

INTERMOLECULAR INTERACTION OF A NEUTRAL POLYMERIC BONDING AGENT CONTAINING *N*-VINYLPYRROLIDONE UNITS WITH AMMONIUM PERCHLORATE AND KETO-RDX

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Abstract The interaction of a new neutral polymeric bonding agent (NPBA) containing *N*-Vinylpyrrolidone units with two types of oxidizers (ammonium perchlorate and Keto-RDX) was investigated by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). NPBA forms a layer of film on the surface of oxidizers. The paper gives hypothetical mechanisms for improving significantly mechanical properties by addition of the neutral polymeric bonding agent (NPBA).

Keywords: XPS; FTIR; NPBA; K₆; AP.

INTRODUCTION

Solid propellants fall into one of two categories. First, there are homogeneous solid propellants that contain fuel and oxidizer in a single phase. Second, there are heterogeneous propellants that are generally in the form of a composite that includes an oxidizing agent, a fuel, and a binder. It is also known to add plasticizers, curing agents, cure catalysts, ballistic catalysts and other additives to such heterogeneous compositions. They are used to provide the propulsive energy for rocket systems, kick motors for satellites, and booster motors for launching cruise missiles and unmanned air vehicles (UAVs)^[1–3].

Because of the incorporation of the considerable amount of solid energetic materials, poor mechanical properties and dewetting are important problems in composite modified double base propellants^[3–6]. Addition of bonding agent is a key technique to solve these problems. The bonding agents decrease the viscosity by evolving gas (*e.g.*, ammonia) that breaks up the thick uncured propellant slurry, making it easier to process^[7–9]. In addition the bonding agent increases the strength of the finished product by physically and chemically attaching the oxidizer to the binder^[10]. Typical bonding agents in a polar binding system where a nitro or a nitrogen group containing plasticizer is used are ineffective since they are too soluble in the polar submix. An effective neutral polymeric bonding agent (NPBA) was synthesized for a polar filler such as crystals of nitramin dispersed in the polar binder by Kim in 1990^[11].

In this investigation in order to achieve greater adsorption, *N*-vinylpyrrolidone (NVP) was added to the polymer structure. NVP is soluble in water and organic solvent, physiologically compatible, essentially chemically inert, temperature-resistant, pH-stable, non-ionic and colorless to yellowish liquid^[12]. It is also known as hydrophilic compounds which are suitable as comonomers. Furthermore it's often used for improving the affinity of polyacrylonitrile for water. Therefore, it has excellent wetting properties and readily forms films. This

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makes it well as a coating or an additive for coatings^[13].

In addition in this study ammonium perchlorate (AP) and K₆ or keto-RDX (2-oxo-1,3,5-trinitro-1,3,5-triazacyclo-hexane) were used as oxidizers. Since AP is inexpensive, easy to formulate, has very tractable ballistics and favorable burn characteristics, and so, despite its limitations, propellants that contain AP have been the backbone of solid propulsion industry for almost fifty years^[14]. Also K₆ is an interesting high explosive with high density ($\rho = 1.93 \text{ g}\cdot\text{cm}^{-3}$)^[15] and suitable heat of formation ($-41.9 \pm 4.2 \text{ kJ}\cdot\text{mol}^{-1}$)^[16]. This compound can be prepared from inexpensive starting materials and has 4% more energy than HMX at early volume expansions. It can be used as a fuel component in inflatable vehicle occupant protection devices with reduced smoke^[15–17].

The Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to study the interaction between oxidizers (ammonium perchlorate and K₆) and the NPBA contacting NCO units. We also understand from literature survey that K₆ is being used for the first time in such a study.

EXPERIMENTAL

Sample Preparation

Figure 1 shows the NPBA structure. It comprises four units: acrylonitrile, methyl acrylate, 2-hydroxy ethyl acrylate, *N*-vinylpyrrolidone. In this work, by adding *N*-vinylpyrrolidone, new NPBA was synthesized using a previously reported procedure^[11]. Sufficiently dried AP and K₆ powders were spread on a Teflon plate in order to make easy to remove the coagulated one later, and bonding agent was dripped on it in the ratio of 1:1 (weight). To disperse bonding agent in oxidizer uniformly, 2 mL acetone was added with stirring. The samples were placed in vacuum at 60 °C, and degassed for 48 h before any analysis.

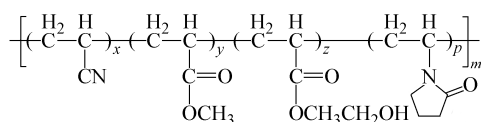


Fig. 1 NPBA scheme

Characterization

FTIR spectra were obtained by preparing KBr pellets, using a Perkin Elmer Spectrum 400 FTIR spectrophotometer in the range of 4000–400 cm^{-1} . The resolution was 4 cm^{-1} , and the number of scans was 16.

