

Deblocking of the Water-Soluble Isophorone Diisocyanate Blocked by Sodium Bisulfite and Its Application

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ABSTRACT: A water-soluble and low stimulation sodium bisulfite blocked isophorone diisocyanate (IPDI) has been prepared. The blocking and deblocking of the blocked IPDI is observed by hot-stage Fourier transform infrared (FTIR) spectrophotometer. The experimental results reveal that IPDI is successfully blocked by sodium bisulfite and the blocked IPDI can regenerate isocyanate groups when the temperature is higher than 80°C. Differential scanning calorimetry analysis indicates that blocked IPDI deblocks initially at around 85°C and reaches the maximum deblocking rate at 117°C. The blocked IPDI in liquid and solid states are stable after being stored for 12 months at room temperature. The blocked IPDI is used as curing agent for waterborne hydroxyl polyurethane, which has good adhesive performance and long pot life. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Waterborne polyurethanes, as nontoxic and nonflammable materials, had been abundantly used as environmental friendly coatings and adhesives showing an excellent range of properties.¹ A curing agent with isocyanate groups was often used in preparing waterborne polyurethane and polyacrylate coatings, adhesives, and textile finishing agents.² The high reactivity of isocyanate groups made the products have a limited pot life and the high toxicity of isocyanate groups also did harm to the operators' health.³ One solution to the problems was to adopt blocked isocyanates.^{4,5} The blocked isocyanates usually were prepolymers which had low amounts of reactive groups and needed high temperature to deblock and regenerate the —NCO groups. Although these shortcomings could be solved if blocked isocyanate was monomer.

A number of patents and reported disclosed that compounds such as *N*-methylaniline, oxime, pyrazole, methyl ethylketoxime, and phenols had been used as blocking agents for isocyanates.^{6–9} However, these blocking agents had some disadvantages. For instance, isocyanate groups blocked by phenols and oxime needed high deblocking temperature and demanded to take free phenol or oxime into consideration. What's more, oxime as blocking agent was more costly. In contrast, sodium bisulfite was inexpensive, easily available, nonpolluted and with lower deblocking temperature.

Ahmad et al.¹⁰ synthesized blocked isophorone diisocyanate (IPDI) using 2-butoxyethanol as blocking agent, but the final

product was not waterborne. Welsh et al.¹¹ reported a water-soluble, blocked diisocyanate, prepared as a bisulfite adduct ($\text{Na}_2\text{S}_2\text{O}_5$) to 1,6-hexamethylene diisocyanate, which proved to be stable for several weeks in aqueous acidic chitosan solutions at room temperature, but it was apparent that crosslinking agent was inefficient in the dry, solid state.

In this article, water-soluble blocked IPDI, which had high amount of reactive groups and low deblocking temperature, was prepared using sodium bisulfite as blocking agents. The solid powder blocked IPDI, which had seldom stimulation and easy transportation, could be obtained after vacuum drying. The prepared products could be widely used in preparing one-component waterborne adhesives with long pot life and reduced the emission of volatile organic components.¹²

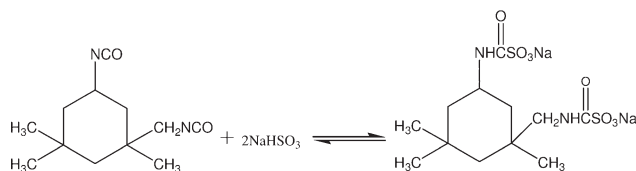
EXPERIMENTAL

Materials

IPDI was purchased from Bayer (Germany). Isopropanol, sodium bisulfite, and ethyl acetate were obtained from Shanghai Sinopharm Chemical Reagents, and used as received without further treatment.

Synthesis of Water-Soluble Blocked IPDI

Sodium bisulfite (69.8 g) was dissolved in 180 mL water, and then the solution and 30 mL isopropanol were added into a three-necked flask with stirring. Dry nitrogen was bubbled into the flask for 10 min. The mixture of IPDI (67.8 g) and ethyl acetate (20 mL) were added into the reactor dropwise over a



Scheme 1. Blocking and deblocking of blocked IPDI.

period of 1 h at 20°C. After the addition was complete, the reaction mixture was stirred at room temperature until theoretical content of —NCO was reached. The change of —NCO content during reaction was detected through a standard dibutylamine back titration method. The reaction activity of diisocyanate with NaHSO_3 was much higher than that of H_2O . Water did not generally react with isocyanate in the existence of NaHSO_3 .¹¹ The solid powder of the product was obtained by vacuum drying at 50°C to constant weight. The powder state of blocked IPDI was used in the following analysis.

