

Identification of Isocyanate Numbers on IPDI and TDI Influenced by Storage Duration and Their Impact on Composite Solid Propellant

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Abstract

*The mechanical properties of composite propellants are greatly influenced by the curing ratio (NCO/OH), which represents the ratio of isocyanate groups in the curing agent to hydroxyl groups in the polyol. Augmenting the NCO/OH ratio will enhance strength and hardness while diminishing the strain. Hence, it is crucial to establish the quantity of isocyanate present in the curing agent compound during propellant formulation, since it directly influences the mechanical characteristics of the prepared propellant. It is pivotal to evaluate the quantity of isocyanate in the samples stored for a specific duration, as it has a strong tendency to react with water vapor. This work evaluated the quantity of IPDI and TDI isocyanates after being kept for a duration of 84 and 90 months. The FTIR analysis detected the existence of NCO functional groups at 2240 cm^{-1} for TDI samples and 2243 cm^{-1} for IPDI samples after being held for 84 and 90 months, respectively. The quantity of isocyanate dropped by 1-2% over a six-month of storage. The decrease in isocyanate content will alter the composition of **the propellant** formulation, leading to propellants with distinct characteristics due to their influence on the curing ratio (NCO/OH).*

Keywords: isocyanate, IPDI, TDI, polyurethane, curing agent, composite propellant

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INTRODUCTION

Isocyanates are widely recognized for their versatility. CA Wurtz first synthesized them in 1848 by reacting diethyl sulfate and potassium cyanide (Gabriel et al., 2014; Lenzi et al., 2022). As the derivatives of isocyanic acid, isocyanates are chemicals that consist of NCO groups. (Gabriel et al., 2014; Kapp, 2024). Two adjacent double bonds unite nitrogen (N), carbon (C), and oxygen (O) atoms to form the chemical structure. Due to its unusual location between the two

electronegative elements N and O, the C atom acquires a comparatively substantial positive charge, which produces a significant electrophilic effect. Thus, the combination of the N atom's nucleophilic nature and the C atom's high electrophilicity makes isocyanates distinctive and extensively utilized (Lenzi et al., 2022). The extensive application of isocyanates belonging to the non-formaldehyde class in the coatings and adhesives industry can be attributed to their favorable bonding properties, water resistance,

resistance to aging, and excellent manufacturability. Furthermore, the exceptionally reactive properties, have caused isocyanate-derived materials to be widely applied in self-healing compounds, graphene-based composites, nanocomposites, etc. (Y. Ma et al., 2017).

In fact, isocyanates have been recognized for decades as a polyurethane building block (Lenzi et al., 2019). In order to produce polyurethane, diisocyanate, a monomer containing two NCO groups as the primary reactive sites, is required. (Gabriel et al., 2014; Spence & Plehiers, 2022). The reaction mechanism involving diisocyanate and polyol to produce polyurethane is illustrated in Figure 1. Specifically, Figure 1a depicts the reaction between polyol and toluene diisocyanate (TDI), whereas Figure 1b illustrates the reaction of polyol and isophorone diisocyanate (IPDI). The reaction occurs when a nucleophilic compound containing an active hydrogen atom attacks the carbon atom from NCO. The hydrogen atom is added to the nitrogen, by which breaks the double bond. The reactivity is based on the high electronegativity of nitrogen and oxygen atoms, which displace the molecule's electron density (Gabriel et al., 2014).

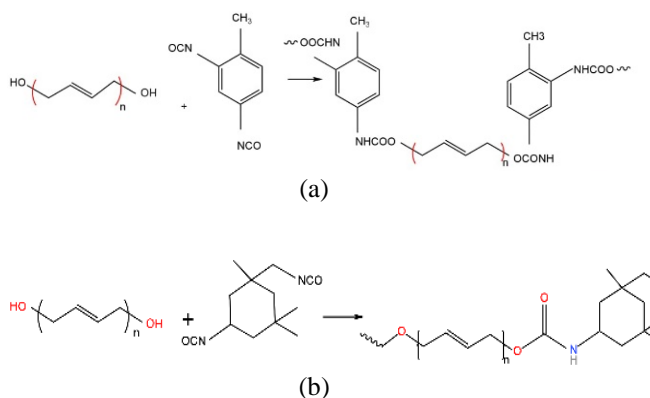


Figure 1. Reaction mechanism of diisocyanate and polyol to form polyurethane (a) TDI vs polyol (b) IPDI vs polyol (Quagliano Amado et al., 2022).