X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out on a VG Microtech Twin Anode XR3E2 X-ray source and a concentric hemispherical analyzer operated at a base pressure of 5×10^{-10} mbar using Al K α ($h\nu = 1486.6 \text{ eV}$). The experimental data were curve fitted with Gaussian-Lorentzian combination peaks after subtracting a linear background. Binding energies were referenced to C1s peak at 284.6 eV. Low resolution survey spectra, as well as higher resolution spectra of C, N, O and Cl were collected and all presently obtained binding energies are available in Table 1.

Table 1. Binding energies of C1s, N1s and O1s of NPBA functional groups

Element/transition	Peak energy (eV)	Peak area counts (eV/s)	FWHM (eV)	Concentration (%)	Assignment
C1s	284.95	225.4	1.50	11.8	—CH ₂
	286.05	830.8	1.58	43.7	—C*—C=O, —C*—CN
	286.89	632.3	1.50	33.2	—C—OH, —CN
	287.90	120.1	1.79	6.3	O=C—N
	289.00	94.0	1.66	4.9	O—C=O
N1s	399.05	224.5	1.44	50.8	—NCO
	399.68	217.3	1.49	49.2	—CN
	530.39	38.5	1.00	3.9	—N—C=O
O1s	531.97	362.5	1.50	36.3	O—C=O*
	532.81	387.2	1.52	38.8	C—OH
	533.76	210.1	1.50	21.1	O*—C=O

RESULTS AND DISCUSSION

FTIR Study of NPBA

The middle IR spectrum was used to identify NPBA (Fig. 2). O—H vibrations appear as an intense broad envelope in the high energy region with maximum at 3450 cm^{-1} . The C—H asymmetric stretching vibration at 2954 cm^{-1} is clearly seen. The weak band at 2230 cm^{-1} is attributed to —CN functional group in NPBA. There are clear structure bands at 1652 and 1733 cm^{-1} , these are assigned to C=O stretching modes. The relative intense peak at 1450 cm^{-1} is assigned to —CH₂ bending mode. Moreover, C—O—C asymmetric stretching vibration bands are seen at 1124 , 1199 and 1169 cm^{-1} . The band situated at 1077 cm^{-1} is due to the stretching vibration of C—O belonging to ester groups of NPBA (Table 2).

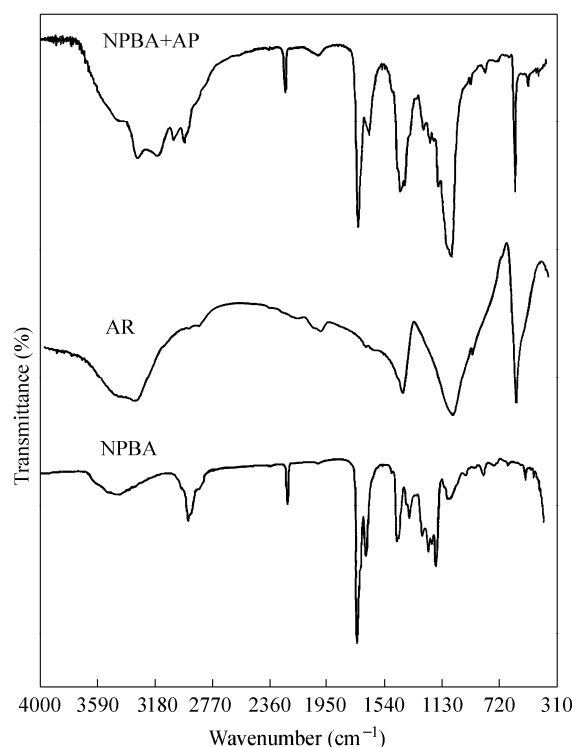


Fig. 2 FTIR spectrum of AP, NPBA and NPBA + AP

Table 2. Experimental FTIR vibrational signals and assignments of AP, NPBA and the mixture of them

AP FTIR (cm^{-1})	NPBA FTIR (cm^{-1})	NPBA + AP FTIR (cm^{-1})	Assignment ^a	Note
{ 3415 3303	3450	3400	ν O—H	Appear as shoulder in mixture
		{ 3284 3144	ν N—H	N—H stretching vibration splitting the effect of NCO unites
		3032		New band
	2954	2955	ν^{as} C—H	
	2230	2176	ν C $\equiv$ N	Shifted downward
	1733	1732	ν C=O	
	1652	1673	ν C=O	Formation of hydrogen bonding
1423	1450		β CH ₂	
			γ N—H	
		1434	β^{as} CH ₂ + γ N—H	
	1386	1403	β^{s} CH ₃	
	1366		γ CH ₂	

