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SYNTHESIS AND PROPERTIES OF IMIDAZOLE-BLOCKED TOLUENE DIISOCYANATES

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Key Words: Imidazole; Toluene diisocyanate (TDI); Blocked isocyanate; Hydroxyl-terminated polybutadiene (HTPB); Gel time; Thermal dissociation

ABSTRACT

Imidazole-, 2-methyl imidazole-, and benzimidazole-blocked toluene diisocyanates (TDI) were prepared and characterized by elemental analysis, IR, and NMR spectroscopy. Simultaneous TGA/DTA results showed that the thermal stability of the adduct decreases in the following order: imidazole-TDI > 2-methylimidazole-TDI > benzimidazole-TDI. Gelation test involving imidazole-blocked adducts and hydroxyl-terminated polybutadiene were also carried out. The cure rate of the adduct increases from the imidazole- to the 2-methylimidazole- and to the benzimidazole-blocked adduct. It is also found that the benzimidazole-blocked adduct shows better solubility in the polyols.

INTRODUCTION

The extreme reactivity of isocyanates with hydroxy compounds makes them attractive crosslinking agents for making different polyurethanes in the form of fibers, soft and hard elastomers, coating for many purposes, adhesives, binders, and highly crosslinked plastics. In some of the above applications it is necessary to

delay the desired isocyanate–hydroxyl reaction until the final stages of the fabrication or use. In order to achieve this objective, blocked isocyanates are used to generate the isocyanate functionality at the proper stage [1]. The dissociation or deblocking temperature of the blocked isocyanates is one of the limiting factors in industrial applications [2]. The thermal dissociation temperature of urethane in very general terms varies in the following order [3]:

Alkyl–NHCOO–Alkyl:	250°C
Aryl–NHCOO–Alkyl:	200°C
Alkyl–NHCOO–Aryl:	180°C
Aryl–NHCOO–Aryl:	120°C

Two reviews [4, 5] have been published in which a large number of patents describe the applications of blocked polyisocyanates.

Blocked polyisocyanates are preferred for many technical and economical reasons. They are essentially not sensitive to moisture. The storage stability of blocked polyisocyanate-based systems is generally high. Powder coating is one of the main areas where blocked polyisocyanates are extensively used because here extensive storage stability is a must [2].

Aromatic reactants are attractive to use as blocking agents for an isocyanate since the urethane linkages formed from the aromatic reactants are unstable at elevated temperature [6]. Phenols are extensively studied for phenyl isocyanate and toluene diisocyanates [7–10]. A number of patents disclose that heterocyclic compounds such as triazoles, imidazolines, and imidazoles have been used as blocking agents for isocyanates [11–14]. Frisch and Damusis [11] patented molded elastomers based on benzotriazole-blocked prepolymers crosslinked with bisaromatic amines. Wegner and coworkers [15] disclosed the use of 1,2,4-triazole as a blocking agent for an isophorone diisocyanate prepolymer in a powder coating which is said to cure in 30 minutes at 140°C. 2-Phenyl-imidazoline-blocked isophorone diisocyanate is reported to unblock at 20–30°C lower temperatures than the caprolactam-blocked diisocyanate [12]. 2-Ethyl-imidazole-blocked isocyanate has been patented for water-soluble applications [16]. A very recent report [17] discloses the use of imidazole-blocked 2,5-bis[(*n*-alkyloxy)methyl]-1,4-benzene diisocyanates to prepare rigid rod-like polyimides in which the reaction of imidazole-blocked isocyanate with pyromellitic dianhydride leads to polyimides. Such a type of reaction of imidazole-blocked isocyanate differs from the reaction of polyurethane formation, and this may open a new area of application. In this report we describe the preparation and properties of some imidazole-blocked toluene diisocyanate adducts that may be used in many thermally curable systems.

EXPERIMENTAL

Materials

The diisocyanate used for the preparation of adducts was a mixture of isomers containing 80% 2,4-toluene diisocyanate and 20% 2,6-toluene diisocyanate (TDI) (Aldrich). Imidazole (Qualigens), 2-methyl imidazole (Fluka), and benzimidazole (Merck) were used without further purification. Propylene-oxide-based polyols and hydroxy-terminated polybutadiene (HTPB) containing 0.1% moisture were gift

samples from Manali Petrochemicals Limited and Vikram Sarabhai Space Centre, respectively. Solvents were purified by standard procedures [18].