Application of Water-Soluble Blocked IPDI

Two grams of water-soluble blocked IPDI or 5.5 g curing agent (AH-0201 C) were mixed with 100 g waterborne hydroxyl polyurethane. The —NCO mol amount of water-soluble blocked IPDI and curing agent (AH-0201 C) was equal. The two types of adhesive were used to bond the interface of PVC film and medium-density fiberboard, respectively. The adhesive was sprayed on the surface of medium-density fiberboard at about 7 g/m², the medium density fiberboard was placed in an oven at 100°C for 3 min, and then the PVC film and medium-density fiberboard were bonded.

Fourier Transform Infrared Spectroscopy

Infrared spectroscopic information of the blocked IPDI was obtained using NICOLET 8700 Fourier transform infrared (FTIR) analyzer (America) in KBr pellets in the range of 400–

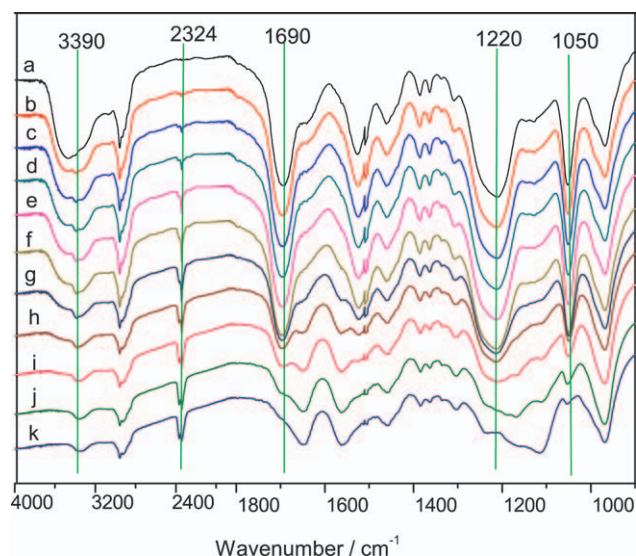


Figure 1. FTIR spectra of the blocked IPDI at different temperature: a: 30°C, b–k: 80–170°C (with 10°C interval). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

4000 cm^{-1} . The sample was heated from 80 to 170°C at a heating rate of 5°C min^{-1} , the information was recorded at 10°C interval.

Differential Scanning Calorimetry

Calorimetric analysis of the blocked IPDI was performed using a Mettler Toledo differential scanning calorimetry (DSC)-821 e/400 differential scanning calorimeter with a heating rate of 20°C min^{-1} .

Peel force

Peel force was observed using a CMT 4304 mechanical tester with a 200 N load cell at the detachment rate of 300 mm min^{-1} .

RESULTS AND DISCUSSION

Deblocking of Blocked IPDI

The overall reaction of blocking and deblocking of IPDI blocked by sodium bisulfite was shown in Scheme 1.

The —NHCO— and —NCO groups, which were detected by hot-stage FTIR spectrophotometer, corresponded to blocking and deblocking IPDI, respectively. The results were shown in Figure 1. Absorption at 3390 cm^{-1} , 1690 cm^{-1} , and 1050 cm^{-1} corresponded to the stretching vibrations of free NH, carbonyl (C=O), and C=O group combined with NH, respectively.⁶ In the spectrum of 30°C, there was no absorption in the 2270 cm^{-1} range,¹³ which indicated that the —NCO groups of IPDI were completely blocked by sodium bisulfite. The absorption of —NCO group at 2324 cm^{-1} was observed obviously when the test temperature was higher than 100°C, and the corresponding absorption increased with the increasing of temperature. Although the absorption of —NHCO— groups at 3390 cm^{-1} , 1690 cm^{-1} , and 1050 cm^{-1} decreased with the increasing of temperature. These experiment results clearly indicated the deblocking of blocked IPDI. The band at 1220 cm^{-1} was S=O vibration, and that it began to disappear at 150°C indicated decomposition of NaHSO_3 .

