

# Synthesis of Water-soluble Highly Blocked ( $\geq 98\%$ ) Isophorone Diisocyanate Using $\text{NaHSO}_3$ and Its Effects on Paper Properties

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Isocyanate blocking can improve the long-term stability of isocyanate and reduce its toxicity for use in aqueous systems. The current isocyanate blocking technique has a low blocking degree, and this study designed a reasonable process route using tetrabutylammonium bromide (TBAB) as the phase transfer catalyst in isopropyl alcohol (IPA) solvent to prepare water-soluble isophorone diisocyanate (IPDI) blocked by  $\text{NaHSO}_3$  with a blocking degree of  $\geq 98\%$ . This work used 1% m (TBAB) / m ( $\text{NaHSO}_3$ ) with a m (IPA): m ( $\text{H}_2\text{O}$ ) ratio of 1 : 1; the  $\text{NaHSO}_3$  was prepared in a 15% aqueous solution. The n ( $\text{HSO}_3^-$ ) : n (-NCO) ratio was greater than 1 : 1. The stirring speed was 200 r/min, the reaction temperature was 30 °C, and the reaction time was 2.5 h. FT-IR was used to analyze the changes in the main functional groups during the blocking reaction. TG and DCS were used to analyze the deblocking characteristics of water-soluble blocked IPDI. This paper also studied the effect of the blocked IPDI on paper properties. Experimental results showed that the strength and water resistance of paper made from the treated fiber can be remarkably improved by using water-soluble blocked IPDI.

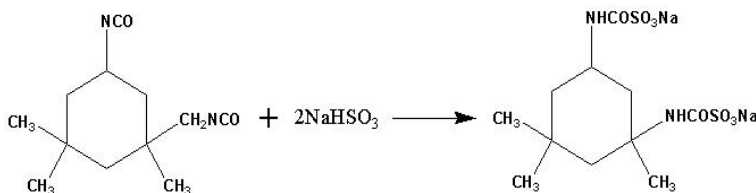
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## INTRODUCTION

The chemical activity of isocyanates is based on the -NCO group. This group has a highly unsaturated bond structure ( $-\text{N}=\text{C}=\text{O}$ ) with an overlapping double bond arrangement that can react with various active hydrogen-containing compounds. Therefore, isocyanate is widely used in the preparation of coatings, adhesives, and other materials (Zuo *et al.* 2008; Jung *et al.* 2018; Matsuura *et al.* 2018; Chowdhury *et al.* 2019). Isocyanates can easily react with water because of the extremely active chemical nature of the -NCO group; this restricts isocyanates in many applications. The -NCO group can be protected *via* blocking, which makes it inactive. When necessary, the blocked compound is deblocked under certain conditions to regenerate the isocyanate group. This approach is favorable for reducing the toxicity of the monomer and increasing long-term storage stability (Delebecq *et al.* 2013). In recent years, some new technologies have been applied to protect isocyanate (He *et al.* 2019; Ma *et al.* 2019; Lubis *et al.* 2020). However, the chemical blocking method is still the most widely used in industry (Xiong *et al.* 2005; Lu *et al.* 2016). The commonly used blocking agents are mainly alcohols, phenols, terpenes, amines and amides, active

methylenes, pyrazoles, and triazoles (Liu and Ma 2019). Inorganic salt blocking agents promote the development of isocyanate blocking techniques from organic materials to inorganic materials because of their low pollution and easy separation. The blocking mechanism is shown in Fig. 1 (Huang *et al.* 2011; Yang *et al.* 2011).



**Fig. 1.** Reaction mechanism of sodium bisulfite blocking (-NCO)

In particular, the isocyanate blocked with bisulfite offers good water dispersibility, low blocking temperature, and rapid deblocking when heated (Sun *et al.* 2008). This is a green process with low energy consumption, high stability, and simple operation. Prior results show that the blocking degree of different isocyanates blocked by bisulfite ranges from 56% to 85% (Huang *et al.* 2011), but full blocking cannot yet be achieved because some -NCO groups remain completely lost. Increasing the blocking degree to more than 98% is conducive to the long-term stability of isocyanates with a broadened scope of use.

Plant fibres contain many hydroxyl groups that can easily absorb water and swell; this limits their utility in paper-based packaging materials (paper used as a packaging material must have good strength and water resistance). At the same time, the hydroxyl groups on the fibre surface can undergo urethane polymerization with isocyanate (Han *et al.* 2020) (Eq. 2). This provides a new solution for fibre modification: The hydroxyl groups in fibre undergo a urethane reaction with isocyanate under certain conditions, and the hydrogen bonding between the fibres is replaced by a more stable polyurethane structure. This enhances the physical strength of the paper and increases water resistance.



**Fig. 2.** Urethane reaction between isocyanate and hydroxyl group

In this paper, sodium bisulfite was used to block isophorone diisocyanate (IPDI) in the preparation of blocked-type water-soluble IPDI. The blocking degree was increased by optimizing the chemical addition method, catalyst, stirring speed, blocking temperature, blocking time, amount of solvent, concentration of blocking agent, amount of catalyst, and molar ratio of  $\text{HSO}_3^-$  and -NCO groups. Furthermore, the  $\text{NaHSO}_3$  produced highly blocked water-soluble IPDI to modify the fibre and study its impact on fibre strength and permeability resistance.

The study has a certain theoretical and practical value. First, the water-soluble isocyanate with high blocking degree ( $\geq 98\%$ ) was provided, which was remarkably higher than 56 to 85% in actual production. Second, when the blocked water-soluble isocyanate obtained in this study was used to prepare waterborne polyurethane materials, water was used as the reaction medium instead of organic solvent, which has advantages of being safer, environmentally friendly, and saving of energy. Third, this experiment provided a simple and rapid method to enhance the strength of plant fiber.

## EXPERIMENTAL

### Materials

The isopropanol alcohol (IPA) labelled as analytically pure grade and used as a reaction solvent was purchased from the chemical reagent factory Tianjin FuYu (Tianjin, China). The sodium bisulfite ( $\text{NaHSO}_3$ ) labelled as analytically pure grade and used as isocyanate sealant was purchased from the chemical reagent factory Shanghai Macklin (Shanghai, China). Isophorone diisocyanate (IPDI, 99% pure) was purchased from the chemical reagent factory Shanghai Macklin (Shanghai, China). Tetrabutyl ammonium bromide (TBAB, 98% pure), hexadecyl trimethyl ammonium bromide (CTAB, 98% pure), and hexadecyl trimethyl ammonium chloride (CTAC, 98% pure), used as the phase transfer catalyst, were purchased from the chemical reagent factory Shanghai Bidepharm (Shanghai, China). Wood fiber as a type of eucalyptus pulp was provided by a pulp mill in Shandong province (Weifang, China).

