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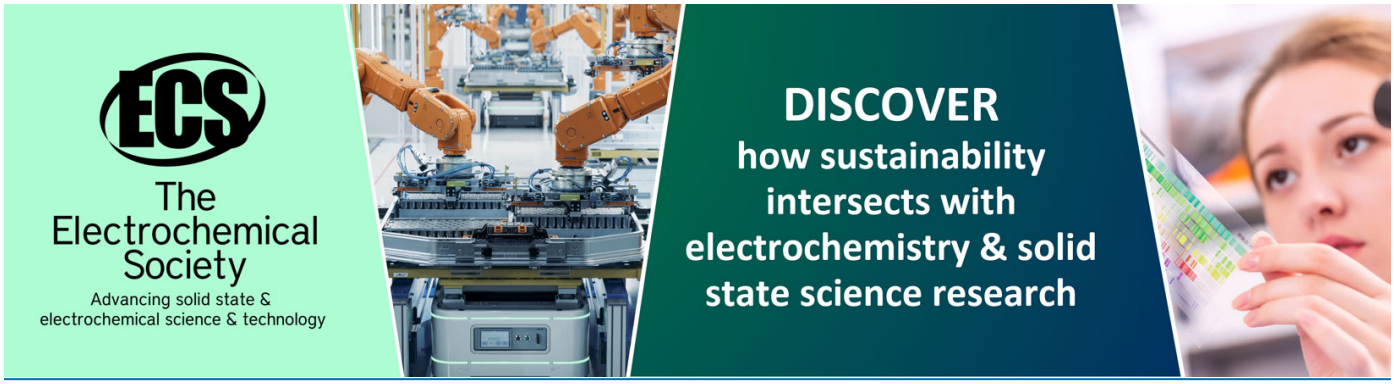

Coating effect and characterization of anionic polymer bonding agent on TKX-50

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Abstract. Different types of TKX-50/PBA-I composite materials were prepared by the solution-water suspension method, and the influence of the content of anionic groups on the coating effect was explored by SEM, FT-IR, XPS and TGA. The results showed that PBA-I were successfully coated on the crystal surface of TKX-50, and the content of anionic group -COOH increased, which was conducive to the coating effect of the bonding agent on TKX-50. Among the different anionic bonding agents, PBA-I-3 had the best coating effect.

1. Introduction

5,5'-bitetrazol-1,1'-dihydroxyamine (TKX-50) is a new type of energetic ionic salt explosive, which has the characteristics of high energy level, low stimulation response, environmental protection and cleaning[1]. It's an important research object for the development of energetic materials in the future. However, TKX-50 has not been widely used in composite energetic materials such as solid propellants and mixed explosives because of the weak interaction between TKX-50 and binder[2-4].

Polymer bonding agents can be freely selected and regulated in structure and chain segments through free radical polymerization, which has the advantage of performance-oriented preparation. It also meets the development trend of long-chain binder molecules required in the research of energetic materials, and can better play the entanglement effect in composite energetic materials in order to improve the macro properties of the composite system[5-6].

Based on the positive charge on the crystal surface of TKX-50[7], it was coated with polymer bonding agent containing anionic groups. The effect of anionic content on the properties of coated samples was explored by SEM, FT-IR, XPS and TGA in order to improve the surface properties of TKX-50.

2. Experimental

2.1. Materials and instruments

The anionic polymer bonding agents PBA-Ⅰ-1, PBA-Ⅰ-2, PBA-Ⅰ-3(with different composition ratios, the anionic groups -COOH increase sequentially) used in the research were self-synthesized. TKX-50 were provided by Gansu Yinguang Chemical Industry Group Co., Ltd. Acetone and ethanol were produced by Beijing Tongguang Fine Chemical Co., Ltd, and the accuracy were Analytical Reagent.