The differential scanning calorimeter was also used to investigate deblocking of the blocked IPDI, the results were shown in Figure 2. An endothermic peak at 47°C could be due to the dissociation of hydrogen bonds existed among IPDI blocked by

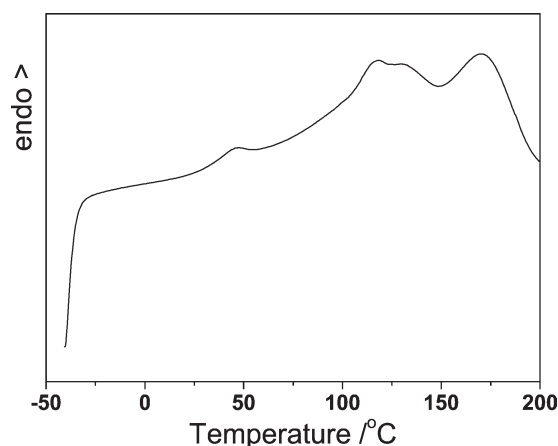


Figure 2. DSC curve of the blocked IPDI.

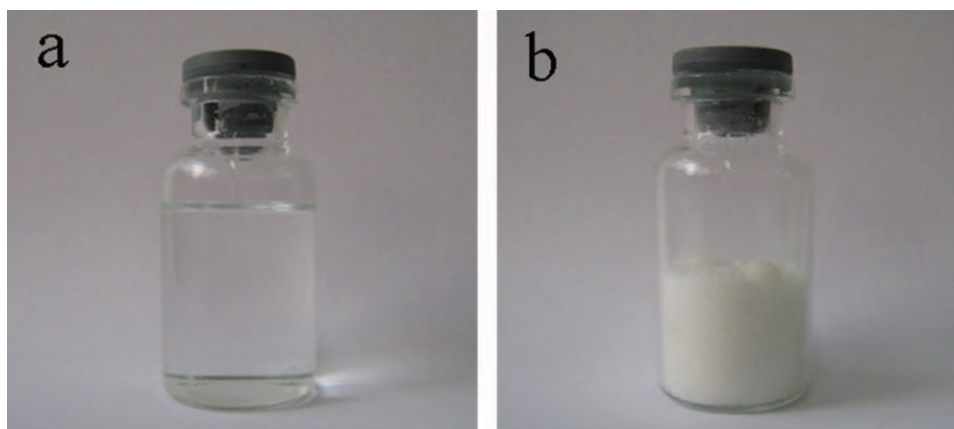


Figure 3. Appearance of liquid (a) and solid (b) states of blocked IPDI after stored 12 months at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sodium bisulfite. The broad endothermic transition in the range of 85–140°C corresponded to the deblocking of the water-soluble blocked IPDI monomer. The broad endothermic transition range was due to the slow deblocking rate of blocked IPDI. Initial deblocking temperature of blocked IPDI was around 85°C, and reached the maximum deblock rate at 117°C. The third endothermic transition around 170°C should attribute to decomposition of NaHSO_3 .¹⁴

Storage Stability

The storage stability of liquid and solid states of the water-soluble blocked IPDI was observed at regular time intervals, respectively. As were in Figure 3, they had no obvious changes after being stored 12 months at room temperature. Both liquid and solid states of blocked IPDI were stable at room temperature, because it did not meet the deblocking temperature.

Application of Water-Soluble Blocked IPDI

The water-soluble blocked IPDI and curing agent (AH-0201 C) were mixed with hydroxyl waterborne polyurethane to prepare adhesive for bonding PVC film and medium-density fiberboard, respectively. The —NCO mol amount of water-soluble blocked IPDI and curing agent (AH-0201 C) was equal. The peel force of two types of adhesives were shown in Table I. It revealed that the peel force of water-soluble blocked IPDI system was considerably higher than that of curing agent (AH-0201 C) system.

CONCLUSIONS

A water-soluble and low stimulation IPDI blocked by sodium bisulfite was obtained. The initial deblocking temperature of the water-solubility blocked IPDI was 80°C characterized by tem-

perature-dependent FTIR and 85°C by DSC. Experiment results revealed that sodium bisulfite blocked IPDI in liquid and solid states could be stored for more than 12 months at room temperature. Application experiment results indicated that the blocked IPDI using as curing agent had good adhesive performance and long pot life.

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Table I. The Peel Force of Adhesives

Curing agent	Peel force (N/15 mm)
Blocked IPDI	19.3
AH-0201 C	18.0