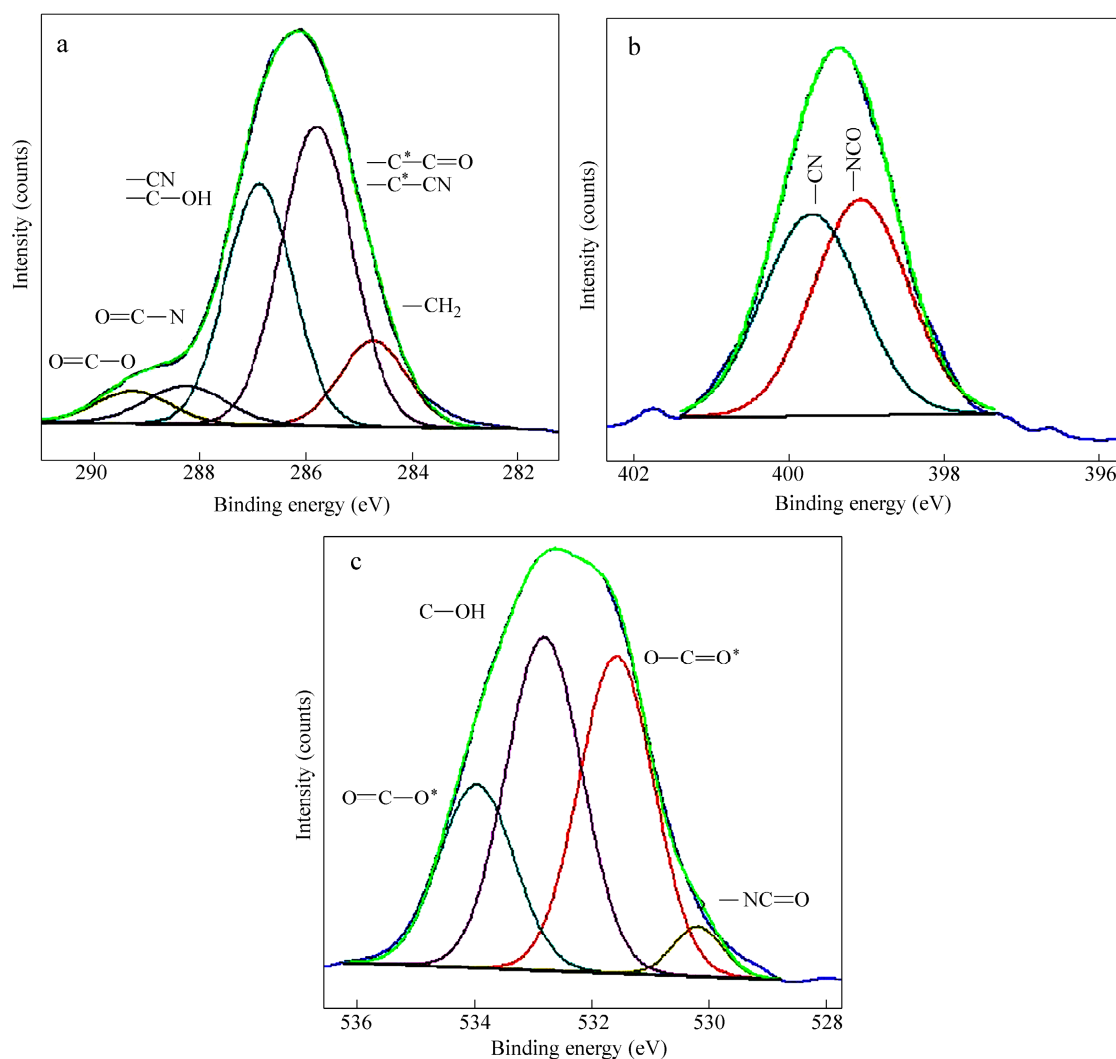
Table 2. Continued

AP FTIR (cm^{-1})	NPBA FTIR (cm^{-1})	NPBA + AP FTIR (cm^{-1})	Assignment ^a	Note
	1269	1270	ν C—N (NCO)	
	$\left\{ \begin{array}{l} 1224 \\ 1199 \\ 1169 \end{array} \right.$	$\left\{ \begin{array}{l} 1224 \\ 1197 \\ 1166 \end{array} \right.$	ν^{as} C—O—C	
	1077	1078	ν C—O + ν ClO ₄ [−]	Intensive reduction in broadening
1071			ν C—O	
625		625	ν ClO ₄ [−]	
			β ClO ₄ [−]	Intensive reduction in broadening

^a Vibrational modes: ν , stretching; β , bending in plane; γ , bending out-of-plane; superscript s, symmetric; superscript as, asymmetric

XPS Study of NPBA

XPS spectra of all NPBA atoms are shown in Figs. 3(a), 3(b) and 3(c). Binding energies (BE) are summarized in Table 1. The binding energies for NPBA are in good agreement with earlier solid-state measurements^[18–22]. Curve fitting analysis of the C1s, N1s and O1s spectra was performed using Gaussian curves as fitting functions.

