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OBSERVED INFRARED ABSORPTIONS OF OH SPECIES IN A MAGNESIUM OXIDE-DOPED SUCROSE-KNO_3 COMPOSITE PROPELLANT

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ABSTRACT

Infrared spectroscopy was used to analyse a sucrose-potassium nitrate composite propellant (KNSU) doped with varying percentages 5, 10, and 15 MgO. The pre-doped KNSU as control and the triplicate 5 %, 10 %, and 15 % were all synthesized using the re-crystallization method. The FTIR results obtained showed the presence of OH species, isolated non-H bonded 3563 cm^{-1} and 3697 cm^{-1} vibrations. An internally bonded OH species at 3559 cm^{-1}. Hydrogen-bonded OH vibrations with the characteristic U shape were identified at 3384-3321 cm^{-1}. Other functional groups identified but of less importance in this presentation were aliphatic CH stretching and magnesium bending. Previous studies have inferred that OH absorptions above 3600 cm^{-1} are attributed to inorganic/mineral composite interactions between MgO and the KNSU matrix. These interactions inhibit hygroscopic behavior, making MgO-doped KNSU a promising candidate for military propulsion systems.

Keywords: Composite propellant, Sucrose-KNO_3, Hydroxyl species, Infrared spectroscopy, Military application, Vibrational stretching

INTRODUCTION

Fourier Transform Infrared Spectroscopy (FTIR) is an important analytical technique for investigating the chemical composition and molecular structure of materials (Siddique, 2024). In composites and propellants, FTIR acts as a vital tool for understanding the chemical interactions, curing processes, degradation mechanisms, and the incorporation of various additives or fillers (Phondekar, & Biswas, 2024) FTIR gives detailed spectra of molecular vibrations, which can be used to identify functional groups, monitor curing or aging processes, and assess the compatibility of matrix and filler materials (Cholake et al. 2014). Until recently, infrared spectroscopy had no broad application as a technique of identification of minerals and related species. The main reason for this was the lack of adequate reference books and databases in this area of minerals and metal composites (Chukanov 2013) (Chukanov & Chervonnyi, 2016). Since infrared spectroscopy is widely used by organic chemists for qualitative chemical elucidation, it is generally accepted that they are proficient in the deductive and elucidative characterization of infrared spectra (Mohan, 2004). This belief was put to the test when a sucrose potassium nitrate (KNSU) composite doped with MgO was analyzed using FTIR (Iguniwei, 2024). The species of interest in the ir spectra were the OH functional groups whose origins may have arose from trapped water molecules, sucrose OH groups and the MgO interaction via hydrogen bonding with the water molecules. Two types of hydroxyls are expected to be formed by heterolytic dissociation of water on Mg^{2+}--- O^{2-} pairs. As described by Chizallet et al. (2007), the heterolytic dissociation of water on Mg^{2+}—O^{2-} pairs can be represented as follows:

$$Mg^{2+}\text{---}\ O^{2-} + 2H_2O \rightarrow Mg^{2+}\ 2(OH^-) + 4H^+\ O^{2-}$$

The recrystallization method was employed to synthesize the MgO-doped KNSU propellant (Smiley, 2013), a novel assumption that magnesium at elevated temperature could undergo heterolytic rearrangement and prevent hydrogen bonding between water molecules and hydroxyl species were highlighted (Chizallet et al., 2007).

MATERIALS AND METHODS

Materials

Table sugar (500 g), industrial grade potassium nitrate (1000 g), heating pan, heat resistant thermometer, glass stirrer and ramming tool, measuring tape and ruler, hand gloves, goggles, dust mask, ceramic mortar and pestle, weighing crucibles, desiccator and ceramic tiles, magnesium oxide (500 g) and moulds

Equipment

Heating mantle, heating pan and stirring scoop, (ii) Digital Weighing Balance, Rossell Hobbs Electrical blender (Model # 22251, year 2014) Agilent Cary FTIR spectroscope (Model # 630, year 2011, serial # MY14470031)

Sample Preparation

The composite propellant samples were prepared using sucrose ($C_{12}H_{22}O_{11}$) as the fuel, potassium nitrate (KNO_3) as the oxidizer, and magnesium oxide powder (MgO) as the dopant. The MgO content varied by weight at 0%, 5%, 10%, and 15%. To increase surface area, the sucrose and potassium nitrate were thoroughly ground in a ceramic mortar and pestle. Batches of 100 g each were weighed and stored.

Recrystallization

Sixty-five grams of KNO_3 and 35 grams of sucrose were weighed and mixed to form a standard 100g batch. It was transferred to a heating pan containing 200 ml of water to dissolve. The mixture was heated with gentle stirring to dry~~ing~~ and was transferred into a mould to cool and which also served as the control. The MgO/KNSU batch was produced with variations in the percentages as listed under sample preparation. As presented in Table 1 and transferred into ziploc polyethylene bags separately, labeled and kept securely.

