absorption degree was calculated. The results are shown below.

Tabelul 2.

Water absorption for EtAc/AAc after 24h

EtAc/AAc	**m initial, mg**	**m final after 24h, mg**	**Water absorption, %**
3:7	8.3	10.1	21.68
5:5	10.0	12.0	20
7:3	12.3	16.7	11.38

From the values from the tables above it can be observed that the water absorption percentage is low. It can be also observed that the percentage value decreases with increasing percentage of polymer EtAc.

2.4.5. Solubility test – solvents

The binders synthesized must be soluble in a solvent, because to be able to apply them on the explosive crystals first they have to be solubilised, then mixed with the explosive and after the solvent shall be evaporated.

The binders obtained were introduced in different solvents (polar and non polar) to determine if they are or not soluble. The explosives from the ammunitions can be recovered from a solvent, but this method is expensive and the process is more complicated.

The solvents used were: toluene, methanol, absolute ethanol, hexane, propylene glycol, acetone, petroleum ether, ethyl acetate, ethylene glycol, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and chloroform.

The polymers were introduced in 5 mL of solvent during 24h at room temperature. The results obtained are shown in the table below.

Table 3.

Polymers solubility after 24h

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

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

From the table above it can be observed that in methanol, hexane, petroleum ether and chloroform none of the polymers dissolved. In absolute ethanol only EtAc/AAc dissolved. In propylene glycol completely dissolved the polymers EtAc/AAc, with molar ratios 3:7 and 5:5, the other polymer being insoluble in this solvent.

In acetone dissolved only EtAc/AAc molar ratios 5:5 and 7:3. 2EHA/AAc molar ratio 3:7 partially dissolved.

In ethyl acetate dissolved only EtAc/AAc, molar ratio 7:3. The others polymers were insoluble in this solvent.

In ethylene glycol dissolved only the polymers EtAc/AAc with molar ratios 3:7 and 5:5. The other polymer was insoluble in this solvent.

In dimethyl sulfoxide (DMSO) and DMF all polymers dissolved.

2.4.6. Solubility test – alkaline solution

This paper has the main aim to obtain a binder which is soluble in an alkaline solution without modifying the physical and chemical properties of explosives. The classical binders used in present exhibit very good mechanical, physical and chemical properties, but during the recovery process of explosives at the end life of ammunitions, this properties change.

For this test a few milligrams of polymers were introduced in tubes of 15 mL. These are filled with alkaline solution. The tubes with polymer and alkaline solution were sealed with rubber stoppers and maintained for 24 h at room temperatures, at 30˚C and at 50 ˚C. The results obtained are presented in the table below:

Table 4.

Polymers solubility after 24 h

SOLVENT	EtAc/AAc		
	3:7	5:5	7:3
pH 14, 20	+	+	+
pH 13, 20	+	+	+
pH 12, 20	-	-	-
pH 11, 20	-	-	-
pH 13, 30	+	+	+
pH 12, 30	-	-	+
pH 11, 30	+	-	-
pH 13, 50	+	+	+

pH 12, 50	+	+	+
pH 11, 50	+	-	-

***(-) polymers not dissolved**
(+) polymers dissolved

From the table above it is observed that at pH 14, at room temperature, all three polymers dissolved.

At pH 13, at room temperature, all polymers dissolved. It can also be observed that at room temperature the synthesized polymers did not dissolve in the alkaline solutions with pH12 and pH11.

At 30˚C in the alkaline solution with pH 12 dissolved only EtAc/AAc molar ratio 7:3.

It is important to observe that polymer EtAc/AAc with molar ratio 3:7 dissolved in the alkaline solution with pH11 at 30˚C. Explosives have high melting and self-ignition temperatures depending on the impurities. This temperature of 30 ˚C is a low value so the explosives can be handled safely.

In the alkaline solution with pH 12, at 50 ˚C all polymers dissolved.

At 50 ˚C for the alkaline solution with pH 11 dissolved EtAAc/AAc molar ratio 3:7.

3. CONCLUSION

Synthesized polymers were characterized by infrared absorption spectrometry and Differential Scanning Calorimetry (DSC). They should be insoluble in water at neutral pH, and because of this the water absortion method was studied. Also it’s been studied the solubility of these polymers in various solvents and also in alkaline solution of NaOH (pH 11 ÷ 14) to determine polymer / polymers which are solubilized at pH 11.

The characteristic band of each polymers was observed using IR analysis. As a result of IR specter analysis has been confirmed the initial molar ratio of the monomers used for producing each polymer. The thermograms analysis of synthesized polymers made possible the observation that the glass transition temperature (Tg) Tg values vary between sites homopolymers components.

Furthermore, we noticed that the Tg's value increases with the increasing molar ratio of acrylic acid binder. It has been observed that the Tg's for polymer with molar ratios 3:7 exceeds the Tg for pure polyacrylic acid, although IR spectrals show the presence of BuAc copolymer. This is probably due to dehydration with formation of intramolecular anhydride copolymer cycles during DSC analysis, which leaded to higher Tg values than expected.

After testing the water absorption was observed that the percentage of water absorbed is reduced. Also it can be seen that the percentage of absorbed water increases with the increasing percentage of AAc polymer.

In the case of solubility tests in various solvents (polar and non-polar) has been observed that the solvent in which the all three synthesized polymers were dissolved was dimethylformamide. The only solvents in which none of the binders obtained dissolved were methanol, petroleum ether and chloroform.

The last test performed, and most importantly, has been the solubility in an alkaline solution. The polymers were introduced into alkaline solutions of NaOH (pH 11÷14) for 24 hours, in ambient temperature of 30 ° C and 50 ° C. It is important to note that the polymer EtAAc / AAc with molar ratio of 3:7 was dissolved in an alkaline solution with pH 11 at a temperature of 30 ° C.

In conclusion, three polymers were syntetized based on acrylic acid and ethyl acrylate, at various molar ratios. One of these, EtAAc / AAc with molar ratio 3: 7, was dissolved in an alkaline solution with pH 11 at a temperature of 30 ° C, thus achieving the main objective of this study.

The study has reached his purpose, continuing with achieving further energetic compositions (10% and 90% binder material for energy) and to study the mechanical, explosive and solubilization properties.

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