**Fig. 3** XPS (a) C 1s, (b) N 1s and (c) O 1s spectra of NPBA

NPBA core level spectra are identical and consist of various components, labeled in increasing BE order. NPBA carbons can be divided into five groups: aliphatic C—C carbons, carbons of the NPBA attach to —CN and —C=O groups, highly antiscreened —C≡N carbons and carboxyl groups of NPBA, N—C=O carbons of *N*-vinylpyrrolidone and O—C=O carbons of NPBA. The N1s spectra consist of two peaks corresponding to —C≡N and —NCO groups. In the O1s spectrum the first peak is related to —NCO groups, also oxygen contributions from the ester group indicated as 533.76 eV and 531.97 eV in the O1s spectrum (Fig. 3) are well resolved with a splitting of 1.79 eV and hydroxyl groups are evidenced by peak at 532.81 eV.

Interaction of AP with NPBA

Figure 2 shows the spectrum of NPBA+AP. It is readily observable that fundamental spectral changes have occurred at the frequencies of AP and NPBA. The frequencies of the OH stretching vibrations of NPBA (3450 cm^{-1}) and N—H stretching vibration in AP (3415 and 3303 cm^{-1}) changed (Table 2). The comparison between original spectrum and difference spectrum of AP in interaction with NPBA revealed that the peak superposing a stretching mode of the hydroxyl group shifted by approximately 50 cm^{-1} to lower frequencies and appeared as a shoulder. This is shown that the intermolecular bonding force arises from the hydrogen bonding force in the case of NPBA (Fig. 4).

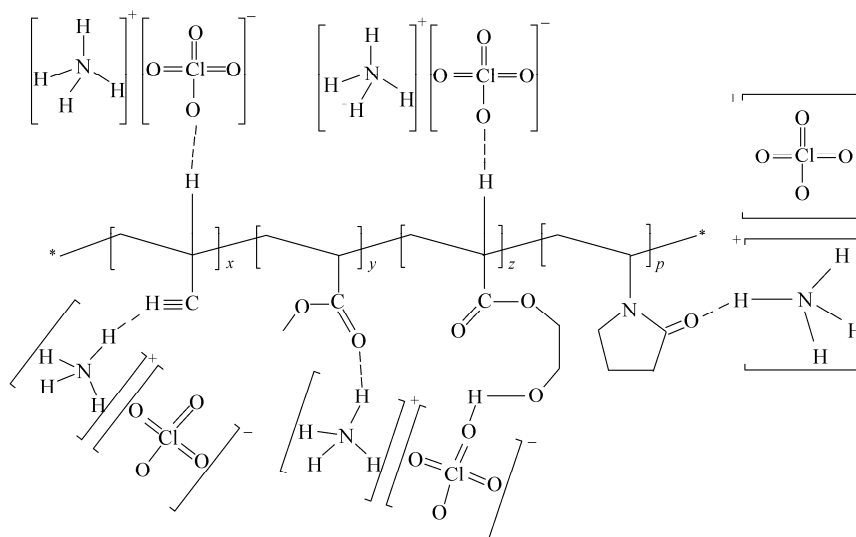


Fig. 4 Hypothetical interaction between AP and NPBA

The new absorption band, 3032 cm^{-1} is assigned to N—H stretching vibration, which is the evidence for the hydrogen bonding occurrence due to —NCO polar group interaction with AP molecule. Therefore, these new absorption bands suggest the presence of —NC=O...H—N interaction and the shift towards lower wavenumber may manifest the formation of hydrogen bonded structure as shown Fig. 4.

The weak band at higher frequency at 2955 cm^{-1} can be ascribed to the C—H stretching vibration in FTIR. The intensity of —CN stretching vibration in FTIR spectrum shifted downward from 2230 cm^{-1} to 2167 cm^{-1} . Also, there exist clear structure bands at 1673 and 1732 cm^{-1} in NPBA+AP spectrum, these are assigned to C=O functional groups. Because of hydrogen bonding interaction C=O bending mode shifted downward. Characteristic bands of —ClO₄[−] ion in the low frequency region are the 1078 and 625 cm^{-1} peaks in FTIR spectrum (Table 2).

Ammonium perchlorate as interaction with NPBA, the broadening of the ClO₄[−] bands reduced. Although there is evidence for surface interaction of the perchlorate ion, the results clearly justify by XPS study.