### Selection of Chemicals Addition Methods

The effect of chemicals addition methods on the IPDI blocking degree was explored under the following conditions. The amount of  $\text{NaHSO}_3$  and IPDI was controlled at  $n(\text{HSO}_3^-): n(-\text{NCO}) = 1:1$ , and the amount of *tetrabutyl ammonium bromide* (TBAB) was controlled at  $m(\text{TBAB}): m(\text{NaHSO}_3) = 1\%$ . The  $\text{NaHSO}_3$  was prepared in an aqueous solution with a concentration of 15%, and the amount of IPA was controlled at  $m(\text{IPA}): m(\text{H}_2\text{O}) = 1:1$ . The stirring speed was 500 r/min, the reaction temperature was 30 °C, and the reaction time was 3 h.

### Selection of Phase Transfer Catalysts

It was difficult to block isocyanate using  $\text{NaHSO}_3$  directly, because the raw materials were in the water phase and the organic phase separately, and the two were incompatible with each other. Phase transfer catalysis can make ionic compounds react with water-insoluble organic substances in low-polarity solvents or accelerate these reactions. Quaternary ammonium salt catalysts are commonly used phase transfer catalysts that play a key role in the blocking reaction (Zhang and Zhao 2010). Preliminary experiments also compared the performance of the three phase transfer catalysts TBAB, CTAB, and CTAC.

The effect of different phase transfer catalysts on the IPDI blocking degree was explored under the following conditions. The amount of  $\text{NaHSO}_3$  and IPDI was controlled at  $n(\text{HSO}_3^-): n(-\text{NCO}) = 1:1$ , The  $\text{NaHSO}_3$  was prepared in an aqueous solution with a concentration of 15%, and the amount of IPA was controlled at  $m(\text{IPA}): m(\text{H}_2\text{O}) = 1:1$ . The stirring speed was 350 r/min, the reaction temperature was 30 °C, and the reaction time was 3 h. The amount of phase transfer catalysts was controlled at  $m(\text{catalyst}): m(\text{NaHSO}_3) = 1\%$ , where “catalyst” is TBAB, CTAB, and CTAC. The chemicals were added in method c (Fig. 3.).

### The Effect of Different Factors on the IPDI Blocking Degree

A single factor experiment was used to study the effect of IPA, stirring rate, reaction temperature, reaction time, concentration of  $\text{NaHSO}_3$ ,  $n(\text{HSO}_3^-): n(-\text{NCO})$ , and TBAB on the IPDI blocking degree, as shown in Table 1. The amount of IPA used in the IPDI blocking reaction system was controlled by changing the mass ratio of IPA to water, namely,  $m(\text{IPA}): m(\text{H}_2\text{O})$ . The amount of TBAB used as phase transfer catalyst was

controlled by changing the mass ratio of TBAB to NaHSO<sub>3</sub>, namely, m(TBAB)/m(NaHSO<sub>3</sub>). The amount of NaHSO<sub>3</sub> and IPDI were controlled by changing the mole ratio of HSO<sub>3</sub><sup>-</sup> to -NCO, namely, n(HSO<sub>3</sub><sup>-</sup>): n(-NCO).

**Table 1.** Single Factor Experimental Design Table

|   | m(IPA):<br>m(H <sub>2</sub> O) | Stirring<br>Speed<br>(r/min) | Temper-<br>ature<br>(°C) | Time<br>(h) | NaHSO <sub>3</sub><br>(%) | n(HSO <sub>3</sub> <sup>-</sup> ):<br>n(-NCO) | m(TBAB)/m<br>(NaHSO <sub>3</sub> )<br>(%) |
|---|--------------------------------|------------------------------|--------------------------|-------------|---------------------------|---|---|
| a | 0 : 1                          | 200                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 0.5 : 1                        | 200                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 200                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1.5 : 1                        | 200                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 2 : 1                          | 200                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
| b | 1 : 1                          | 100                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 200                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 300                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 500                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 600                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
| c | 1 : 1                          | 400                          | 15                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 20                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 25                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 35                       | 2.5         | 15                        | 1 : 1   | 1   |
| d | 1 : 1                          | 400                          | 30                       | 1           | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 1.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2           | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 3           | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 3.5         | 15                        | 1 : 1   | 1   |
| e | 1 : 1                          | 400                          | 30                       | 2.5         | 5                         | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 10                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 20                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 25                        | 1 : 1   | 1   |
| f | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1.125 : 1                                     | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1.25 : 1                                      | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1.375 : 1                                     | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1.5 : 1                                       | 1   |
| g | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1 : 1   | 0   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1 : 1   | 0.5                                       |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1 : 1   | 1   |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1 : 1   | 1.5                                       |
|   | 1 : 1                          | 400                          | 30                       | 2.5         | 15                        | 1 : 1   | 2   |

### Synthesis of Water-soluble Highly Blocked IPDI

The experimental procedure of NaHSO<sub>3</sub>-blocked IPDI was as follows: NaHSO<sub>3</sub> was weighed and placed in a beaker followed by the phase transfer catalyst TBAB. After the mixture was stirred evenly, IPA was added to obtain a mixed solution. The IPDI was placed in a dry four-necked flask that was purged with nitrogen and heated in an oil bath. The mixed solution containing “NaHSO<sub>3</sub>/TBAB/IPA” was placed in a constant-pressure dropping funnel and slowly added into a four-necked flask at a rate of 2 to 3 mL/min. The stirring rate and reaction time were controlled. After the reaction, no precipitated solids were observed at the bottom of the four-necked flask, and the solution was clear with no layers. The NaHSO<sub>3</sub>-blocked water-soluble IPDI was thus obtained.