Preparation of Blocked Diisocyanates

In a typical synthesis, 50 mL of 1.6 M solution of the blocking agent was taken in a three-necked flask fitted with a condenser and a magnetic stirrer. Dry nitrogen was passed through the other neck for 1 minute. Then 50 mL of 0.8 M diisocyanate solution was added drop by drop over a period of 2 hours at reflux temperature, and the reaction was continued for an additional hour. The product was effectively precipitated by adding petroleum ether (60–80°C) and dried in air. Details of the reaction conditions and results are given in Table 1.

Characterization Methods of the Blocked Diisocyanates

IR spectra of the adducts were recorded by the potassium bromide pellet method in a Nicolet impact-400 FT-IR spectrophotometer. ¹H-NMR spectra were recorded in a Bruker 300 MHz spectrometer. The chemical shift values were reported relative to the methyl group of TDI. Elemental analyses were carried out with a Heraeus CHN-RAPID analyzer. The melting points of the adducts were determined in a Toshniwal melting point apparatus.

Thermal Analysis

TGA/DTA were carried out simultaneously in a Seiko TGA/DTA 200 thermal analyzer using α -alumina as a reference. The sample weight was 3–5 mg. The work was performed from 30 to 600°C at a heating rate of 10°C/min in a nitrogen atmosphere with a gas flow rate of 100 mL/min.

Gel Time Studies

HTPB (2×10^{-3} M) was taken separately in three beakers, each of 30 mm diameter. To this, 2×10^{-3} M of blocked diisocyanates was added and mixed thoroughly. Then the beakers were placed in an oil bath maintained at 160°C. The beakers were inverted at regular time intervals to observe the flow behavior of the solutions. The time at which the solution ceased to flow was taken as the gel time. A duplicate experiment was conducted for each adduct to ensure the accuracy of the data collected.

Solubility Test

The solubilities of the adducts in various polyols were determined according to the reported procedure [9].

RESULTS AND DISCUSSION

The reaction mixtures of experiments conducted with the 2-methyl imidazole and benzimidazole were found to be heterogeneous even at the reflux temperature of chloroform. *N,N'*-Dimethylformamide was added to homogenize the reaction

TABLE 1. Preparation of Imidazole-Blocked TDI Crosslinkers

Blocking agents	Solvent	Temperature	Yield, %	Elemental analysis, %						Melting point, °C
				Calculated			Found			
				C	H	N	C	H	N	
Imidazole	CHCl ₃	Reflux	90	57.8	4.8	26.9	57.1	4.2	26.8	—
2-Methylimidazole	CHCl ₃ + DMF (9:1)	Reflux	60	60.3	5.3	24.9	59.5	6.0	24.9	100–105
Benzimidazole	CHCl ₃ + DMF (9:1)	Reflux	90	67.3	4.4	19.8	66.5	4.4	19.8	140–145

mixture. Since the blocking agents used in this study are highly reactive with isocyanate and are also basic in nature, no catalyst was added to avoid any undesirable side reactions such as dimerization or trimerization of isocyanate.

The IR spectra of the adducts are given in Fig. 1. All the spectra are identical and do not show absorption in the 2270 cm^{-1} range. This indicates that the NCO