The C1 2p XPS spectrum from AP is shown in Fig. 5. The energy splitting of a photoelectron peak is commonly found in an XPS spectrum, because of the interaction between the spins of the electron, s, (up or

down) and its orbital angular momentum, l . This interaction leads to a splitting of the degenerate state into two components. The corresponding Cl 2p peak^[23], exhibiting spin-orbit splitting, have binding energies of 207.65 eV and 209.19 eV (Fig. 5a). The data show a continual change in the observed Cl 2p, binding energy over a range of 203.0–211.0 eV. Chlorine peaks have undergone changes after exposure to surface interaction of NPBA (Fig. 5b). The intense peak of chlorine has decreased in intensity; also shape and the binding energy peak of Cl 2p have changed. It can be concluded that the resonance structure of the perchlorate ion due to interaction with NPBA's hydrogen has changed, and in consequence the binding energy of the chlorine atom has changed (Table 3). Therefore ammonium perchlorate is in the strong intermolecular interaction with NPBA.

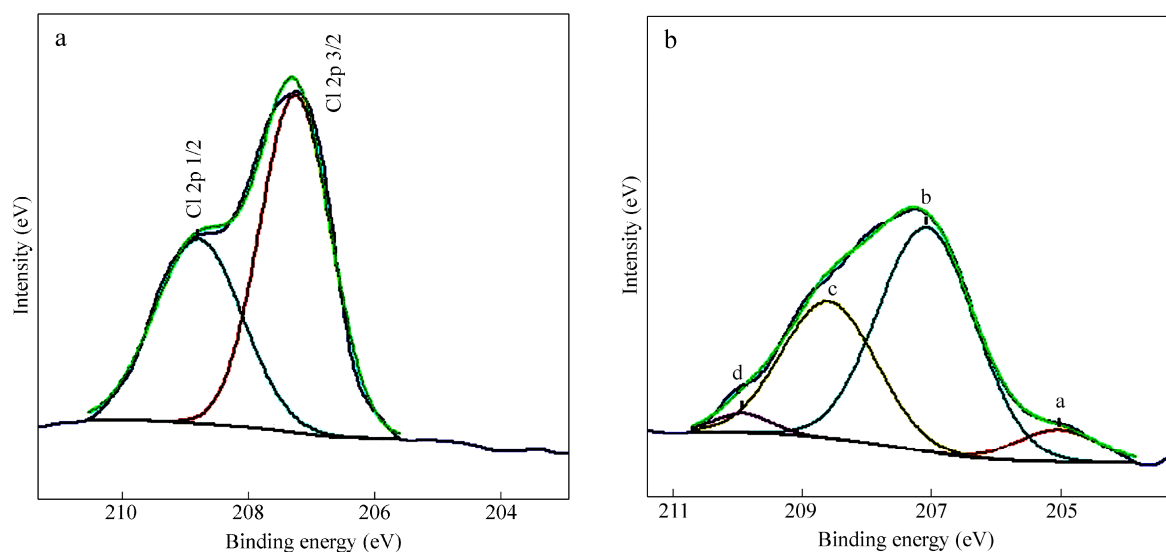


Fig. 5 XPS Cl 2p spectra of (a) AP and (b) AP + NPBA

Table 3. Binding energies of Cl 2p of AP and AP/NPBA

Compound	Element/ transition	Peak energy (eV)	Peak area counts (eV/s)	FWHM (eV)	Concentration (%)
AP	Cl 2p	207.65	62.2	1.33	59.7
		209.19	41.9	1.64	40.3
NPBA/AP	Cl 2p	205.02	2.6	1.50	6.8
		207.07	211.5	1.78	56.7
		208.59	12.8	1.72	33.6
		209.93	1.1	1.03	2.9

Interaction of K_6 with NPBA

The FTIR spectrum of K_6 is characterized by intense and sharp vibrational bands (Fig. 6). The most probable attributions of these bands are shown in Table 4. The C–H asymmetric stretching modes appear in the high energy region with maxima at 3056 and 2992 cm^{-1} . Also the C–H in plane bending vibration is observed at 1457 cm^{-1} , and the C–H out of plane modes appear at 1282 and 896 cm^{-1} . The intense band due to the C=O stretching vibration produces a maximum at about 1765 cm^{-1} . Strong bands at 1604 and 1282 cm^{-1} can be assigned to the $-\text{NO}_2$ asymmetric and symmetric stretching modes, respectively. The bands at 1368, 1320, 1305, 1035 and 957 cm^{-1} are attributed to $-\text{N}-\text{NO}_2$ stretching mode. These modes of vibrations, contributions of in plane and out of plane C–H bending vibration are observed as illustrated in Table 4.