### Blocked Ratio Test of Isocyanate

The test steps were as follows (Gu *et al.* 2006):

- a. A total of 0.1 g of sample was added into a dry and clean Erlenmeyer flask.
  - b. Next, 18 mL of water was added into the Erlenmeyer flask, and 30 mL of IPA was added after a homogeneous solution was formed after stirring.
  - c. Iodine solution was used for titration. The titration was stopped and data V<sub>1</sub> was recorded when the solution in the Erlenmeyer flask became light yellow.
  - d. Then, 10 mL of 7.5 mol/L NaOH was added into the Erlenmeyer flask and the solution was shaken well. After the solution was allowed to stand for 10 min, 1 drop of 1% phenolphthalein solution was added into the Erlenmeyer flask. Then, the solution in the Erlenmeyer flask became red.
  - e. A total of 2.5 mol/L H<sub>2</sub>SO<sub>4</sub> was added dropwise until the red color disappeared. A few more drops of dilute H<sub>2</sub>SO<sub>4</sub> were then added to ensure that the solution was acidic.
  - f. The titration was then continued with iodine solution. When the solution in the Erlenmeyer flask became light yellow, the titration was stopped and V<sub>2</sub> data were recorded.
- Steps a through c were used to determine the content of the remaining sodium bisulfite that did not block -NCO.

Steps d through f determined that the content of sodium bisulfite generated after deblocking of -NH-CO-SO<sub>3</sub><sup>2-</sup> under the action of NaOH; free -NCO was eventually converted to -NH-CO-NH-.

$$S = V_2 / (V_1 + V_2) \times 100\% \quad (2)$$

$$I = S \times f_x \quad (3)$$

where  $S$  is the reaction rate of -NH-SO-SO<sub>3</sub><sup>2-</sup>,  $I$  is the blocking degree of -NCO group, and  $f_x$  is the molar ratio of NaHSO<sub>3</sub> to -NCO

### Preparation of Modified Fibre by Water-soluble Highly Blocked IPDI

Eucalyptus pulp fibre was transformed into a circular fibre sheet with a basis weight of 100 g/m<sup>2</sup> on a sheet former (RK-3A; Protein Technologies, Inc., Tucson, Austria). The fibre sheet was evenly impregnated with the prepared water-soluble blocked IPDI on an automatic coater at room temperature (Model AFA-IV; Wanjiang Weida Instrument Business Department, Dongguan, China) with a dose of 15 g/m<sup>2</sup>. The fibre sheet was dried at 30 °C for 6 h, and then hot pressing was performed using a hot press (CREE-6014A; Kerui Instrument Technology Co., Ltd., Dongguan, China) at 0.01 MPa for 10 min to deblock the IPDI; the released isocyanate groups (-NCO) underwent a urethane reaction with the hydroxyl group (-OH) of cellulose to produce a IPDI-modified fibre sheet.

The tensile strength of modified fiber sheet was measured using the method of GB/T 12914 (2008) by the tensile strength testing instrument (Code 066, Lorentzen & Wettre, Sweden). The specimens were 25 mm long and 15 mm wide. The tensile elongation rate was (20±5) mm/min.

The tearing strength of modified fiber sheet was measured using the method of GB/T 455 (2002) by tearing tester (Elmendorf, TSE-A007B, China). The sample is 75 mm long and 63 mm wide.

The water absorption of the modified fiber sheet was measured using the method of GB/T 1540 (2002). The sample is with a diameter of (125±5) mm.

## Methods

### *Fourier-transform infrared spectroscopy (FT-IR)*

The NaHSO<sub>3</sub>-blocked IPDI solution was freeze-dried, and a small amount of the freeze-dried sample was ground with KBr into a powder at a ratio of 1:60 to prepare the test sample for IR measurements (Tensor 37; Bruker, Karlsruhe, Germany). At the same time, IR measurement was performed on the samples after deblocking the IPDI. The functional group changes of the IR spectra of IPDI before and after deblocking were detected. The measurement used a scan range of 600 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>, with a resolution of 4 cm<sup>-1</sup>, and 32 replicate scans.

### *Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) analysis*

In an alumina crucible, 5 to 10 mg of freeze-dried NaHSO<sub>3</sub>-blocked IPDI sample was added, and TG analysis (STA449 F3; NETZSCH, Selbu, Germany) was performed by heating up to 200 °C at a rate of 10 K/min under N<sub>2</sub>. The measurement conditions included a measurement temperature of 35 to 200 °C, heating rate of 10 K/min, and nitrogen scan rate of 50 mL/min.

### *Scanning electron microscopy (SEM)*

A fibre was hot pressed and evenly impregnated with NaHSO<sub>3</sub>-blocked IPDI at 140 °C; the resulting sample was analysed with SEM (Quanta 200; FEI, Hillsboro, OR, USA) to observe its surface morphology. The working voltage of the SEM was 5 KV.

## RESULTS AND DISCUSSION

### **Selection of Chemical Addition Methods**

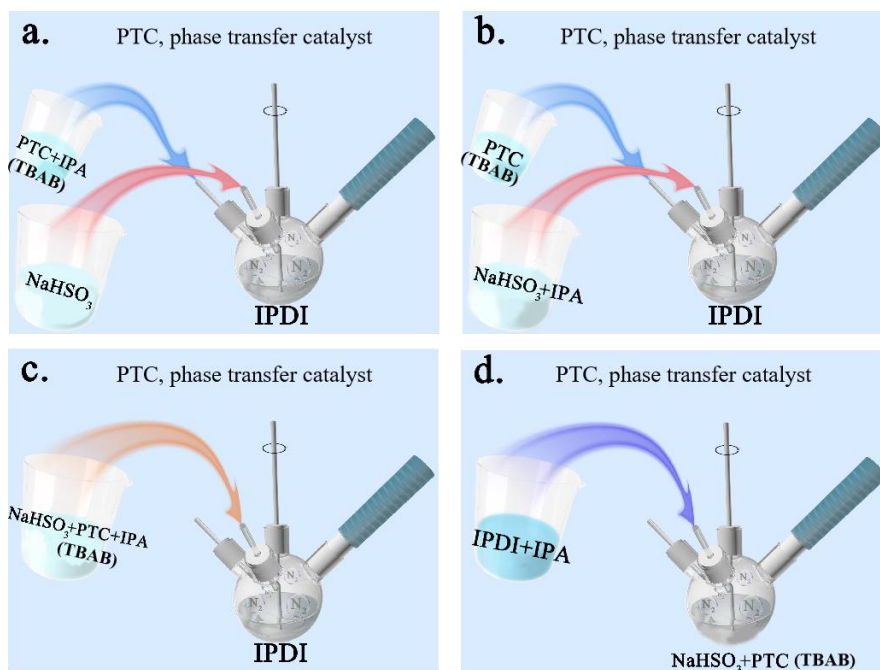
The method of chemical addition is shown in Fig. 3.

Method a: The TBAB and IPA were mixed first, then dropped into IPDI with NaHSO<sub>3</sub> aqueous solution. The blocking degree of IPDI prepared by method a was 84.7%.