Fourier Transform Infrared Spectroscopy (FTIR)

One (1) mg each of the control (0 %), MgO/KNSU (5 %, 10 %, and 15 %) composite Propellant was ground with a transparent KBr (10 mg) matrix and transferred to a sample holder that had all moisture removed. It was inserted into the instrument placeholder and then powered on to commence the analysis. Results were obtained.

RESULTS AND DISCUSSION

Results

Table 1: KNSU Composite Propellant doped with MgO

Variations Symbols	MgO Modifier	(% of a 100 g) KNSU
MgO A1	5	95
A2	10	90
A3	15	85
KNSU	0	100

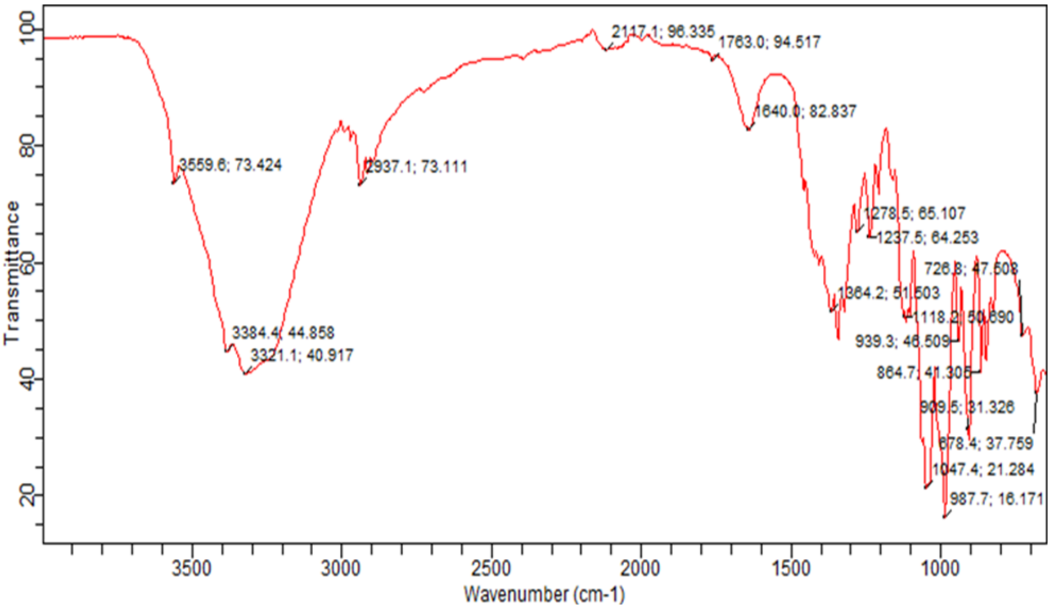

Figure 1a: Pre doped KNSU FTIR Spectrum

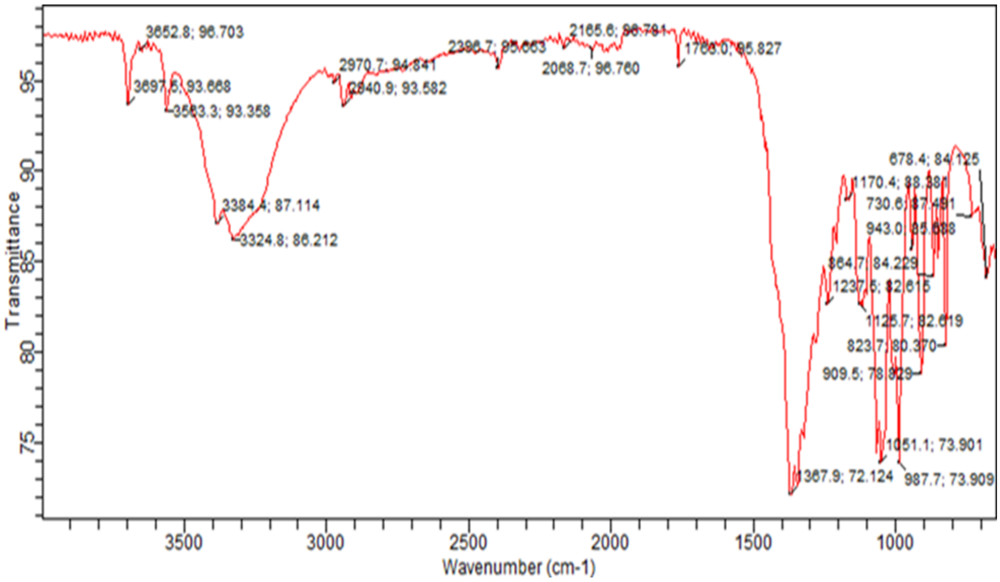

Figure 1b: 5% MgO/KNSU FTIR Spectrum

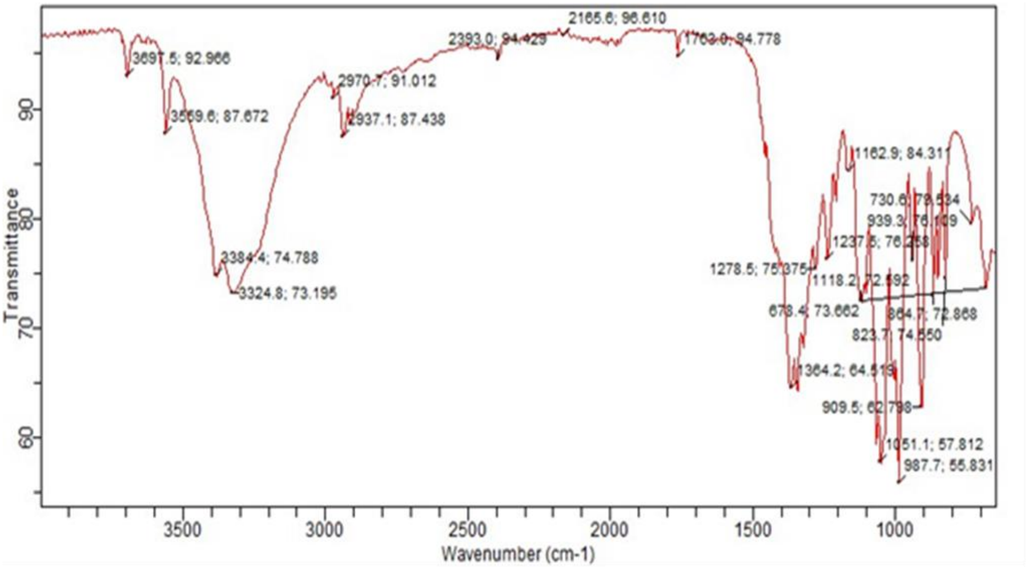

Figure 1c: 10% MgO/KNSU FTIR Spectrum