SU8200 field emission scanning electron microscope was provided by Hitachi High Tech Co., Ltd., Japan. Nicolet iS 50 Fourier transform infrared spectrometer was provided by Thermo Fisher Scientific

Co., Ltd. PHI QUANTERA-II SXM X-ray photoelectron spectroscopy analyzer was provided by ULVAC-PHI, Inc., Japan. DTG-60(H) differential thermal gravimetric synchronous analyzer was provided by SHIMADZU Co., Ltd., Japan.

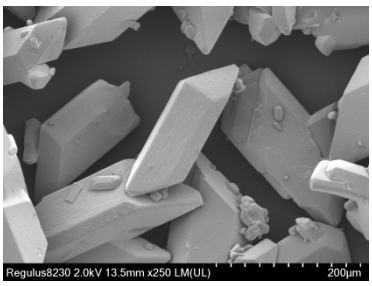
2.2. Preparation of the TKX-50 coating sample

The coating sample were prepared according to the following method[8]: the mixture of TKX-50 and deionized water are weighed with a mass ratio of 1:1.5. The system temperature is heated to 40 ℃ at a magnetic stirring speed of 120r/min. Take the mixed solution formed by dissolving different kinds of PBA-Ⅰ (named PBA-Ⅰ-1, PBA-Ⅰ-2, PBA-Ⅰ-3 respectively) in acetone. Keep the temperature and stir for 25~30min, and then filter and wash the product. Air dry at room temperature for 1d, and then dry in a 60 ℃ vacuum oven for 6h to obtain white hard particles.

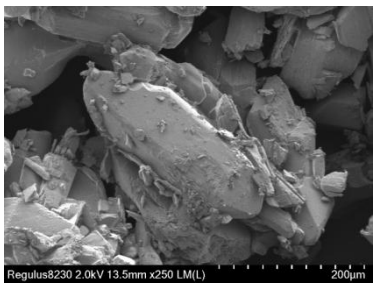
3. Results and Discussion

3.1. Morphological analysis（SEM）

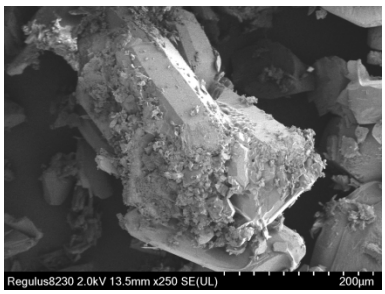
The TKX-50/PBA-I coating samples were characterized and observed by the SU8200 field emission scanning electron microscope (FESEM) of Hitachi High-Tech Co., Ltd. of Japan. Test condition parameters: the sample is sprayed with gold, and the test voltage is <3.0kV. **Figure 1** is the SEM electron micrograph of the TKX-50 coated by PBA-I.



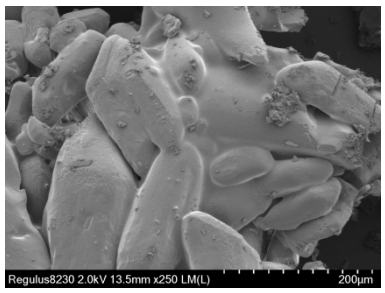
(a)TKX-50



(b)TKX-50/PBA-Ⅰ-1



(c)TKX-50/PBA-Ⅰ-2



(d)TKX-50/PBA-Ⅰ-3

Figure 1. The coating of PBA-Ⅰ on TKX-50

It can be seen from Figure 1-(a) that the main forms of TKX-50 raw crystals are long prismatic, long flaky, and long rod-shaped, most of which belong to the four-sided rhombohedral prism with smooth surface and regular shape. From Figure 1-(b), 1-(c), 1-(d), PBA-Is were successfully coated on the surface of the TKX-50 crystal, and the coating effect became better in turn. Among them, PBA-I-3 in Figure 1-(d) had the best coating effect on TKX-50 crystals. The bonding agent adhered to the crystal surface and precipitated in film shape. The coated surface was more uniform and glossy. This was due to the increase of the anionic groups -COOH in the bonding agent. The wettability between the bonding agent and TKX-50 was improved, PBA-Ⅰ-3 precipitated on the surface of TKX-50 at a relatively more stable rate and was adsorbed on the crystal surface of TKX-50 through binding interaction.

