

SURFACE STRUCTURE AND PROPERTIES OF GLOW-DISCHARGE PLASMA TREATED 1,3,5,7-TETRANITRO-1,3,5,7-TETRAAZACYCLOOCTANE IN DISPERSED STATE

A.P. Korobko, I.V. Levakova, and S.V. Krashenninikov

*Karpov Institute of Physical Chemistry, State Scientific Center of the Russian Federation,
ul. Vorontsovo pole 10, Moscow, 105064, Russia, korobko@cc.nifhi.ac.ru*

INTRODUCTION

Dispersed powders of various chemical nature are widely used as fillers for polymer composite materials. The parameters of polymer composite materials are dependent to a great extent on the surface properties of fillers and their interaction with the polymeric matrix. Optimum interaction can be achieved in many cases by modifying the surface properties of fillers. Among various modification techniques, the treatment of surface by low-temperature glow-discharge plasma is of particular importance.

In this work, the plasma-chemical procedure was applied for surface treatment of powdered 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), one of the cyclic nitramines of considerable practical interest. We studied the influence of discharge parameters on the change in surface energy and functionalization of HMX particles. We consider also some aspects of the structure dynamics of the modified layers.

EXPERIMENTAL

The β -polymorph of crystalline HMX was a product with particles of rounded form and size ranging from about 2 to 80 μm obtained by known procedure.

The plasma treatment was conducted in a vacuum plasma reactor operating in flow mode, using 1-kHz or 50-Hz ac glow discharge. During treatment the powder was in the fluidized mass state. Purified air and argon at a pressure of 6-14 Pa were used as plasma gases. Discharge current and exposure time were variable parameters.

For contact angle measurements we used pellets made of the original and the modified powders and liquids with known surface tensions. Equilibrium (Θ_e), advancing (Θ_a), and receding (Θ_r) contact angles were measured by the goniometric procedure with the use of a horizontal microscope.

In wetting hysteresis measurements contact angles were measured by tilting the pellet by 35° .

To study functionalization of HMX particles the technique of Fourier transform IR photoacoustic spectroscopy (FTIR-PAS) and X-ray photoelectron spectroscopy (XPS) were employed. The IR spectra were measured on a Bruker IFS 113v IR spectrometer equipped with a Photoacoustic MTEC 200 cell filled with helium. X-ray photoelectron spectra were recorded on a Kratos 800 XPS electron spectrometer.

MAIN RESULTS AND DISCUSSION

One of the most important parameters characterizing surface properties of solids is the free surface energy

$$\gamma_s = \gamma_s^d + \gamma_s^p,$$

(superscripts d and p denote the dispersion and polar components of the γ_s , respectively).

In order to determine γ_s of original and modified HMX we used the Kaelble's equation in a form convenient for processing of experimental data on wetting:

$$\frac{W_{LS}}{2a} = \frac{\gamma_L(1 + \cos\Theta_e)}{2a} = (\gamma_s^d)^{1/2} + (b/a)(\gamma_s^p)^{1/2} \quad (1)$$

where

$$a = (\gamma_L^d)^{1/2}, \quad b = (\gamma_L^p)^{1/2}$$

and subscripts S and L refer to the solid and liquid surfaces, respectively. Function $W_{LS}/2a=f(b/a)$ is the straight line with a slope and an intercept determined $(\gamma_S^p)^{1/2}$ and $(\gamma_S^d)^{1/2}$, respectively.

Table 1 presents the results of measurements of surface energy and its components for the HMX powder, depending on the conditions of treatment in air plasma. Numerical values for the coefficients of equations (1) were obtained by the least-squares procedure from seven points (dodecane, hexadecane, epoxy resin (diglycidyl ether of bis-phenol A), diiodomethane, ethylene glycol, glycerol, water) for the original powder and four points (hexadecane, epoxy resin, glycerol, water) for each of the modified samples.

Table 1. Total surface energy and its components (mJ/m²) for original and modified samples (discharge current 60 mA).

| Treatment time, min | Dispersion component γ_S^d | Polar component γ_S^p | Total energy γ_S |
|---------------------|-----------------------------------|------------------------------|-------------------------|
| 0 | 26.27 | 12.81 | 39.08 |
| 2 | 25.64 | 31.08 | 56.72 |
| 4 | 26.10 | 33.19 | 59.29 |
| 6 | 25.76 | 36.67 | 62.43 |
| 10 | 25.44 | 37.93 | 63.37 |

The data in table 1 show that the contribution of the polar component to the surface energy of the original HMX is sufficiently large (~30%). The increase in overall surface energy with increasing treatment time is almost totally determined by an increase in the contribution of the polar

components. The dispersion component varies very little. Crucial changes in γ_S take place within first 2-4 min of treatment. Varying the discharge current at a fixed duration of treatment slightly affects the surface energy.