Method b: The IPA and NaHSO<sub>3</sub> aqueous solution were mixed first, then dropped into IPDI with TBAB. The blocking degree of IPDI prepared by method b was 83.5%.

Method c: The IPA, TBAB, and NaHSO<sub>3</sub> aqueous solution were mixed first, then dropped into IPDI. The blocking degree of IPDI prepared by method c was 90.9%.

Method d: The IPDI and IPA were mixed first, then dropped into the mixture of TBAB and NaHSO<sub>3</sub> aqueous solution. The blocking degree of IPDI prepared by method d was 88.6%.



**Fig. 3.** Different chemical addition methods for synthesis of water-soluble blocked IPDI using  $\text{NaHSO}_3$

In summary, method c was clearly better. The chemicals were added in method c so that the TBAB that was used as phase transfer catalyst could be added to the aqueous solution of  $\text{NaHSO}_3$  first; thus, the  $\text{NaHSO}_3$  can combine with TBAB, which has a lipophilic chemical structure. As a result,  $\text{NaHSO}_3$  was better dissolved in IPA. Thus, the chance of  $\text{NaHSO}_3$  reacting with IPDI in IPA increased so that the blocking degree was improved.

### Selection of Phase Transfer Catalyst

The results are shown in Table 2. The TBAB showed good performance as a phase transfer catalyst.

**Table 2.** Effects of Different Phase Transfer Catalyst on the Blocking Degree of IPDI

| Type of Catalyst            | No Catalyst | TBAB  | CTAB  | CTAC  |
|-----------------------------|-------------|-------|-------|-------|
| Blocking Degree of IPDI (%) | 67.43       | 97.95 | 95.78 | 94.61 |

### The Effect of Different Factors on the IPDI Blocking Degree

#### *The effect of IPA on the IPDI blocking degree*

The IPDI is an oily hydrophobic substance, and  $\text{NaHSO}_3$  is an ionic compound that dissolves in water. The two are incompatible with each other. As a reaction solvent, IPA can be miscible with both IPDI and water to provide a homogeneous system for chemical reactions between IPDI and  $\text{NaHSO}_3$  ( $\text{NaHSO}_3$  can be transferred from the aqueous phase to the IPA solvent phase under the action of a phase transfer catalyst). The results are shown in Fig. 4(a). As the amount of IPA used increased, the IPDI blocking degree first increased and then decreased. The blocking degree was quite low when the amount of IPA was excessively low; this was because a small amount of IPA led to a small capacity to contain

IPDI and NaHSO<sub>3</sub>, which cannot cause all IPDI and NaHSO<sub>3</sub> in the system to fully contact to trigger a chemical reaction. Thus, there was a decrease in the blocking degree. The blocking degree also decreased when the amount of IPA used was excessively large. The results showed that with an increasing amount of IPA, NaHSO<sub>3</sub> could precipitate out of the reaction system in the form of crystals to reduce the occurrence of the chemical reaction of NaHSO<sub>3</sub> and IPDI. This decreased the blocking degree. According to the literature (Wang 2010), the ratio of hydrophilic groups and hydrophobic groups in the solvent molecular system will affect the solubility of the solute. Adding alcohol to an aqueous solution will reduce the polarity of the solvent. Thus, the solubility of the solute dropped according to the principle of “like dissolves like.” This is why NaHSO<sub>3</sub> will gradually precipitate in the form of crystals from the system as the amount of used IPA increases. In summary, the IPDI blocking degree was the highest (86.96%) when m(IPA): m(H<sub>2</sub>O) was 1 : 1.

#### *The effect of stirring rate on the IPDI blocking degree*

The experimental results are shown in Fig. 4(b). With increasing stirring speed, the blocking degree gradually increased because a relatively high stirring rate was conducive to the dispersion and dissolution of IPDI and NaHSO<sub>3</sub> in the reaction system. This increased the reaction probability of the two. The blocking degree did not change substantially when the stirring rate exceeded 400 r/min; thus, a stirring rate of 400 r/min was suitable. At this time, the highest blocking degree was 98.65%.

#### *Effect of reaction temperature on the IPDI blocking degree*

The experimental results are shown in Fig. 4(c). The blocking degree first increased and then decreased as the temperature was increased. When the temperature was relatively low, the solubility of NaHSO<sub>3</sub> in the solvent system decreased, and the NaHSO<sub>3</sub> crystals precipitated. There was incomplete chemical reaction with IPDI. In addition, at low temperature conditions, the rate of chemical reaction between NaHSO<sub>3</sub> and IPDI was also low so that the blocking degree was low. The blocking degree decreased when the temperature was higher than 30 °C. Although an increase in reaction temperature improved the reaction between NaHSO<sub>3</sub> and IPDI, it also increased the probability of the reaction between IPDI and water. This combined effect led to a decrease in the blocking degree. In summary, the optimal temperature for blocking IPDI with NaHSO<sub>3</sub> was 30 °C, and the highest blocking degree was 98.65%.