Civil and military applications of polyurethane have generated considerable interest. In civil applications sector, polyurethane is used in various domains, such as thermal insulation, coatings, and foams, among others. At this moment, its exceptional characteristics are being touted as a material of interest for military applications. An example of this is a composite solid propellant composed of polyurethane polymeric binders (Touidjine et al., 2023).

Diisocyanate serves as a curing agent for polyurethane in composite solid propellant. Diisocyanate containing aromatic groups, such as TDI, and aliphatic diisocyanate, such as IPDI, are highly favored and extensively employed (Ma et al., 2020). Table 1 presents various examples of isocyanate compounds utilized in composite solid propellants.

Table 1. Some examples of isocyanate applied as composite solid propellant curing agent

Diisocyanate	Reference
Toluene Diisocyanate (TDI)	Budi & Budiman, 2021; Li et al., 2024; Restasari et al., 2022
Isoporone Diisocyanate (IPDI)	Cardoso et al., 2023; Pinalia et al., 2021; Prianto et al., 2021
Dimeryl Diisocyanate (DDI)	S. Ma et al., 2020; Sheibani, 2022
Hexamethylene diisocyanate (HDI)	H. Ma et al., 2020; Toudjine et al., 2023
Methylene diphenyl diisocyanate (MDI)	Barnhart et al., 2022

Throughout the manufacturing, transportation, storage, and operation processes, both propellants and rocket motors will be subjected to static and dynamic loads and stresses. Rocket motors are mostly composed of a viscoelastic substance called propellant, which accounts for approximately 80 to 94% of the motor's total mass. The propellant must possess adequate mechanical properties to avoid the formation of cracks in the propellant and unattached regions or spaces in the liner, insulator, or motor casing. Cracks, voids, or unbounded areas in the propellant grain of a rocket motor can lead to excessive pressure build-up due to increased surface burning during combustion. This can result in failure during both testing and operation.

The curing ratio (NCO/OH) is a crucial determinant for achieving favorable mechanical properties, which refers to the ratio between the isocyanate number on the curing agent and the hydroxyl number on the

polyol. It plays an important function in facilitating the formation of crosslinks and interchain interactions within the polymer matrix. Increasing the NCO/OH ratio will enhance strength and diminish strain (Lysien et al., 2021). In addition, it has been found that the hardness value increases with an increase in the NCO/OH ratio (Restasari & Ardianingsih, 2021).

Therefore, the NCO number provides a vital role in propellant formulation. Thus, it is imperative to carefully ascertain the precise value of NCO present in the curing agent. Given the highly unstable nature of isocyanate (Coureau et al., 2021), it is essential to determine the concentration of isocyanate in the curing agent compound.

The inherent instability of isocyanate has been previously indicated in prior study. Nuryawan and Alamsyah (2018) found that isocyanate readily undergoes reaction with hydrogen in both water and alcohol. Previous studies have also addressed the safety and management considerations of isocyanate, including its storage (Corbett, 1963). Nevertheless, the precise discussion of the influence of storage on the concentration of isocyanate number and its subsequent effect on propellant composites has not been explicitly addressed. Therefore, the primary objective of this study is to identify the quality of TDI and IPDI, with a specific focus on the isocyanate number parameter and examine its impact on composite propellants.