A sensitive characteristic of surface properties of solids is the contact angle hysteresis determined as the difference

$$\Delta\Theta = \Theta_a - \Theta_r$$

The wetting hysteresis is one of the characteristic of energy irregularity of a solid surfaces as Θ_a and Θ_r respond to areas having enhanced or reduced surface energy in different

Table 2. Hysteresis of contact angle (deg) upon plasma treatment of HMX powder (discharge current 60 mA).

| Treatment time, min | Water | | | Glycerol | | | Epoxy resin | | |
|---------------------|------------|------------|----------------|------------|------------|----------------|-------------|------------|----------------|
| | Θ_a | Θ_r | $\Delta\Theta$ | Θ_a | Θ_r | $\Delta\Theta$ | Θ_a | Θ_r | $\Delta\Theta$ |
| 0 | 72 | 62 | 10 | 58 | 50 | 8 | 41 | 31 | 10 |
| 2 | 43 | 38 | 5 | 31 | 28 | 3 | 27 | 21 | 6 |
| 4 | 40 | 36 | 4 | 23 | 20 | 3 | 20 | 14 | 6 |
| 6 | 33 | 31 | 2 | 20 | 15 | 5 | 18 | 14 | 4 |
| 10 | 30 | 28 | 2 | 19 | 13 | 6 | 25 | 19 | 6 |

manner. $\Delta\Theta$ measured for the three liquids are listed in table 2.

The data in table 2 indicate that the greatest energy irregularity is observed for the original sample.

As the treatment time increases, the heterogeneity is reduced. The most distinct reduction of hysteresis is observed for water, the most polar liquid. It is likely that the decrease in energy irregularity of the treated samples is indicative of the selective character of surface chemical reactions induced by reactive plasma species.

In order to clarify the reasons for the change in surface energy of the HMX powder by the action of discharge, we studied changes in chemical composition and structure of HMX surface layers as a result of plasma treatment.

IR spectra allows for detailed qualitative analysis of such changes. Figure 1 shows the difference spectrum between spectra of original and air plasma-treated HMX samples, which

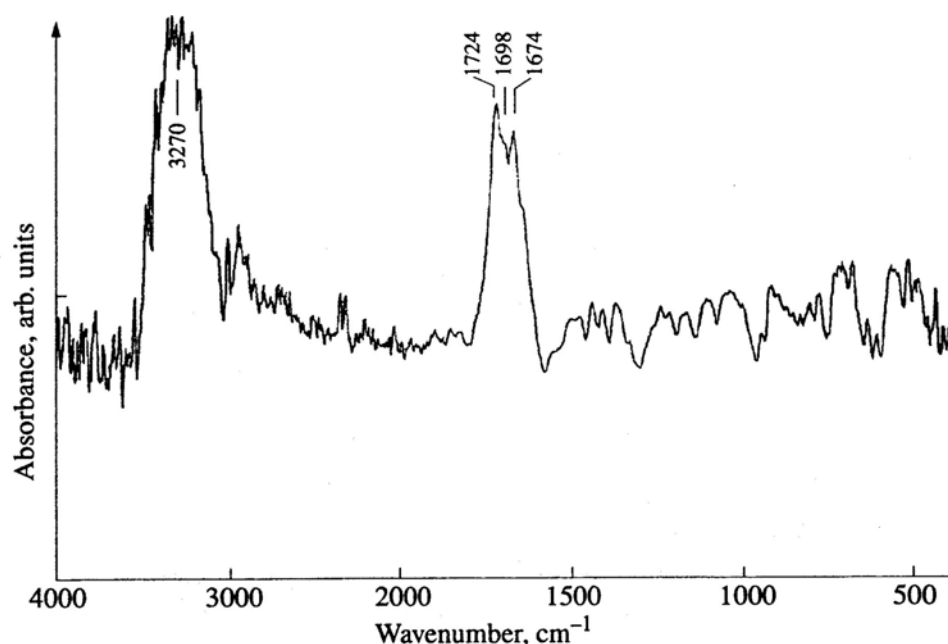


Fig. 1. Difference IR spectrum for the original HMX powder and its sample modified in air plasma.

displays two sets of new bands due to the modified compound. In the region of 1700 cm^{-1} the band at 1724 cm^{-1} characterizes carbonyl group vibration of the ketone, urea or aldehyde type. Conjugation of these groups can be displayed at a lower frequency (1698 cm^{-1}). The low-frequency band at 1674 cm^{-1} is most likely due to the imino group $\text{C}=\text{N}$ stretching mode. The broad band in the region $3100\text{--}3500\text{ cm}^{-1}$ (centered at 3270 cm^{-1}) has a complex structure and, most likely, is due to stretching vibration of primary and secondary amino groups and bound hydroxyl groups. Besides, the results of IR study indicate that in the HMX surface layer active species of a glow discharge induces chemical reaction resulting in cleavage of the eight-membered cycle and a decrease in number of N-nitro groups.