3.2. FT-IR spectroscopy analysis

The samples were scanned by Nicolet iS50 Fourier Transform Infrared Spectrometer from Thermo Fisher Scientific, USA. Test condition parameters: the infrared spectrum resolution 4 cm^{-1}, test temperature 25°C, scanning times 30 times. **Figure 2** is the infrared spectrum of the TKX-50/PBA-I coated samples measured by the KBr method. It can be seen that the main infrared absorption characteristic peaks of TKX-50 are 3220 cm^{-1} and 1577 cm^{-1} which are the stretching vibration peaks and Flexural vibration peaks belonging to N-H. It is also shown that the C-N stretching vibration peak, C=N characteristic peak and N=N characteristic peak which belong to TKX-50[9]. Different TKX-50/PBA-I samples had no obvious deviation from the peaks of TKX-50 raw materials. The specific peak assignments are shown in **Table 1**. The chemical structure of TKX-50 had no effect by PBA-I.

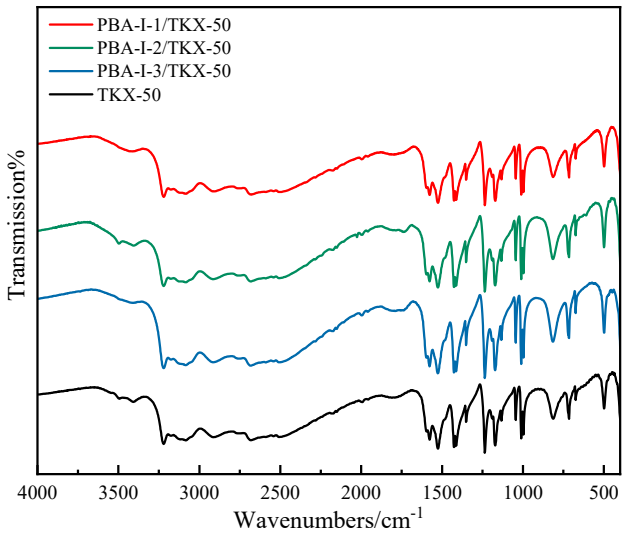


Figure 2. FT-IR of TKX-50/PBA-Ⅰ coating samples

Table 1. FT-IR peaks assignment of TKX-50 and TKX-50/PBA-I coating samples

TKX-50		TKX-50/PBA-Ⅰ	
peak position(cm^{-1})	peak assignment	peak position(cm^{-1})	peak assignment
3220.5	ν(N-H)	around 3220.5	ν(N-H)
1577.4	δ(N-H)	around 1579.4	δ(N-H)
1236.1	ν^{as}(C-N)	around 1236.1	ν^{as}(C-N)
1172.5	ν^{s} (C-N)	around 1172.5	ν^{s} (C-N)
1427.1	ν(N=N)	around 1427	ν(N=N)
1525.4	ν(C=N)	around 1527.3	ν(C=N)

3.3. X-ray photoelectron spectroscopy analysis（XPS）

The surface elements of the samples were analyzed by PHI QUANTERA-II SXM X-ray Photoelectron Spectroscopy Analyzer. Test condition parameters: the X-ray source is AlKa (Al target, 1486.6eV, linewidth 0.68eV), and the vacuum degree of the sample cavity is 10^{-7} Pa. Before XPS analysis, the samples were etched with Ar +, with an etching depth of 1nm and an etching area of 2mm × 2mm.