#### *Effect of reaction time on IPDI blocking degree*

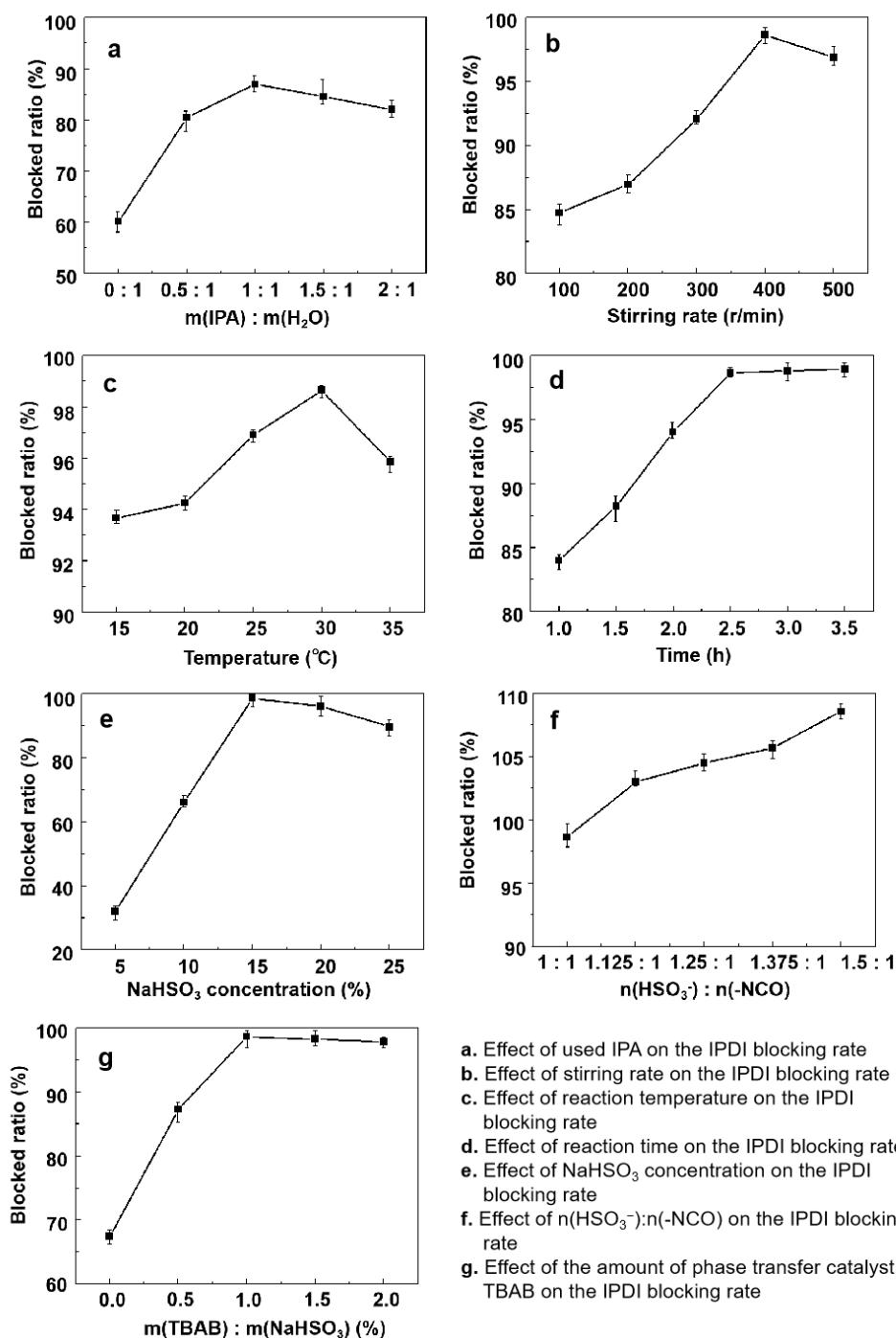
The blocking degree gradually increased and stabilized with longer reaction time, as shown in Fig. 4(d). The blocking degree no longer increased when the reaction time reached approximately 2.5 h, indicating that the reaction was completed. The blocking degree was 98.65% at this time.

#### *Effect of NaHSO<sub>3</sub> concentration on IPDI blocking degree*

The experimental results are shown in Fig. 4(e). With increasing NaHSO<sub>3</sub> concentration, the blocking degree tended to increase first and then decrease. The blocking degree was low when the NaHSO<sub>3</sub> concentration was relatively low because there was a large amount of water in the reaction system; thus, the chance of IPDI reacting with water increases. The amount of water in the reaction system was low when the concentration of NaHSO<sub>3</sub> was high. These conditions were not conducive to the dissolution of NaHSO<sub>3</sub>. As a result, NaHSO<sub>3</sub> precipitated in the form of crystals, and the chance of NaHSO<sub>3</sub> reacting



with IPDI was reduced; thus, the blocking degree was also low. In summary, the blocking degree was the highest (98.65%) when the concentration of  $\text{NaHSO}_3$  was 15%.



**Fig. 4.** The effect of different factors on the IPDI blocking degree

#### *Effect of $n(\text{HSO}_3^-) : n(-\text{NCO})$ on the IDPI blocking degree*

The results are shown in Fig. 4(f). The blocking degree was relatively low when  $n(\text{HSO}_3^-) : n(-\text{NCO})$  was less than 1.125:1; flocculent precipitates were found at the bottom after the solution was allowed to stand for a period of time. The amount of  $\text{NaHSO}_3$  was

small, and the -NCO group of IPDI could not be completely blocked when the blocking degree was low. There was sufficient  $\text{HSO}_3^-$  to react with -NCO when  $n(\text{HSO}_3^-) : n(-\text{NCO})$  was greater than 1.125:1; the blocking degree was as high as 103%. However, excessive  $\text{NaHSO}_3$  will precipitate out of the reaction system in the form of crystals (Zhang *et al.* 2011). The amount of  $\text{NaHSO}_3$  should not be too high to save raw materials.

#### *Effect of the amount of phase transfer catalyst TBAB used on the blocking degree of IPDI*

The results are shown in Fig. 4(g). With increasing TBAB content, the blocking degree showed a gradual increase, which then stabilized. The blocking degree was low (only 65%) when no TBAB was used; while the blocking degree was 98.65% with 1% TBAB, demonstrating that the phase transfer catalyst was conducive to the blocking reaction.

In summary, the better experimental conditions for preparing water-soluble blocked IPDI using  $\text{NaHSO}_3$  were as follows:  $m(\text{TBAB})/m(\text{NaHSO}_3)$  was 1%,  $m(\text{IPA}) : m(\text{H}_2\text{O})$  was 1:1, the concentration of the  $\text{NaHSO}_3$  solution was 15%, the stirring speed was 400 r/min, the reaction temperature was 30 °C, and the reaction time was 2.5 h. When  $n(\text{HSO}_3^-) : n(-\text{NCO})$  was 1:1, the blocking degree was 98.3%. When  $n(\text{HSO}_3^-) : n(-\text{NCO})$  was 1.125:1, the blocking degree was 103%.

### IR Spectral Analysis

To determine the structural changes of the functional groups before and after IPDI blocking and the reaction mechanism, the authors performed IR spectroscopy on the blocked samples and the deblocked samples (Fig. 5).