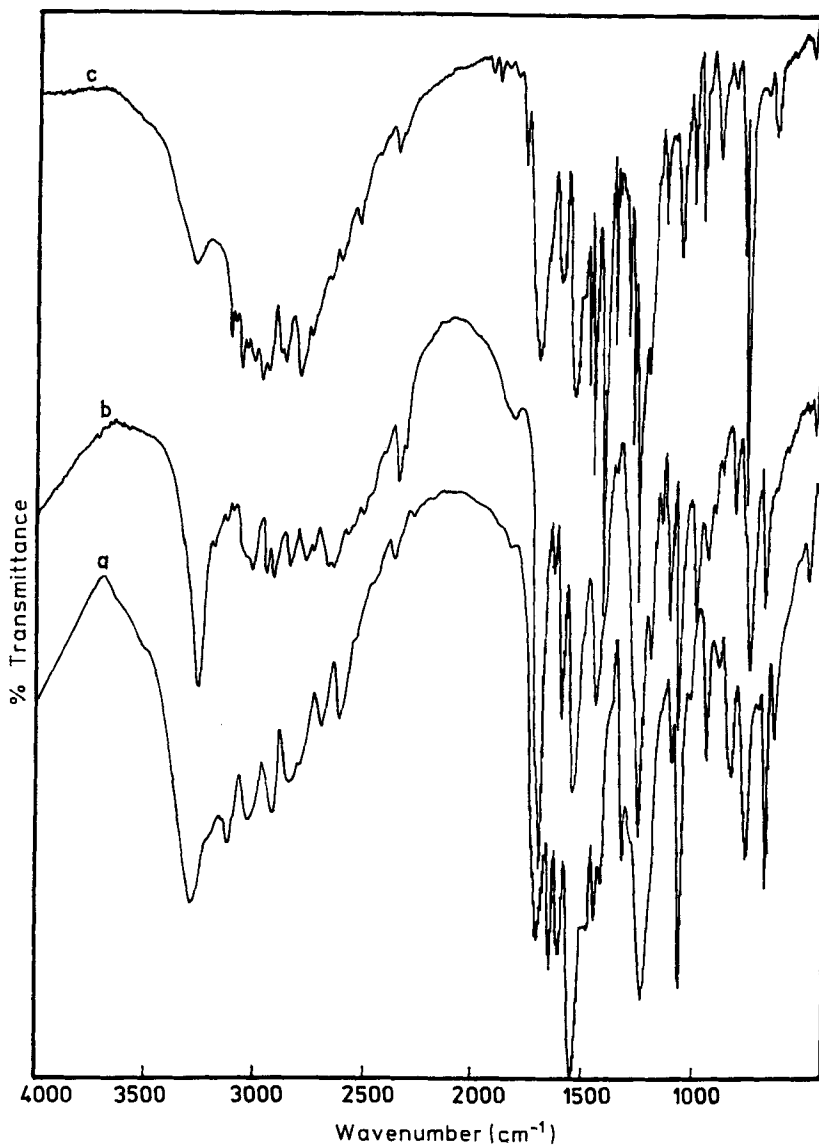


FIG. 1. IR spectrum of (a) imidazole-TDI adduct, (b) 2-methylimidazole-TDI adduct, and (c) benzimidazole-TDI adduct.

groups of the original TDI molecule are completely blocked with the imidazole. Strong absorptions at 1700 cm^{-1} (C=O stretching), $3250\text{--}3300\text{ cm}^{-1}$ (N–H stretching), $1530\text{--}1560\text{ cm}^{-1}$ (N–H bending), and $1210\text{--}1240\text{ cm}^{-1}$ (the stretching vibration of the C=O group of urethane combined with the N–H group) [19] confirm the imidazole-blocked TDI adducts formed.

The $^1\text{H-NMR}$ spectra show a peak at $2.0\text{--}2.2\text{ ppm}$ due to the methyl protons of the TDI moiety. The methyl protons of the imidazole moiety appear at $2.2\text{--}2.3\text{ ppm}$. All aromatic protons appear as multiplets at $6.8\text{--}7.8\text{ ppm}$. The solvent and the chemical shift values for the individual compounds are given in Table 2.

The elemental analyses data for the blocked isocyanates are given in Table 1. The results agree well with the calculated values, indicating that the compounds are pure.

The TGA and DTA traces (Figs. 2a, 2b, 2c) obtained simultaneously show that the imidazole-blocked adduct follows two-stage dissociation. The first stage dissociation reaction starts at 140°C and continues to nearly 50% weight loss. The second stage dissociation starts at 290°C and continues to nearly 90% weight loss. The 2-methylimidazole-blocked adduct also follows two-stage dissociation, but the first stage dissociation is extended to higher conversion whereas the benzimidazole-blocked adduct follows a single stage dissociation reaction. This two-stage dissociation reaction may be due to the different reactivities of the two urea groups present in the adduct. The urea group close to the methyl group of the TDI molecule will dissociate initially. Mukaiyama and Iwanami [20] and the authors [21] have reported that the ortho substituents in the isocyanate moiety accelerate dissociation and facilitate deprotonation of the urethane linkage. In the case of the 2-methylimidazole-blocked adduct, the methyl substituent on the blocking agent will labilize

TABLE 2. $^1\text{H-NMR}$ Chemical Shifts of Imidazol-Blocked TDI Crosslinkers

Blocked isocyanate	Chemical shifts, ppm
	DMSO- d_6 2.0–2.3 (3H, 1); 6.9–7.2 (5H, 2); 7.3–7.8 (6H, 3)
	DMSO- d_6 2.1–2.2 (3H, 1); 2.2–2.3 (6H, 2); 6.8–7.0 (3H, 3); 7.1–7.3 (4H, 4); 7.4–7.5 (2H, 5)
	DMSO- d_6 2.1–2.2 (3H, 1); 6.9–7.3 (11H, 2); 7.4–7.8 (4H, 3)