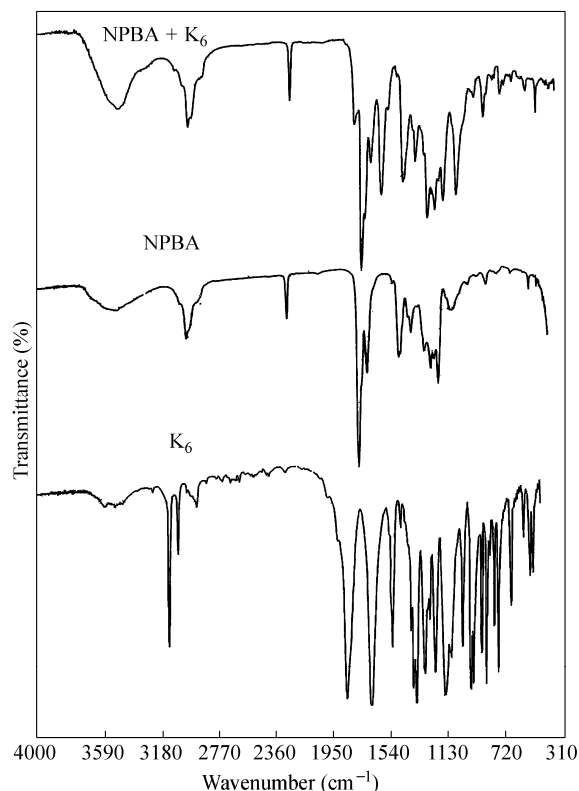


Fig. 6 FTIR spectra of K6, NPBA and NPBA + K₆

Table 4. Experimental FTIR vibrational signals and assignments of AP, NPBA and the mixture of them

K ₆ FTIR (cm ⁻¹)	NPBA FTIR (cm ⁻¹)	K ₆ + NPBA FTIR (cm ⁻¹)	Assignment ^a	Note
	3446	3417	ν O—H	Red shift
3056			ν^{as} C—H	Disappear
2992			ν^{as} C—H	Disappear
	2954	2932	ν^{as} C—H	Red shift
	2230	2215	ν C $\equiv$ N	Red shift
1765		1765	ν C=O	Appear as a shoulder
	1733	1733	ν C=O	
		1712	ν C=O	New band
	1652	1674	ν C=O	Blue shift
1604		1597	ν^{as} NO ₂	Red shift
1457	1450	1449	β CH ₂	Blue shift
	1386		β^{s} CH ₃	Disappear
1368			ν N—NO ₂	Disappear
	1366	1364	γ CH ₂	
1320			ν N—NO ₂	Disappear
1305		1305	ν N—NO ₂	
1282		1277	ν^{s} NO ₂	
	1269		ν C—N (NCO)	Disappear
	1224	1225	ν^{as} C—O—C	
1223			ν^{as} N—C—N	Disappear
	1199	1202	ν^{as} C—O—C	

Table 4. Continued

K ₆ FTIR (cm ⁻¹)	NPBA FTIR (cm ⁻¹)	K ₆ + NPBA FTIR (cm ⁻¹)	Assignment ^a	Note
1190			$\nu^{\text{as}} \text{N}-\text{C}-\text{N}$	Disappear
	1169	1169	$\nu^{\text{as}} \text{C}-\text{O}-\text{C}$	
1151			$\nu^{\text{as}} \text{N}-\text{C}-\text{N}$	Disappear
1077	1077	1077	$\nu \text{C}-\text{O} + \nu^{\text{as}} \text{N}-\text{C}-\text{N}$	
1035			$\beta \text{CH}_2 + \nu \text{N}-\text{NO}_2$	Disappear
957			$\beta \text{CH}_2 + \nu \text{N}-\text{NO}_2$	Disappear
896			γCH_2	Disappear
875			R_g breathing	Disappear
821			$\nu \text{C}-\text{N}-\text{C}$	Disappear
783			$\nu \text{N}-\text{C}-\text{N}$	Disappear
728			βrg	Disappear
701			βrg	Disappear

^a Vibrational modes: ν , stretching; β , bending in plane; γ , bending out-of-plane; superscript s, symmetric; superscript as, asymmetric

FTIR spectrum of K₆ + NPBA is shown in Fig. 6. The absorption band at 3417 cm⁻¹ related to an O—H group is shifted downward as a result of intermolecular interaction and the hydrogen bonding formation between K₆ and NPBA. Due to intermolecular interaction in the component of NPBA the absorption at 1652 cm⁻¹ belonging to a carbonyl group shifted to around 1674 cm⁻¹ (Fig. 7). The bands of C—H stretching vibrations of K₆ disappeared. Exception of intramolecular interaction and van der Waals force it is suggested that a strong intermolecular interaction between hydrogens of K₆ and functional groups of NPBA such as —CN, C=O, —OH and NCO has occurred (Fig. 7).