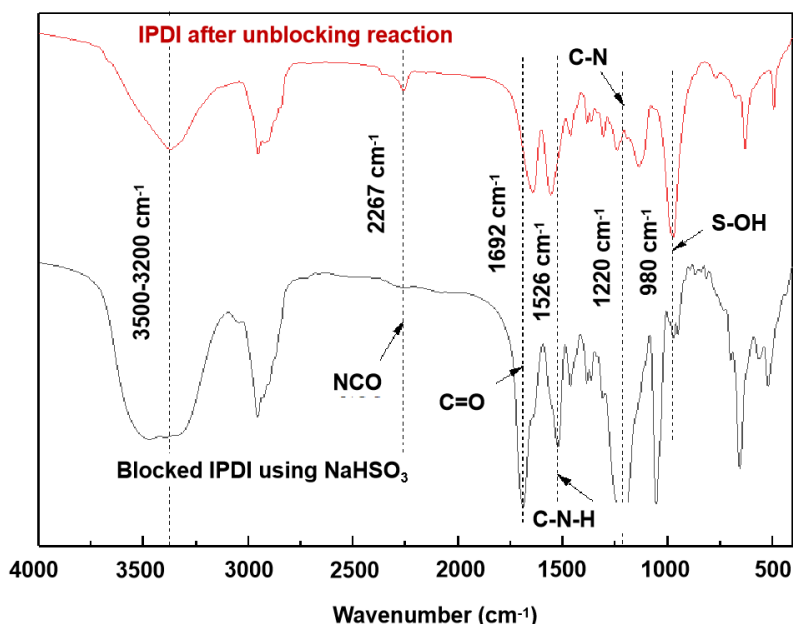


Fig. 5. IR spectra of blocked IPDI before and after deblocking

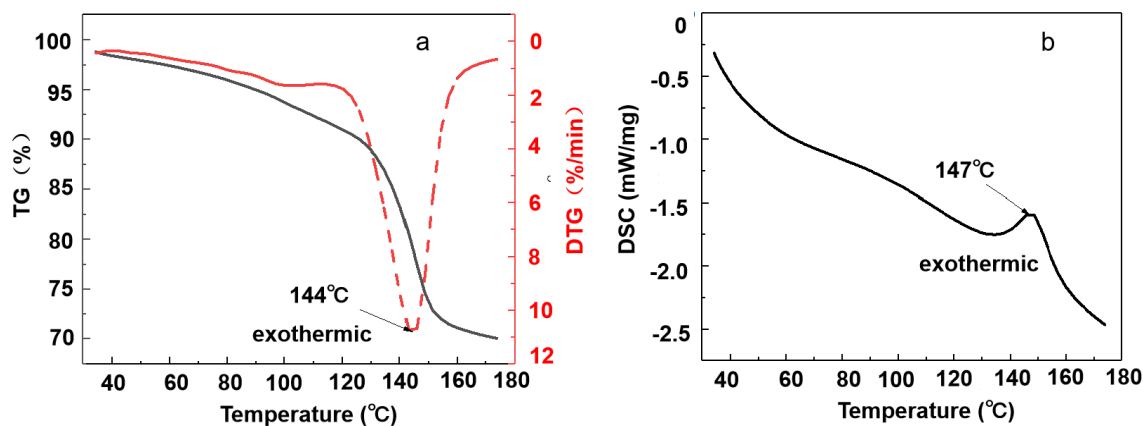
The FT-IR spectrum of the blocked IPDI shows that the peak intensity at 980  $\text{cm}^{-1}$  was considerably reduced; this peak corresponded to the stretching vibration absorption peak of S-OH, indicating that  $\text{NaHSO}_3$  was remarkably consumed. The peak at 2267  $\text{cm}^{-1}$  disappeared, and this peak was assigned to the vibration absorption peak of -NCO, indicating that the characteristic functional group -NCO of IPDI was almost completely

blocked. In addition, the absorption peak at  $3500\text{ cm}^{-1}$  to  $3200\text{ cm}^{-1}$  broadened. This peak is the absorption peak of N-H. When  $\text{NaHSO}_3$  was used to block IPDI, there was an electrophilic substitution reaction between  $-\text{NCO}$  and  $\text{HSO}_3^-$ . The active hydrogen of  $\text{HSO}_3^-$  was transferred to N, and one N-H bond was formed. The absorption vibration peak of  $\text{C}=\text{O}$  was at  $1692\text{ cm}^{-1}$ , the bending vibration absorption peak of C-N-H was at  $1526\text{ cm}^{-1}$ , and the stretching vibration absorption peak of C-N was at  $1220\text{ cm}^{-1}$ . The appearance of these peaks indicated that  $\text{HSO}_3^-$  was connected to  $-\text{NCO}$  to produce the -NHCO- structure.

The IPDI deblocked at a specific temperature. The FT-IR spectrum shows that the absorption peak of  $-\text{NCO}$  reappeared at  $2267\text{ cm}^{-1}$ . This indicated that the IPDI blocked by  $\text{NaHSO}_3$  can be deblocked under certain conditions (Hatakeyama *et al.* 1995).

### TG and DSC Analysis

The samples prepared *via* the optimal conditions above were first freeze-dried to obtain solid powder samples. This helped identify the optimal deblocking temperature for blocked IPDI. The samples were then analyzed by TG and DSC (Fig. 6).



**Fig. 6.** TG analysis (a) and DSC analysis (b) of the blocked IPDI

The TG analysis curve in Fig. 6(a) shows that the thermal degradation began at  $120\text{ }^{\circ}\text{C}$ , and the thermal degradation efficiency was highest at  $144\text{ }^{\circ}\text{C}$ , indicating that a decomposition reaction occurred. The DSC curve in Fig. 6(b) also shows an endothermic peak at  $120\text{ }^{\circ}\text{C}$ ; the peak was highest when the temperature rose to  $147\text{ }^{\circ}\text{C}$ . This shows that the process was endothermic. In summary, the blocked IPDI prepared here undergoes an endothermic decomposition reaction and successfully releases  $-\text{NCO}$  so that the deblocking occurred at approximately  $145\text{ }^{\circ}\text{C}$  (Zhang *et al.* 2011). The blocked IPDI prepared here had a higher blocking degree, and there were more -NHCO- bonds formed in the solid sample. The interaction force between the molecules was strong, and the molecules were difficult to decompose resulting in a higher decomposition temperature than other reports.

### Improvement of Fibre Properties

The fibre was modified by water-soluble blocked IPDI in this paper. The tensile index and tearing index were increased, and the Cobb value decreased, as shown in Fig. 7, which indicated the strength and water resistance of the fiber can be remarkably improved using water-soluble blocked IPDI. Each index achieved the best value under a temperature

of 145 °C that was the optimal unblocked temperature of water-soluble blocked IPDI. The blocked IPDI totally released the isocyanate groups (-NCO) to react with the hydroxyl group (-OH) of cellulose to form polyurethane structure with good strength and water resistance when hot pressing was performed to 145 °C.