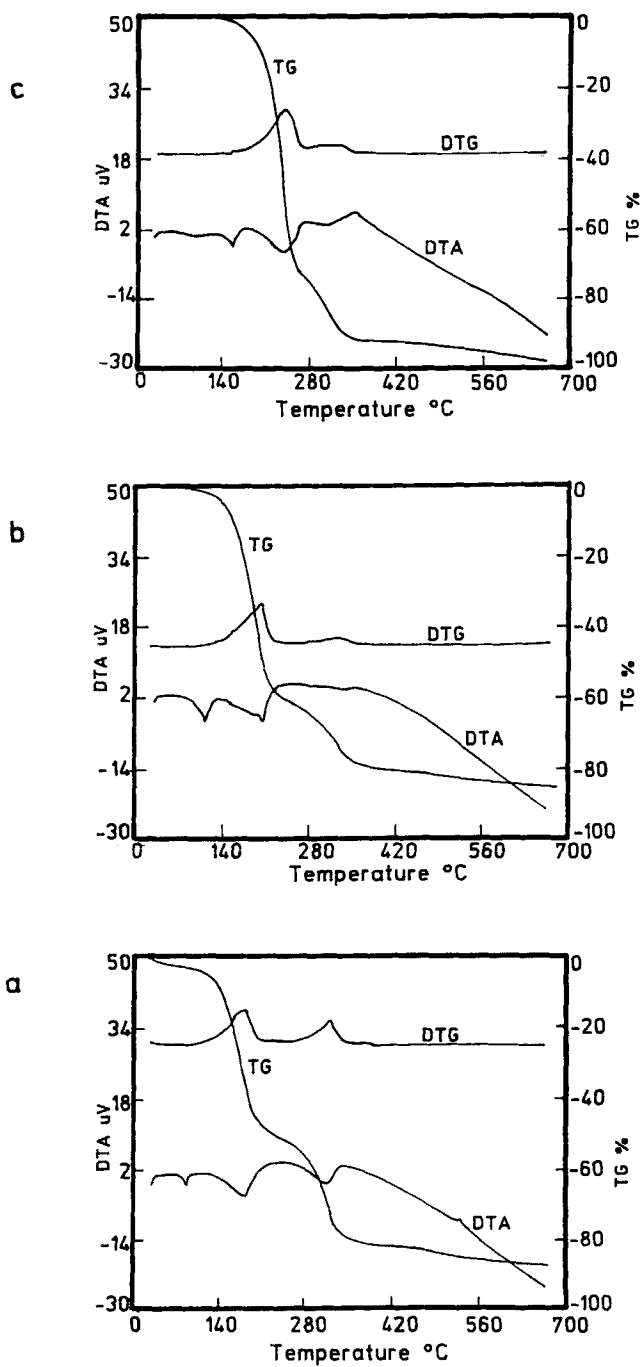


FIG. 2. TG/DTA curve of (a) imidazole-TDI adduct, (b) 2-methylimidazole-TDI adduct, and (c) benzimidazole-TDI adduct.

TABLE 3. Gel Time and Decomposition Temperature of Imidazole-Blocked TDI Crosslinkers

Blocked isocyanate	Gel time, hours	Decomposition temperature, °C	
		50% weight loss	75% weight loss
Imidazole-TDI	> 12	243	318
2-Methylimidazole-TDI	10	202	315
Benzimidazole-TDI	5	237	254

the bond formed between the carbonyl carbon and the nitrogens of imidazole and result in a high degree of dissociation compared to the imidazole-blocked adduct. The accelerating effect of the ortho substituent in phenol of phenol-blocked isocyanate has been reported [9]. The single stage dissociation reaction of a benzimidazole-blocked adduct can be better understood by the presence of an aromatic substituent. Such a substituent reduces the negative charge density on the nitrogen atom attached to the carbonyl carbon through the resonance and weakens the bond formed between them. Ultimately, the adduct will dissociate at a relatively lower temperature with a higher rate than the imidazole- and methylimidazole-blocked adducts.