MATERIALS AND METHOD

Materials

The materials utilized in this research were diisocyanate, specifically isophorone diisocyanate (IPDI) and toluene diisocyanate (TDI) produced by Convestro, LLC, US. Both chemicals have been stored in a steel drum for 80 and 90 months. In addition, several materials were also used for diisocyanate characterization including 37% hydrochloric acid from Smart Lab Indonesia, di-n butylamine from Sigma-Aldrich Germany, toluene from Sigma-Aldrich Germany, sodium hydroxide and isopropyl alcohol from Smart Lab Indonesia, as well as bromophenol blue from Himedia Laboratories Pvt., Ltd. This study examined the impact of various NCO numbers on physical properties of propellant. The composite propellant samples were prepared using IPDI and TDI for isocyanate identification, ammonium perchlorate (AP), hydroxyl terminated polybutadiene (HTPB), aluminum powder, and dioctyl adipate (DOA) with specified solid content composition and curing ratio as summarized in Table 2.

Table 2. Solid content and curing ratio of propellant

Propellant sample	Solid content (%)	Curing ratio (NCO/OH)
CP-A	82.50	0.99
CP-B	82.50	0.87
CP-C	82.50	0.77

Method

Isocyanate Identification

This study employed the Fourier-Transform Infrared (FTIR) Spectrometer Bruker Alpha II to accurately identify the NCO group.

Isocyanate number (%NCO) was analyzed to observe the changes of the isocyanate content of TDI and IPDI throughout the storage period. TDI and IPDI are stored in sealed drum containers at room temperature for 84 and 90 months. The procedure follows the steps outlined in Figure 2.

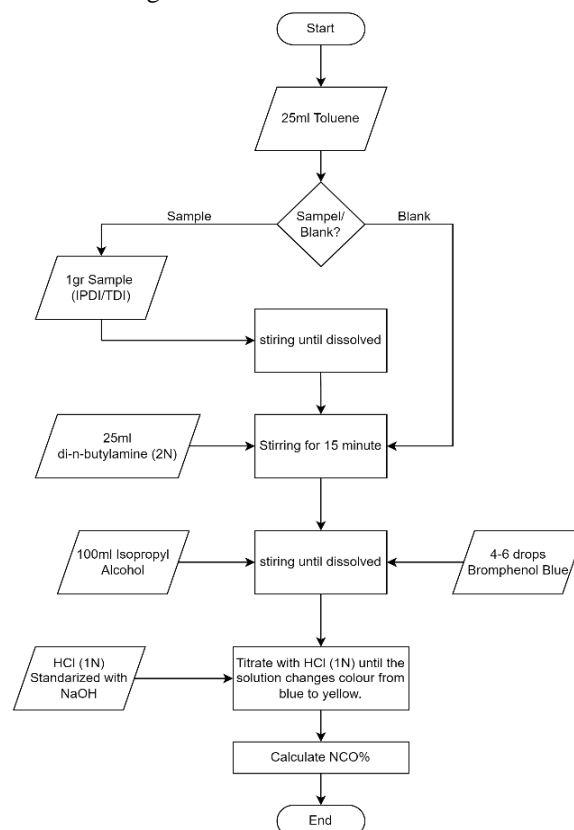


Figure 2. Acid-base titration flowchart for NCO% determination

Subsequently, the resulting titration volume was utilized to determine the isocyanate number using equation (1).

$$NCO\% = \frac{[(B-V) \times N \times 0.042] \times 100}{w} \quad (1)$$

where B is HCl volume for blank titration (ml), V is HCl volume for sample titration (ml), N is HCl normality, 0.042 milliequivalent weight of NCO, and w is weight of the sample (g).

Propellant sample preparation and characterization

The propellant samples were prepared by mixing all ingredients gradually for one and a half hours until a slurry is formed. The slurry was then cast and cured in an oven for 72 hours to produce propellant samples suitable for characteristic tests. These mechanical properties of the samples were determined using Tensilon RTG-1250 5 KN UTM.

RESULTS AND DISCUSSION

Functional Group Analysis

Functional group analyses were performed by FTIR on TDI and IPDI that had been stored for 84 and 90 months. Their FTIR spectra are depicted in Figure 3.