According to the XPS results, the relative mass fraction of the surface elements of each measurement sample can be obtained. Based on the difference in the molecular structure and element composition of different substances, the coating degree of TKX-50/PBA-I can be calculated by the characteristic signal difference of the N element [10], the calculation formula is shown as follow:

$$N_{TKX\text{-}50}(1\text{-}R)+N_{PBA\text{-}I}R=N \quad (1)$$

Where: R is the coating degree of the sample; N_{TKX-50} is the N element content in TKX-50; N_{PBA-I} is the N element content in PBA-I; N is the N element content in the coating sample. The larger the R value, the greater the coverage degree of the sample. The XPS results and coating degree of TKX-50/PBA-Ⅰ are shown in **Table 2**.

Table 2. XPS results and coating degree of TKX-50/PBA-Ⅰ[a]

Sample	$C_{modified}$(%)	$N_{modified}$(%)	$O_{modified}$(%)	$R_{modified}$(%)
TKX-50	10.73	58.65	27.80	0
TKX-50/PBA-Ⅰ-1	24.15	54.33	19.01	10.72
TKX-50/PBA-Ⅰ-2	24.12	52.33	22.88	13.77
TKX-50/PBA-Ⅰ-3	24.38	51.47	24.03	15.86

[a] The surface atomic mass fraction is calculated based on the sum of C N O 3 elements as 100%. TKX-50 is a blank control.

It can be seen from Table 2 that the order of the degree of coverage is PBA-Ⅰ-3>PBA-Ⅰ-2>PBA-Ⅰ-l. PBA-I contains a large number of groups that can interact with TKX-50 such as -COO-, -COOH, -OH. Among them, -COOH and TKX-50 can form a strong hydrogen bond and electrostatic attraction. As the content of -COOH increased, the interacting groups belonging to PBA-Ⅰ-3 was more than PBA-Ⅰ-1 and PBA-Ⅰ-2. Therefore the degree of coverage of PBA-Ⅰ-3 reached about 15.86% which showed a better coating effect on TKX-50.

3.4. Non-isothermal thermal decomposition kinetics analysis

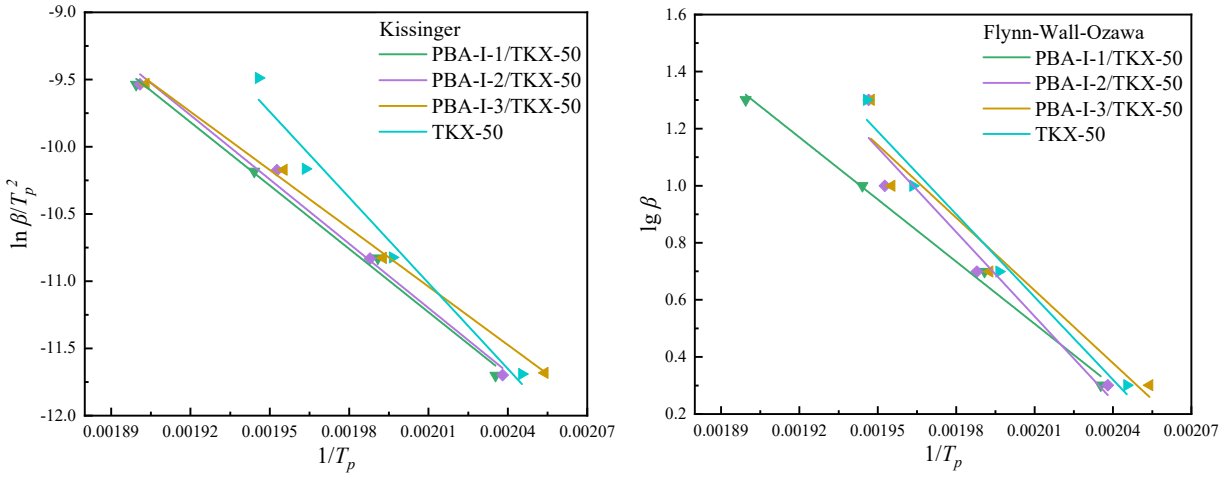
The non-isothermal thermal decomposition performance was tested by DTG-60(H) thermogravimetric analyzer. Test condition parameters: nitrogen atmosphere, gas flow rate 50 mL/min, sample volume <0.7mg, sample cell is an open aluminum crucible, test temperature range is 50~400 ℃, heating rates are 2 K/min, 5 K/min , 10 K/min and 20 K/min.The data results were obtained under four heating rates. The relevant parameters of thermal decomposition kinetics, including activation energy and pre exponential factor, were calculated by Kissinger method and Flynn-Wall-Ozawa method. The thermal decomposition of TKX-50/PBA-Ⅰ were analyzed.

