



Utilization of Waste Nitrocellulose Propellants by Obtaining Porous Materials

Petar SHISHKOV¹, Radi GANEV², Tzveti TZVETKOFF¹
and Ivan GLAVCHEV^{1*}

¹*University of Chemical Technology and Metallurgy,
8 Kl.Ohridski St., 1756 Sofia, Bulgaria*

²*Civil Engineering Higher School,
175 Suhodolska St., 1373 Sofia, Bulgaria*

* *E-mail: ivgl@uctm.edu*

Abstract: Technology for utilization of waste single and double based propellants by obtaining porous propellants was worked out. The technology contains the preparation of solutions of waste propellants with concentration up to 20%, mixing with additives, forming a liquid layer with determined thickness, evaporation of some amount of the solvent, leaching liquid components with water and drying the porous propellants. The time for evaporation of some amount of the solvent was determined from the results of the rates of evaporation. The investigated additives were 1-butanol, ethylene glycol and polyethylene glycol 400. The porous propellants with specific density from 0.5 to 0.7 g/cm³ and regular distribution of voids of dimensions from 0.1 to 500 μm were obtained.

Keywords: waste propellant, porous propellant

Introduction

There are some technologies for obtaining porous propellants, among them are: from mixtures of solutions of propellants/removable fillers [1], mixtures of fine propellant powders/binders/solvents/diluents [2], mixing particles of a high temperature resistant propellant with particles of thermally removable fillers [3], dispersion of propellants solutions in water [4], spray-drying method [5], sol-gel method [6], cross linking [7] and others. Every of these methods has advantages and disadvantages.

The solubility of any polymer in defined solvent depends on its chemical structure, molecular weight and polydispersity, as well as temperature and concentration. The coefficient of the interaction between solvent and polymer χ in the Flory's equation depends on chemical structure of components and temperature. This coefficient determine the value σ_o^s in the equation for fractionation of polymers:

$$\phi_{x\ s}/\phi_{x\ p} = \exp(\sigma_o^{s,x}),$$

where $\phi_{x\ s}$ and $\phi_{x\ p}$ are the polymer phases with longitude of the macromolecule x in the solvent ($\phi_{x\ s}$) and in the precipitate ($\phi_{x\ p}$). In this way it is possible to obtain samples of solid polymer with definite molecular weight from polymer solutions by mixing with precipitator. The polymers are insoluble in precipitators. The mixtures of various amounts of solvents and precipitators have different solubility. This process takes place in ultrafiltration membrane technologies.

During the ageing of nitrocellulose propellants, processes of degradation and destruction of a polymer occur, what cause decrease in the nitrogen content and molecular weight, and increase in polydispersity and solubility, connected with changes in their IR spectra [8].

The mechanism of formation of coatings from polymer solutions has been the subject of interpretation by generally two theoretical schools, from which every one has its experimental support. The first one asserts that the skin on the top of the coating is formed because of an evaporation step involved [9]. The second one suggests precipitation to be the responsible cause [10]. In the literature there is an information how to obtain a three-layer structure consisting of an upper "active" layer, a "sublayer" and a "porous" layer. The thickness of each layer depends on the evaporation conditions [11]. The influence of the originating hydrogen bonds on the concomitant evaporation of several solvents from thin films based on epoxy resins was published elsewhere [12]. It is established, that the rates of evaporation depends not only on the chemical properties of the solvents used, but also on the structure of the formed films [13, 14]. The chamber method (pre-standard ENV 13419-1) showed a possible way to determine the rate of evaporation of solvents and additives [15], but its disadvantage was that some amount of volatile compounds could be lost before starting the measurements [16]. In our previous investigation, gravimetry and gas chromatography were compared as tools for measuring the rate of evaporation of acetone and dioxane from cellulose triacetate thin films and the influence of these rates on both the film formations was estimated [17]. The aim of these investigations was to develop a technology for preparation of porous materials on the base of the rates of evaporation from propellant solutions in the presence of a precipitator.

Experimental

The samples of single and double based propellants – pyroxyline (Pyr.) and nitrocellulose-nitroglycerine (NC-NGI) (“Arsenal”, Bulgaria), made in 1980 year and stored in non-heating army stores, were dissolved in technical grade acetone (Neftochim, Bulgaria). The solutions of concentrations 15 and 20% were mixed with 3 different technical grade additives: n-butanol, (Bu) ethylene glycol (EG) (Neftochim, Bulgaria) and polyethylene glycol with molecular weight 400 (PEG 400) (Verila, Bulgaria). The evaporation rates were determined at room temperature, at relative humidity 60-70% by weight measurement of the samples during 24 h. The liquid layers from the solutions were formed and after defined time some amount of water was added. After dissolving the rests of solvent and additives in water and drying by heating at 105 °C, the density of the obtained porous materials was measured by the standard method. The dimensions and distribution of the obtained voids were determined with scanning electron microscope Philips (The Netherlands).

Results and Discussion

It is well known, that nitrocellulose propellants are very well soluble in acetone. Their solubility decreased in the following compounds: 1-butanol>ethylene glycol> polyethylene glycol. These compounds are soluble in acetone and in this way they are precipitators of nitrocellulose. The samples of 15 and 20% acetone solutions of the propellants were made. Transparent mixtures were made by mixing the solutions with definite amounts of different additives. The evaporation rates were determined by the method, described in [17]. A part of the obtained evaporation rates are in Table 1.