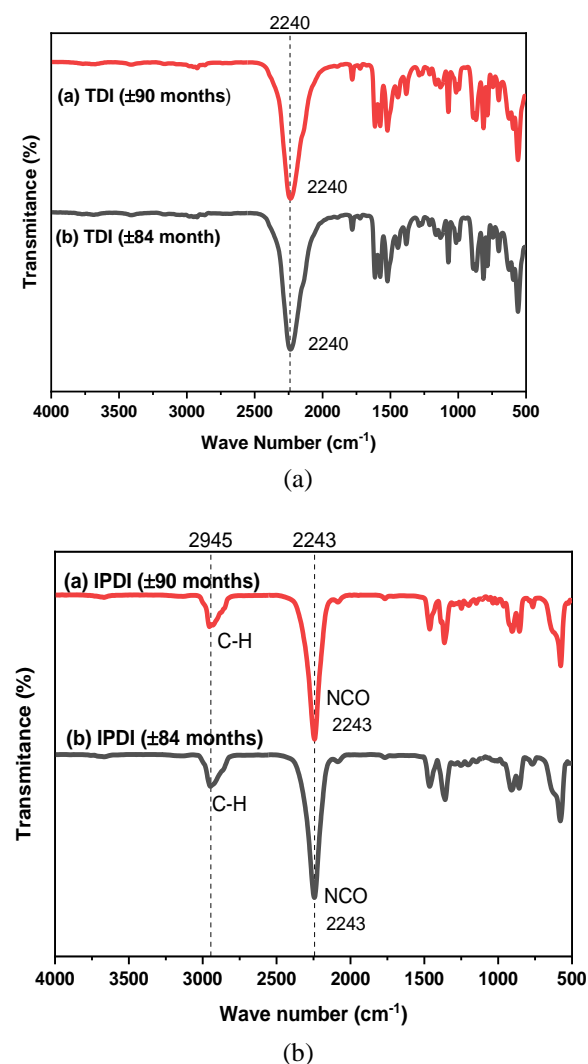


Figure 3. FTIR spectra of TDI (a) and IPDI (b)

The FTIR spectra of TDI (Figure 3.a) show a peak observed at 2240 cm^{-1} , which is a unique characteristic for stretching isocyanate group. Similar results were reported by other researchers which found the $\text{N}=\text{C}=\text{O}$ peak in the range of $2230\text{--}2276\text{ cm}^{-1}$ (Baskara et al., 2023; Kaya et al., 2011). Some additional peaks including C-H vibration (2932 cm^{-1}) and C=N stretch (1605 cm^{-1}) are also shown in TDI spectrum. At 1740 cm^{-1} , a slight peak indicates the presence of C=O stretching in TDI consistent with prior study showing transmittance bands in the C=O stretching area from $1740\text{ to }1620\text{ cm}^{-1}$ (Ling et al., 2008). Quantitative measurement of isocyanates derivatives in the current TDI sample is difficult because of the overlapping C=O groups from urea, urethane, and other secondary products. This study will solely focus on the relative intensity changes of the bands in the C=O area. Urea may have been produced as a result of the storage conditions characterized by elevated humidity. This

enables the isocyanate to react with moisture present in the surrounding environment.

The spectral analysis of IPDI (Figure 3.b) using Fourier Transform Infrared (FTIR) reveals a prominent peak at 2243 cm^{-1} that can be attributed to the isocyanate (--NCO) groups that are characteristic of IPDI. The sharp peaks observed in the FT-IR spectrum at 2945 cm^{-1} can be attributed to the C-H stretching of IPDI. Previous studies (Sultan et al., 2012) have also reported similar spectral findings, indicating the presence of isocyanate groups and C-H stretching peak of IPDI. The IPDI spectrum also displays additional peaks, such as the C=O vibration at 1723 cm^{-1} and the C=N stretch at 1321 cm^{-1} . The spectra obtained from the FTIR analysis are summarized in Table 3.