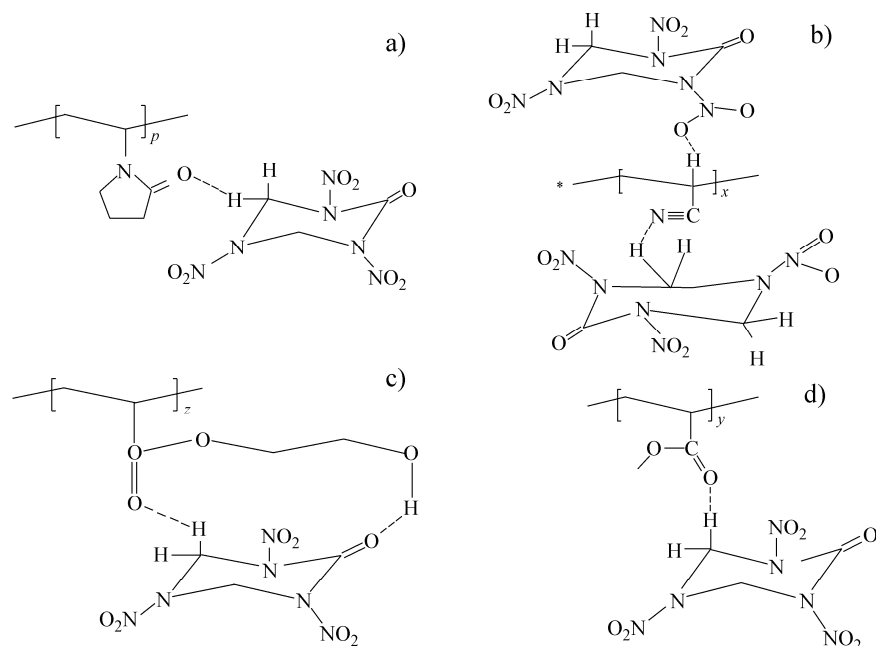


Fig. 7 Hypothetical hydrogen-bonding formation between K₆ and NPBA unites: (a) *N*-vinylpyrrolidone, (b) acrylonitrile, (c) 2-hydroxy ethyl acrylate and (d) methyl acrylate

The —CN groups can be detected as a medium intensity band at 2215 cm⁻¹ which is shifted downward by 15 cm⁻¹. The hypothetical hydrogen bond formation of this group is shown in Fig. 7(b). The frequency of the

C=O stretching at 1765 cm^{-1} for K_6 appears as a very weak band in the mixture which leads us to suggest a hydrogen-bonded structure between K_6 and NPBA as shown in Fig. 7(c). Moreover it is notable that a C=O vibration mode appeared at 1712 cm^{-1} . This new absorption band suggests the presence of —NCO groups and the shifting towards lower wavenumber may manifest the formation of a hydrogen-bonded structure as shown in Fig. 7.

In the lower frequency range (below 1650 cm^{-1}) of NPBA + K_6 FTIR spectrum, two bands can be referred to K_6 . The first one located at 1593 cm^{-1} and assigned to the —NO_2 asymmetric stretching mode is shifted downward from 1604 cm^{-1} . The second band appears at 1277 cm^{-1} which is corresponding to —NO_2 symmetric modes of vibration.

Although small changes for nitro groups interaction are observed in FTIR spectra, wide variation is shown in XPS. The observed XPS N1s spectra of K_6 are summarized in Fig. 8. The peaks shifted to lower binding energy generally indicate a more reduced chemical state, while those shifted to higher binding energy indicate a more oxidized chemical state. Therefore, the lower binding energy peak is suggested to N—C—N belonging to the aliphatic or ring nitrogen atoms while the higher binding energy peaks arises from the nitrogen atom in the nitro group of K_6 (Table 5). Moreover a change in BE is a major factor in determining the electronic structure of molecules. A change in the surrounding matrix of atoms or a change in the degree of electron bond polarization between nearest neighbor atoms will have a significant impact on the BE of XPS. After coating, it is readily observable that fundamental spectral changes have occurred in BE of nitrogen atoms in the nitro group of K_6 . The nitrogen atoms of nitro groups consented the new relative proportional of oxidation state, subsequently appeared at new BEs. The authors have declared that strong intermolecular interaction between oxygen of nitro groups with NPBA's hydrogen, especially hydroxyl groups exists (Fig. 7).