The two non-isothermal thermal decomposition kinetic calculation methods of Kissinger equation and Flynn wall Ozawa equation are shown in formula(2) and formula(3)[11-12]:

$$\ln\left(\frac{\beta}{T_p^2}\right)=\ln\frac{AR}{E_a}-\frac{E_a}{R}\cdot\frac{1}{T_p} \tag{2}$$

$$\lg\beta=\lg\left(\frac{AE_a}{RG(\alpha)}\right)-2.315-0.4567\frac{E_a}{RT_p} \tag{3}$$

Where: β is the heating rate(K/min), T_p is the decomposition peak temperature(K), E_a is the apparent activation energy(J/mol), A is the pre exponential factor, of which the unit is related to the reaction order, and the first-order reaction unit is S^{-1}, R is Planck constant which is equal to 8314 J/(K·mol), $G(\alpha)$ is the integral form of phase boundary reaction mechanism function. The calculated results and fitting curves are shown in **Table 3** and **Figure 3** respectively.



(a) (b)

Figure 3. The a) Kissinger and b) Ozawa curves of TKX-50 and different TKX-50/PBA-Ⅰ

Table 3. Non-isothermal decomposition kinetics results of TKX-50 and different TKX-50/PBA-Ⅰ

Sample	Kissinger		Flynn-Wall-Ozawa		$\bar{E}_a$/(kJ·mol^{-1})	ln(A/s^{-1})
	E_a/(kJ·mol^{-1})	R^2	E_a/(kJ·mol^{-1})	R^2		
TKX-50	126.12	0.9768	127.95	0.9798	127.03	22.15
TKX-50/PBA-Ⅰ-1	130.56	0.9932	132.20	0.9941	131.38	23.09
TKX-50/PBA-Ⅰ-2	134.89	0.994	136.29	0.9947	135.59	24.19
TKX-50/PBA-Ⅰ-3	152.42	0.9411	152.85	0.9466	152.63	28.79

The E_a and A values showed that the coating effect of PBA-Ⅰ improved the activation energy barrier of TKX-50, which was conducive to the thermal stability of the coating samples. It confirmed the good interaction between PBA-Ⅰ and TKX-50. The order of E_a and A values was PBA-Ⅰ-3>PBA-Ⅰ-2>PBA-Ⅰ-l, which was the same with the order of coverage degree in 3.3. The apparent activation energy of TKX-50/PBA-Ⅰ-3 was as high as 152.63kJ·mol^{-1}, and the change of -COOH content in PBA-Ⅰ was positively correlated with the activation energy parameters, which confirmed the correlation between bonding effect and thermal stability again.

4. Conclusions

The coating properties of TKX-50/PBA-Ⅰ were characterized by SEM, FT-IR, XPS and TGA.

(1) SEM results showed that PBA-Ⅰ successfully wrapped TKX-50 crystal in the form of film or fragment and PBA-Ⅰ-3 had the best coating effect on TKX-50.

(2) FT-IR results showed that PBA-Ⅰ had no effect on the molecular structure of TKX-50 crystal which did not affect the safey of TKX-50.

(3) XPS results showed that the three anionic polymer bonding agents can produce good wettability to TKX-50, and the coating degree R increased with the increase of -COOH content. PBA-Ⅰ-3 had the best coating effect on TKX-50, of which the coating degree is up to 15.86%.

(4) PBA-Ⅰ increased the apparent activation energy of TKX-50 in varying degrees. With the increase of -COOH content, the thermal stability of the coating samples showed an increasing trend.

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