Table 3. Summary of FTIR analysis results of Isocyanate

Wavenumber (cm^{-1})		Functional Group
TDI	IPDI	
2932	2945	C-H
2240	2243	$\text{N}=\text{C}=\text{O}$
1740	1723	C=O
1605	1321	C=N

Isocyanate Number Determination

Isocyanate number determination procedure (Figure 2) resulting in a color transition from blue to yellow at the conclusion of the titration process, as depicted in Figure 4.



Figure 4. %NCO Determination

Figure 5 indicates a discrepancy in %NCO values between TDI and IPDI samples stored for 90 months and those stored for 84 months. A storage time difference of 6 months results in a 1-2% decrease in %NCO.

A decrease in %NCO value is likely because of the strong reactivity of isocyanate. Isocyanates feature the $\text{N}=\text{C}=\text{O}$ functional group, which is extremely electrophilic because of the carbon-oxygen double bond. Isocyanates have a high reactivity and easily react with nucleophiles like alcohols, amines, and water (Kapp, 2024).

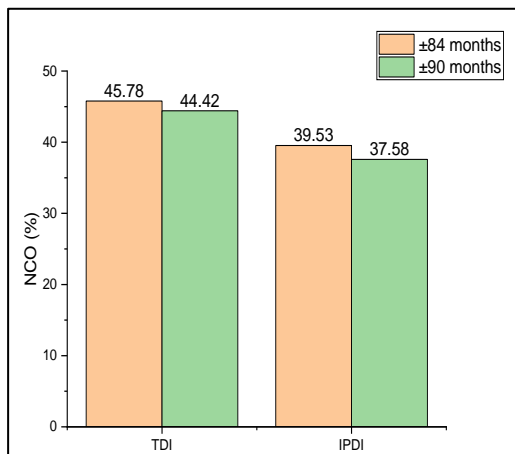


Figure 5. Isocyanate Number Determination of TDI and IPDI after 84 and 90 months storage.

Isocyanates undergo hydrolysis reactions when exposed to moisture or humidity. This reaction can result in the formation of carbamic acid intermediates, which then break down into primary amines and carbon dioxide. A further reaction between the amine and other isocyanates can produce urea (Figure 6). This decomposition can occur spontaneously in the presence of water or moisture, which is why isocyanate-containing materials should be stored in a dry environment and handled carefully to prevent unintended reactions. Indonesia's tropical climate causes humidity levels to range between 60-90 RH, potentially reducing %NCO owing to moisture in the environment.

Additionally, certain isocyanate compounds can be reactive to heat, light, or certain impurities, leading to their instability in specific circumstances. Isocyanates are inherently unstable. Therefore, they require careful handling and storage to avoid undesirable reactions and maintain their stability and efficacy in various applications.

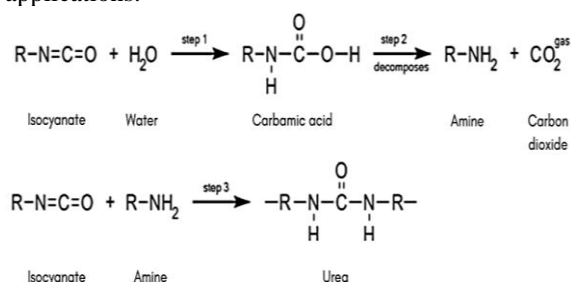


Figure 6. NCO water reaction (Firdaus et al., 2015)

The Effect of NCO Number on Composite Solid Propellant

The effect of the curing ratio on the mechanical properties of the propellants is presented in Table 4. The relationship between curing ratio and mechanical strength is proportional, as indicated by the increase in max. stress with increasing curing ratio.

Table 4. Mechanical properties of composite propellant

Propellant sampel	Curing Ratio	Max. Stress (kgf/cm ²)	Elongation at break (%)	Strain at Max. Stress (%)
CP-A	0.99	6.90	3.59	5.60
CP-B	0.87	6.31	6.61	7.61
CP-C	0.77	5.57	13.56	15.86

The NCO/OH ratio in composite propellants is crucial for ensuring the appropriate crosslinking and curing of the binder system, which directly impacts the mechanical properties, burn rate, and overall performance of the propellant (Noureldin et al., 2020).