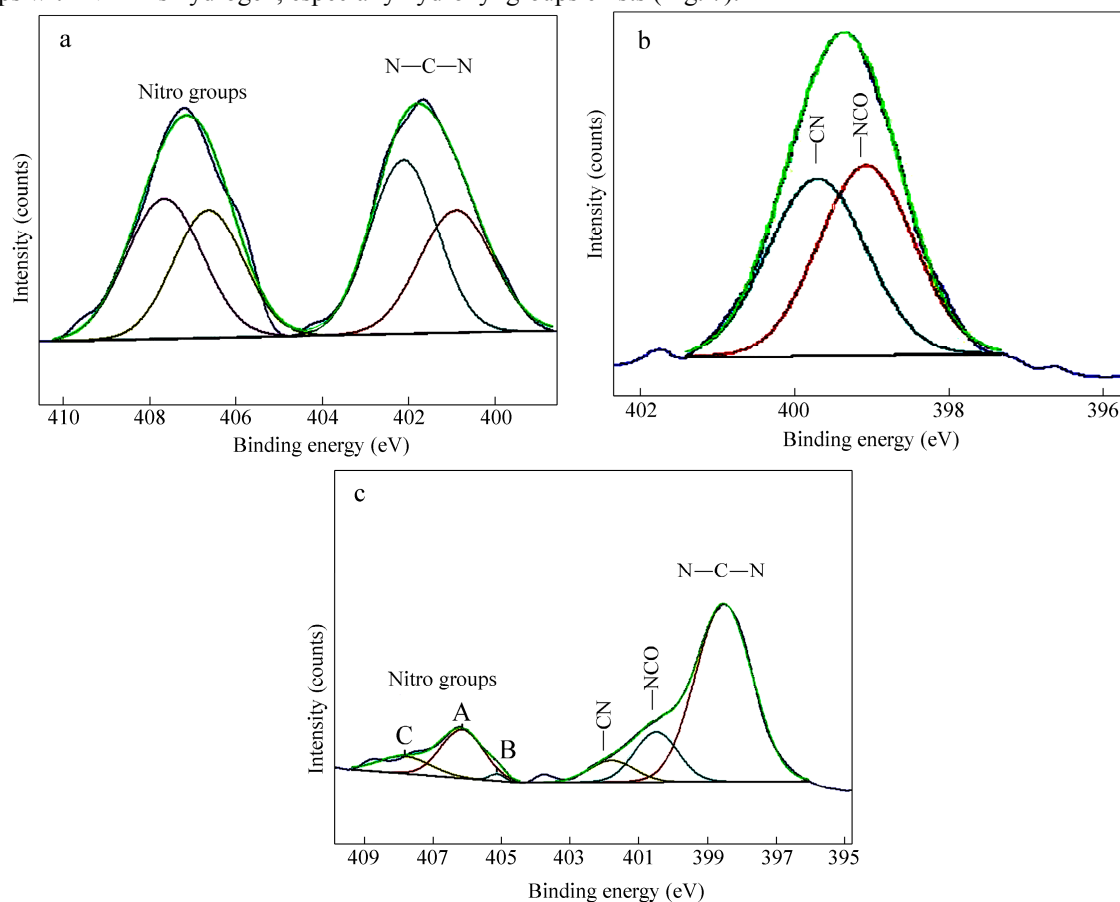


Fig. 8 XPS N 1s spectra of (a) K_6 , (b) AP + NPBA and (c) K_6 + NPBA

Table 5. Binding energies of N1s of K₆ and K₆/NPBA

Compound	Element/ transition	Peak energy (eV)	Peak area counts (eV/s)	FWHM (eV)	Concentration (%)
K ₆	N1s	400.91	57.3	2.00	22.3
		402.12	74.9	1.85	29.2
		406.63	57.1	1.91	22.2
		407.65	67.6	2.06	26.3
K ₆ /NPBA	N1s	398.52	137.5	1.94	76.1
		400.49	29.6	1.50	16.4
		401.79	13.4	1.56	7.4
		406.15	28.5	1.48	67.3
		405.13	1.5	0.53	3.6
		407.82	12.4	1.80	29.2

CONCLUSIONS

FTIR spectra combined with the XPS results show that in addition to van der Waals attractions the hydrogen-bond plays a very important role in the interactions of NPBA and oxidizers. In samples of AP + NPBA and K₆ + NPBA, FTIR spectral evidence is presented which indicates that intermolecular hydrogen-bonding between NH₄⁺ ion of AP, carbonyl and hydrogen of K₆ with NPBA occurs. The XPS data of AP + NPBA and K₆ + NPBA provide evidence for hydrogen bonding between the perchlorate ion of AP and nitro group of K₆ with NPBA which enhances the adsorption of the oxidizer and NPBA. Therefore, if the essential role of bonding agents is placed on producing tough bonding and good interaction at oxidizer surface, the NPBA containing NCO groups is recommended.

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