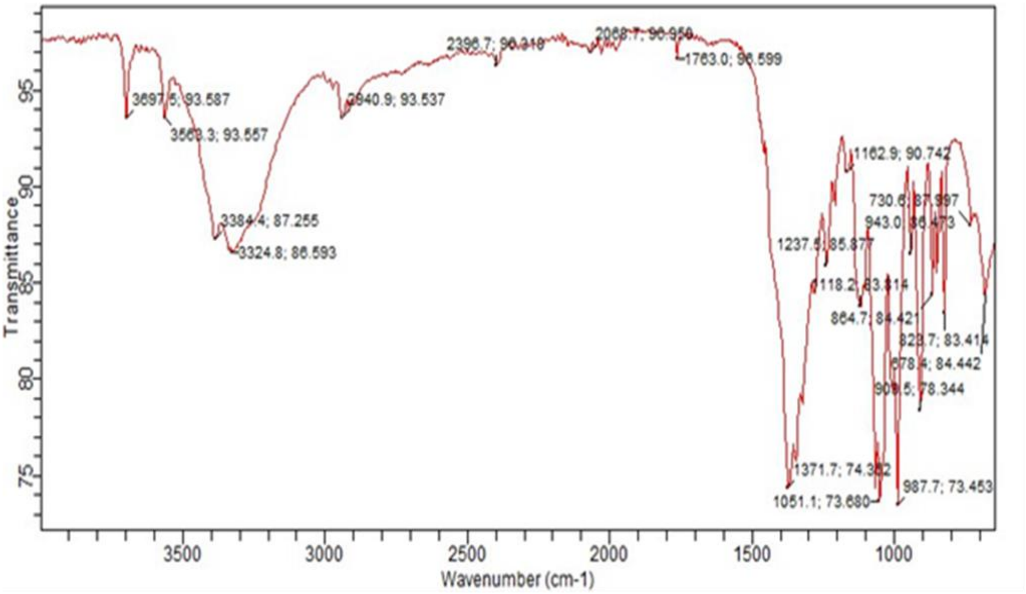

Figure 1d: 15 % MgO/KNSU FTIR Spectrum

Table 2: FTIR Tabulated Results: KNSU control and MgO doped KNSU

% Dopant	Observed Peaks (cm^{-1})	Shape	Interpretation (cm-1)
KNSU	3559	weak	OH stretching (Internally bonded)
(0%)	3384, 3321	Broad, medium	OH symmetrical stretching
	2937	Narrow, weak	CH symmetrical stretching
	1640	Broad, weak	H-O-H bending vibration
5%	3697, 3563	Sharp, weak	OH stretching (none H bonded)
	3384, 3324	Broad, medium	OH symmetrical stretching
	2970, 2940	Narrow, weak	CH Assym/Sym Streching
	1050	Sharp, strong	Mg bonded to OH bending vibration
10%	3563	Sharp, weak	OH stretching (none H bonded)
	As observed for 5%		
	909	Sharp, strong	NH wagging vibration
15%	As observed for 5% & 10%		
	1051	Sharp, strong	C-O ether stretching