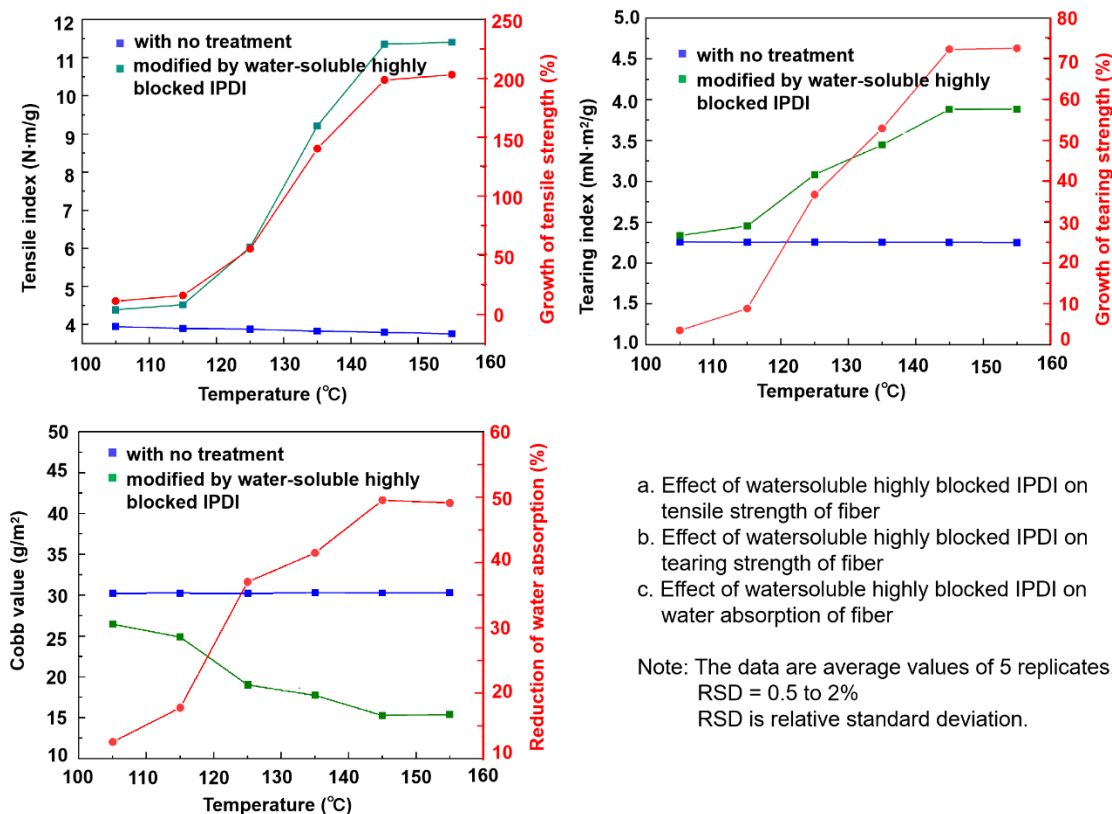


Fig. 7. Effect of water-soluble highly blocked IPDI on fibre properties

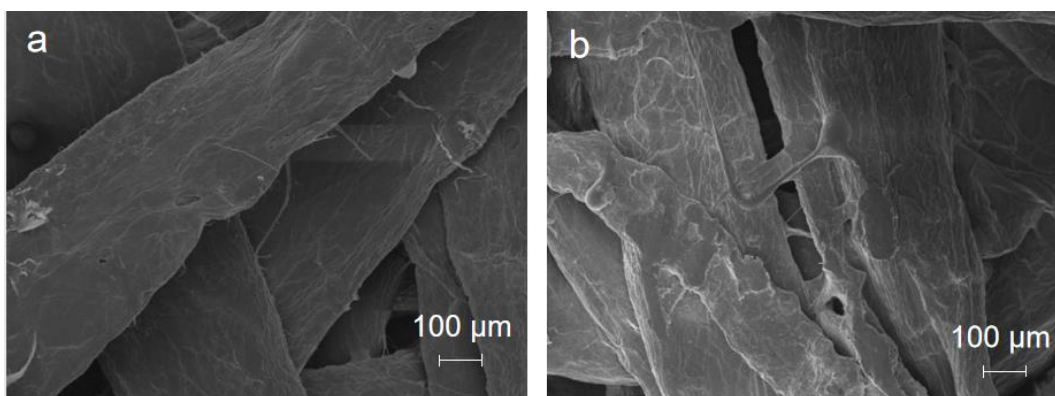


Fig. 8. SEM images of original fibre (a) and IPDI-treated fibre (b)

### SEM Analysis

The authors performed SEM analysis on the original fibre (a) and the IPDI-treated fibres (b) to better observe the chemical binding effect of IPDI on the fibres (Fig. 8). Figure 8(a) shows the smooth fibre surface with fibres disorderedly alternating. Figure 8(b) shows

the fibre surface after IPDI treatment; there were many cements between the fibres. This was because the -NCO that was released after deblocking the blocked IPDI aqueous solution underwent an electrophilic substitution reaction with the -OH group on the surface of the fibre to form -NHCOO-functional groups with a higher binding energy and better hydrophobicity. In addition, there was a stronger chemical bond between the fibres to ensure that the fibre had better strength and water resistance.

## CONCLUSIONS

1. Sodium bisulfite was used as the blocking agent, isopropyl alcohol (IPA) was used as the reaction solvent, and tetrabutylammonium bromide (TBAB) was used as the phase transfer catalyst to prepare water-soluble sodium bisulfite-blocked isophorone diisocyanate (IPDI) with a blocking degree of  $\geq 98\%$ . The chemical addition method, catalyst type, stirring speed, blocking temperature, blocking time, amount of reaction solvent used, concentration of blocking agent, amount of used catalyst, and molar ratio of  $\text{HSO}_3^-$  to -NCO groups were optimized.
2. The blocking degrees were 98.3% and 103% at  $n(\text{HSO}_3^-) : n(-\text{NCO})$  ratios of 1 : 1 and 1.125 : 1, respectively, under the optimized conditions where  $m(\text{TBAB})/m(\text{NaHSO}_3)$  was 1%,  $m(\text{IPA}) : m(\text{H}_2\text{O})$  was 1 : 1,  $\text{NaHSO}_3$  was prepared in a 15% aqueous solution, the stirring speed was 200 r/min, the reaction temperature was 30 °C, and the reaction time was 2.5 h.
3. The  $\text{NaHSO}_3$  strongly blocked the water-soluble IPDI prepared in this experiment and modified the fibre. The results showed that the fibre strength and water resistance were remarkably improved.