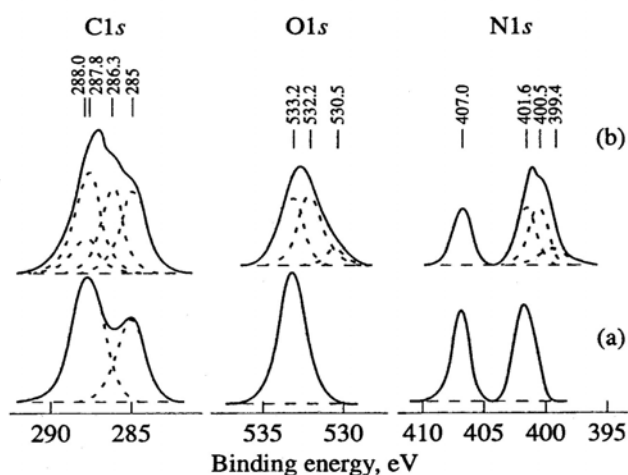


Fig. 2. Envelopes of $\text{C}1s$, $\text{O}1s$, and $\text{N}1s$ spectral lines for (a) the original HMX powder sample and (b) that treated in air plasma.

To obtain quantitative information on the chemical composition of the surface we used the XPS technique. Figure 2 depicts the spectral regions of the binding energies of $\text{C}1s$, $\text{O}1s$ and $\text{N}1s$ electrons in the original (curves (a)) and modified (curves (b)) HMX samples.

The assignment of XPS spectral lines is given in Table 3.

Results of quantitative treatment of the spectral data are given in Table 4.

The XPS data show that amounts of C and N in state III and IV increase and the amounts of H and N in state I and II decrease with increasing discharge current and treatment time. However, the total amount of O and N changes slightly and

with a less expressed trend. At the same time, the amount of O that is not bound to N^{II} increases. In the argon plasma these trends are expressed more strongly.

Surface functionalization of HMX particles by plasma treatment results in the appearance of excess surface energy. Such a system tends to return to the equilibrium state with minimum of interfacial energy. The rate of transition depends on both properties of the system and external conditions.

Table 3. Assignment of XPS spectral lines in original and modified HMX samples.

| Spectral region | Spectral lines, eV | | Assignment |
|-----------------|--------------------|--------------|--------------------------------|
| | Original HMX | Modified HMX | |
| C1s | 287.8 | 287.8 | N-CH ₂ -N |
| | 285.0 | 285.0 | Contamination CH _x |
| | - | 288.0 | C=O |
| | - | 286.3 | C-OH; C=N |
| O1s | 533.2 | 533.2 | NO ₂ |
| | - | 532.2 | C=O |
| | - | 530.5 | C-OH |
| N1s | 407.0 | 407.0 | N ^{II} O ₂ |
| | 401.6 | 401.6 | C-N ^I -C |
| | - | 400.5 | C=N ^{III} |
| | - | 399.4 | N ^{IV} -H |

Table 4. Chemical composition of the surface layer of the samples.

| Sample* | Element content, at % | | | | | | | ΣH (calcd.) |
|------------|-----------------------|------|----------------|-----------------|------------------|-----------------|------|-------------|
| | ΣC | ΣO | N ^I | N ^{II} | N ^{III} | N ^{IV} | ΣN | |
| Original | 17.1 | 28.2 | 14.9 | 12.9 | 0 | 0 | 27.8 | 26.9 |
| Air, 10/2 | 23.0 | 25.1 | 8.7 | 8.7 | 7.1 | 2.3 | 26.8 | 25.1 |
| Air, 20/10 | 24.6 | 27.0 | 7.8 | 7.8 | 7.4 | 2.5 | 25.5 | 22.8 |
| Air, 40/20 | 27.0 | 25.8 | 7.1 | 7.1 | 10.0 | 2.8 | 27.0 | 20.2 |
| Ar, 20/10 | 30.0 | 29.2 | 6.8 | 6.8 | 8.4 | 2.6 | 24.6 | 16.2 |
| Ar, 40/20 | 29.7 | 30.3 | 6.6 | 6.6 | 7.5 | 3.4 | 24.1 | 15.9 |

* Numerator and denominator of fraction are discharge current (mA) and treatment time (min), respectively.

We studied the structure dynamics of surface layers by measuring wetting hysteresis $\Delta\Theta = \Theta_a - \Theta_r$ during sample aging (wetting by water, aging at 20 to 100 °C, relative humidity of 60%). It was shown that the observed picture of structure rearrangement of the modified layer is characteristic of polymers. By rough estimation, the apparent activation energy of the diffusion of polar groups into the bulk and nonpolar groups to the surface, resulting in the rearrangement of the surface structure, is 70-75 kJ/mol. It is in fairly good agreement with the data on activation of relaxation processes in the surface layer for certain plasma polymers.

The thickness of plasma-modified layers was estimated by measuring electrical conductivity of compacted original and plasma-treated powder. It was assumed that low-ohmic (conductive) phase represents infinite percolation cluster with fractal structure. The thickness of such layers is about 10 nanometers.

CONCLUSION

Low-temperature plasma treatment of powdered HMX in nonpolymerizing gases leads to the formation of a layer of products enriched with oxygen- and nitrogen-containing functional groups on the surface of its particles. The thickness of this layer is about 10 nanometers. The bulk properties of HMX remain unchanged during the treatment. The results obtained suggest that the substance formed as a result of plasma treatment is polymeric products of plasma-chemical reactions.