Discussion

Table 1 presents the KNSU control and the magnesium oxide dopant varied as 5 %, 10% and 15 % in formulating the KNSU/MgO composite propellant (KNSU/MgOCP). Figure 1a-1d presents the FTIR results of the pre-doped KNSU, doped MgO/KNSU composite propellant MgO/KNSUCP. Table 2 presents all the absorption wavenumbers of the FTIR spectra (1a-1d). However, the interest is the OH absorption wave numbers 3300 cm^{-1} – 3700 cm^{-1} whose origins may have risen from trapped water molecules, sucrose OH groups and the MgO interaction via hydrogen bonding with the water molecules (Chizallet et al., 2007). The dual wavenumbers of 3384cm^{-1} and 3321 cm^{-1} and 3324 cm^{-1} may be attributed to primary amine asymmetrical and symmetrical stretching (Vlcek Jr et al., 2015), and may also be attributed to hydrogen bonded OH with a U shape on the spectrum. Some Organic chemistry biased researchers attributed these wave numbers up to 3600 cm^{-1} to be hydrogen bonded and some dimeric internally bonded OH species (Coates, 2000; Mohan, 2004). They seem not to recognize the importance of wavenumbers beyond 3600 cm^{-1} in the range of 3650 cm^{-1} – 3750 cm^{-1} (Chukanov & Chervonnyi, 2016). Initially, the wavenumbers 3697 cm^{-1} and 3563 cm^{-1} were misattributed as noise and distortions without significant value.

Chukanov & Chervonnyi, 2016 inferred that values above 3600 cm^{-1} are ascribed to isolated OH species in inorganic and mineral matrix complexes like the composite propellant doped with inorganic MgO. This assertion agrees with the work on Al-OH stretching vibration at 3630 cm^{-1} as reported by Usman & Alkali (2024). Chukanov & Chervonnyi (2016) explained that for potassium-fluor-richterite and K-rich richterites the band of stretching vibrations of OH groups belonging to the cluster MgMgMg–OH–(K) is observed in the range from 3694 cm^{-1} to 3730 cm^{-1}. These values agree with the 3697 cm^{-1} obtained from the potassium nitrate sucrose composite propellant doped with varying percentages MgO (5 %, 10% and 15%). The potassium in the KNO$_3$ plays an interactive role with the Magnesium of the MgO in coordinating with and isolating OH species, observed from the FTIR result of 3697 cm^{-1} in the MgO/KNSU doped composite. Similar high wavenumber bands above 3680 cm^{-1} are ascribed to OH groups adjacent to a filled A-site, [M(1) M(1)M(3)]–OH–A (Jacobsen, 2006), where A is occupied with Na or K (Chukanov & Chervonnyi, 2016, p 19). The wave number 3559 cm^{-1} of the pre-doped KNSU composite propellant was ascribed to internally bonded OH, likely trapped in the matrix of the sucrose composite. It was observed that the shoulder off the U-shaped bonded OH species shifted upfield due to the influence of the magnesium temperature-dependent reaction as elucidated in equation 1. This reaction lead to the absorption becoming distinct sharp and isolated from the U-shaped OH-bonded species as observed in the spectra of figure 1a – 1d. The magnesium reaction has also eliminated the water bending vibration absorption observed at 1640 cm^{-1} in Figure 1a pre pre-doped KNSU spectrum. Its absence in the 1b – 1d spectra confirms the active role played by magnesium's ability to isolate OH species in a coordinating fashion. These observations agree with the research data as espoused by (Mink et al., 2018; Chukanov 2013).

CONCLUSION

This study underscores the significance of infrared absorptions of OH species beyond 3600 cm^{-1}, countering biases from some researchers with organic chemistry perspectives Magnesium oxide doping significantly influences the formation of internally bonded and isolated OH species in sucrose-KNO$_3$ composite propellants (Kas evidenced by increased IR absorptions intensities at 3563 cm^{-1} and 3697 cm^{-1}. The enhanced Mg-OH matrix significantly improves hygroscopic inhibition, positioning MgO-doped sucrose-KNO$_3$ composite propellant (KNSU/MgOCP) as a highly promising propellant for military solid rocket propulsion systems.

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