Table 1. The values of the evaporation rates (%/min)

Compositions \ Time, min	0.5	1	10	60	300
Pyr./Bu	22	1.2	0.15	$2.8 \cdot 10^{-3}$	$3.5 \cdot 10^{-4}$
NC-NGI/Bu	20	1.1	0.13	$2.3 \cdot 10^{-3}$	$3.1 \cdot 10^{-4}$
Pyr./EG	24	1.3	0.2	$5.8 \cdot 10^{-3}$	$5.5 \cdot 10^{-4}$
NC/EG	23.5	1.2	0.19	$5.3 \cdot 10^{-3}$	$5.4 \cdot 10^{-4}$
Pyr/PEG 400	25	1.38	0.22	$6.1 \cdot 10^{-3}$	$6.2 \cdot 10^{-4}$
NC/PEG 400	24.1	1.32	0.21	$5.4 \cdot 10^{-3}$	$5.7 \cdot 10^{-4}$

It is evident that the kind of propellants and additives influence on the evaporation rates. The rates determined were mainly from the evaporation of acetone and the ratio solvent/precipitator decreased during the time. In this way the amount of precipitator increased and solid polymer phase in the solutions was obtained.

The layers from the same compositions were formed. After time determined from the rates of evaporation, the “skin” on the top of the layers was formed and precipitation of polymer by the changing amounts of solvent and precipitator took place. Some amount of water was added on the solid surfaces. The extraction of the rest of acetone and additives from the layers lasted several hours. The obtained samples of the porous propellants were drayed at 105 °C. The samples, made with additive n-butanol have both small and several mm size big voids, distributed irregularly (distances between these voids are different). Dimensions of the big voids in the samples, made with ethylene glycol are around 1 mm and are distributed irregularly too. Only in the samples, made with polyethylene glycol 400 the voids are distributed regularly (distances between these voids are approximately equal) and their dimensions are from 0.1 to 500 μm . (Figures 1 and 2). The values of the density of the samples, made with polyethylene glycol 400 are from 0.5 to 0.7 g/cm^3 . It is possible to decrease the loss of solvents and additives by their recuperation.

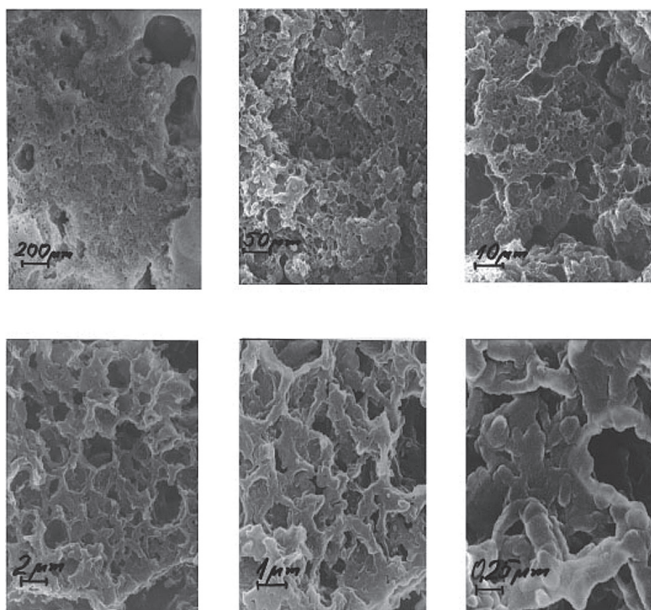


Figure 1. Electron microscopy scan of samples, made from Pyr/PEG 400.

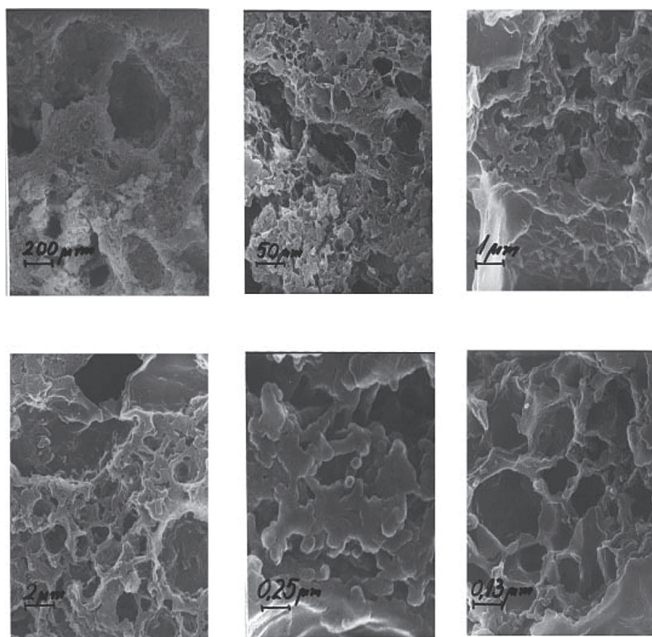


Figure 2. Electron microscopy scan of samples, made from NCNGI/PEG 400.

Conclusion

The porous propellants with small, regularly distributed voids were made by extraction of the rest of solvent and polyethylene glycol 400 from the layer of propellants solutions in water after some time of evaporation of acetone. The technology gives the possibility for production of porous propellants with the economy of the time and finances.

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