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## REFERENCES CITED

- Chowdhury, R. A., Clarkson, C. M., Shrestha, S., El Awad Azrak, S. M., Mavlan, M., and Youngblood, J. P. (2019). "High-performance waterborne polyurethane coating based on a blocked isocyanate with cellulose nanocrystals (CNC) as the polyol," *ACS Applied Polymer Materials* 2(2), 385-393. DOI: 10.1021/acsapm.9b00849
- Delebecq, E., Pascault, J. P., Boutevin, B., and Ganachaud, F. (2013). "On the versatility of urethane/urea bonds: Reversibility, blocked isocyanate, and non-isocyanate polyurethane," *Chemical Reviews* 113(1), 80-118. DOI: 10.1021/cr300195n

- GB/T 455 (2002). "Paper and board - Determination of tearing resistance," Standardization Administration of China, Beijing, China.
- GB/T 1540 (2002). "Paper and board - Determination of water absorption - Cobb method," Standardization Administration of China, Beijing, China.
- GB/T 12914 (2008). "Paper and board - Determination of tensile properties," Standardization Administration of China, Beijing, China.
- Gu, J. Y., Zhang, Y. H., and Gao, Z. H. (2006). "Blocking and unblocking reaction of TDI prepolymer," *Chemistry and Adhesion* 28(2), 67-70. DOI: 10.3969/j.issn.1001-0017.2006.02.001
- Han, F., Xu, B., Shah, S. A. A., Zhang, J., and Cheng, J. (2020). "Thermally reversible crosslinked polyurethanes based on blocking and deblocking reaction," *Macromolecular Materials and Engineering* 305(5), Article ID 1900782. DOI: 10.1002/mame.201900782
- Hatakeyama, H., Hirose, S., and Hatakeyama, T. (1995). "Biodegradable polyurethanes from plant components," *Journal of Macromolecular Science, Part A* 32(4), 743-750. DOI: 10.1080/10601329508010285
- He, Z., Jiang, S., An, N., Li, X., Li, Q., Wang, J., and Kang, M. (2019). "Self-healing isocyanate microcapsules for efficient restoration of fracture damage of polyurethane and epoxy resins," *Journal of Materials Science* 54(11), 8262-8275. DOI: 10.1007/s10853-018-03236-3
- Huang, X. Y., Lu, Y., and Mou, S. Y. (2011). "Blocking of isocyanate with sodium bisulfate by ultrasonic method," *Modern Chemical Industry* 31(9), 50-51, +53. DOI: 10.16606/j.cnki.issn0253-4320.2011.09.019
- Jung, K. I., Kim, B., Lee, D. G., Lee, T. H., Choi, S. Y., Kim, J. C., and Jung, H. W. (2018). "Characteristics of dual-curable blocked isocyanate with thermal radical initiator for low-temperature curing of automotive coatings," *Progress in Organic Coatings* 1(125), 160-166. DOI: 10.1016/j.porgcoat.2018.09.009
- Liu, S., and Ma, X. Y. (2019). "Research progress of blocked solvent-free polyurethane," *Materials Reports* 33(23), 3892-3899. DOI: 10.11896/cldb.18110087
- Lu, L., Yang, P., Liu, Y., Li, J., Zhang, Z., and Li, T. (2016). "Kinetics and thermodynamics of the blocking reaction of several aliphatic isocyanates," *Journal of Macromolecular Science, Part A* 53(9), 574-578. DOI: 10.1080/10601325.2016.1201753
- Lubis, M. A. R., Park, B. D., and Lee, S. M. (2020). "Microencapsulation of polymeric isocyanate for the modification of urea-formaldehyde resins," *International Journal of Adhesion and Adhesives* 100, Article ID 102599. DOI: 10.1016/j.ijadhadh.2020.102599
- Ma, Y., Lu, P., Chen, W., Zhang, Y., and Gu, J. (2019). "Preparation of isocyanate microcapsules as functional crosslinking agent by minimalist interfacial polymerization," *Advanced Powder Technology* 30(10), 1995-2002. DOI: 10.1016/j.appt.2019.05.003
- Matsuura, Y., Sakatani, T., Kado, Y., Takahashi, Y., Muramoto, Y., Fukunishi, S., and Minami, S. (2018). "Modification of polysilane with methacrylate having a protected isocyanate," *European Polymer Journal* 108, 219-224. DOI: 10.1016/j.eurpolymj.2018.08.043
- Sun, Z., Li, G. X., Wang, G., Hua, M. T., and Wang, C. (2008). "Synthesis of water-dispersed and blocked polyisocyanate," *Paint Industry* 38(1), 34-36. DOI: 10.3969/j.issn.0253-4312.2008.01.010.

- Wang, X. W. (2010). *Synthesis and Application of the Water-Soluble Blocked Isocyanate Monomer*, Master Thesis, Hefei University of Technology, Hefei, P. R. China. DOI: 10.7666/d.y1699949
- Xiong, W. B., Liu, R., and Liu, X. Y. (2005). "Study on isocyanate blocking and its deblocking reaction," *Shanghai Coatings* 43(4), 6-8. DOI: 10.3969/j.issn.1009-1696.2005.04.002
- Yang, Y. Q., Chen, Q., Wang, G., and Huang, R. C. (2011). "Preparation and characterization of low VOC waterborne sodium bisulfite-blocked polyurethane curing agent," *Paint & Coatings Industry* 41(7), 33-36. DOI: 10.3969/j.issn.0253-4312.2011.07.008
- Zhang, Y., and Zhao, S. (2010). "Blocking of isocyanate with sodium bisulfite in the presence of phase-transfer catalyst," *Adhesion* 31(4), 62-63. DOI: 10.3969/j.issn.1001-5922.2010.04.018
- Zhang, Y., Gu, J., Jiang, X., Zhu, L., and Tan, H. (2011). "Investigation on blocking and deblocking isocyanates by sodium bisulphite," *Pigment & Resin Technology* 40(6), 379-385. DOI: 10.1108/03699421111180527
- Zuo, X. B., Ning, C. H., Zhou, D., Li, A. Y., Zhang, J. Y., and Zhu, Y. H. (2008). "Preparation and deblocking-reaction of blocked polyisocyanates," *Journal of Chemical Engineering of Universities* 22(3), 543-546. DOI: 10.3321/j.issn:1003-9015.2008.03.032

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