The isocyanate number (NCO) can greatly impact the characteristics of solid composite propellants, especially in connection to the binder system employed in the formulation. A higher NCO number means more available isocyanate groups for crosslinking reactions with polyols or other functional groups in the binder. This can lead to higher crosslinking density (Ni & Thring, 2003) and improved mechanical strength of the propellant (Boshra et al., 2021). In addition, higher NCO numbers generally result in higher curing rates due to the higher concentration of reactive isocyanate groups available for crosslinking reactions (Amran et al., 2021). This can influence the processing conditions and the time required for propellant fabrication.

For the most part, propellants with higher NCO values are characterized by greater crosslinking density, which results in increased mechanical strength and stiffness (Noureldin et al., 2020). Figure 7 illustrates that stress rises as the NCO/OH ratio increases, whereas strain decreases with the same increase in NCO/OH. This aligns with prior research findings (Lee & Kim, 2023; Tanver et al., 2016).

To a certain extent, the thermal stability of the propellant can be affected by the NCO number. The resistance of the propellant to thermal degradation at elevated temperatures can be improved through the use of an adequate NCO number in conjunction with proper crosslinking (Chiou & Schoen, 2002), which is crucial for ensuring reliable performance during storage and operation.

The NCO number should be selected to ensure compatibility with other ingredients in the propellant formulation, such as energetic additives and plasticizers. Compatibility issues can arise if the NCO number is too high or too low, leading to phase separation, poor adhesion, or altered combustion behavior.

Overall, the selection of the NCO number in the binder system of solid composite propellants requires careful consideration of the desired mechanical, thermal, and processing properties,

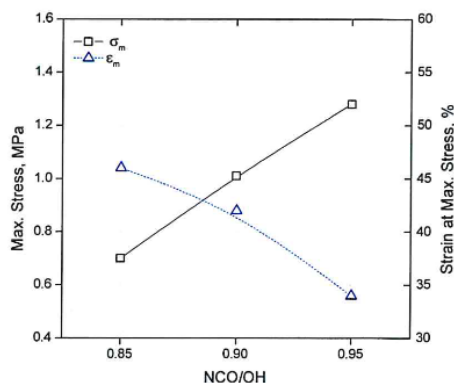


Figure 7. Max. stress and strain at max stress curves versus NCO/OH

as well as compatibility with other ingredients, to achieve optimal performance and stability. It is crucial to determine the NCO number of each curing agent to be employed as it is strongly linked to the formulation intended to create propellants with the necessary qualities.

The reduction in the quantity of NCO number over time will significantly impact the propellant composition. Hence, in order to utilize propellant with a consistent composition, it is essential to rigorously uphold storage conditions to preserve the material's quality during the storage duration.

CONCLUSION

The observation results indicate a reduction in NCO number during the storage period for both TDI and IPDI. There is a difference in the %NCO readings between TDI and IPDI samples stored at different time durations. The TDI that was stored for 84 months had an NCO value of 45.78%, whereas the TDI stored for 90 months had an NCO value of 44.42%. The IDPI stored for a duration of 84 months had an NCO rate of 39.53%, whereas the IDPI stored for a duration of 90 months showed an NCO rate of 37.58%. A storage duration of 6 months leads to a reduction of 1-2% in the concentration of %NCO. This pertains to the strong reactivity of the isocyanate group. Isocyanate readily reacts with moisture in the air when exposed to humid and inadequate storage conditions. The reduction in NCO number will significantly influence the design of propellant compositions. Thus, it is essential to uphold storage conditions to preserve the quality of isocyanate. Isocyanate compounds must be identified periodically as they significantly impact the properties of the propellant produced.

NOTATION

B : volume for Blank titration (ml)
 V : volume for sample titration (ml)
 N : normality
 w : weight of used sample (g)
 NCO% : Isocyanate Number (%)
 NCO/OH : Curing Ratio

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