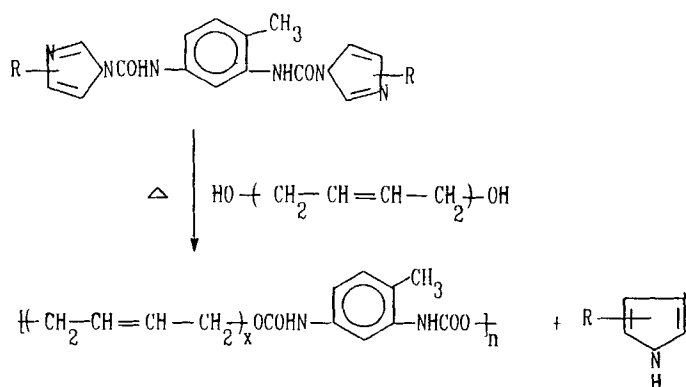
The weight loss temperatures determined from the TG curves are given in Table 3. The 50% weight loss temperature decreases from the imidazole-blocked adduct to the 2-methylimidazole-blocked adduct and increases to the benzimidazole-blocked adduct. In contrast, the 75% weight loss temperature decreases from the imidazole to the 2-methylimidazole- and to the benzimidazole-blocked adduct. The high temperature found at 50% weight loss of benzimidazole may be due to the low volatility of benzimidazole after dissociation, since its melting temperature is higher than those of imidazole and 2-methylimidazole. Compared to DTG traces, DTA curves show an additional endotherm below 150°C due to melting of the adduct, but the melting points determined using the melting point apparatus are lower than the peak temperature of the melting transition of DTA curves. This may be attributed to a low, irregular heating rate and less sensitivity of the apparatus. The endotherm corresponding to the deblocking reaction is broad and starts after completion of the melting endotherm. This pattern confirms that all the adducts dissociate above the melting temperature.

To study the structure-property relationship of the blocked isocyanates synthesized, they were reacted with HTPB, which is a novel binder used in solid rocket propellents. The reason HTPB was chosen is that it makes a short pot-life possible for a system involving an aromatic isocyanate because of the high reactivity of the primary hydroxyl groups of HTPB toward the isocyanate groups. The use of blocked isocyanates instead of isocyanates as such, along with HTPB, increases the pot-life. At elevated temperatures the functionality of the blocked isocyanates will be regenerated and a cure reaction will take place as follows:

TABLE 4. Dissolution Temperatures of Imidazole-Blocked TDI Crosslinkers in Polyols^a

Blocked isocyanate	Dissolution temperature (°C) in					
	PPG-400	PPG-1000	PPG-2000	Empeyol F-3000	HTPB	
Imidazole-TDI	Partially soluble 160	Partially soluble at 160	Partially soluble at 160	Partially soluble at 160	Partially soluble at 160	Partially soluble at 160
2-Methylimidazole-TDI	130	Not completed at 160	Not completed at 160	Not completed at 160	Partially soluble at 160	Partially soluble at 160
Benzimidazole-TDI		Not completed at 160	Not completed at 160	Not completed at 160	Not completed at 160	Not completed at 160

^aPPG = Poly(propylene glycol); Empeyol F-3000, a glycerol-based triol.



During the course of the reaction, the viscosity is increased and at once the free flow is arrested. The times required for gelation of the blocked isocyanate-*HTPB* mixture to occur are given in Table 3. The gel times of 2-methylimidazole- and benzimidazole-blocked adducts are lower than for the imidazole-blocked adduct due to the steric and electronic effects of methyl and phenyl substituents, respectively.

The solubility of the blocked diisocyanates is a limiting factor for uniform curing with the hydroxy coreactants. The solubility tests for blocked TDI adducts were carried out separately in different polyols, and the results are summarized in Table 4. The 2-methylimidazole-blocked adduct shows better solubility than the imidazole-blocked adduct due to the presence of the aliphatic substituent. Improvement in the solubility of blocked isocyanate using a methyl-substituted blocking agent has been reported [9]. The benzimidazole-blocked adduct dissolves more readily than the 2-methyl imidazole adduct. This may be due to the dissociation rather than dissolution of the adduct in the polyols. It was also found that the solubility of the adducts decreased with increasing molecular weight of the polyols.

CONCLUSIONS

1. Imidazole-, 2-methylimidazole-, and benzimidazole-blocked TDI adducts were synthesized and characterized.
2. The thermal properties of the adducts, simultaneously using a TG/DTA technique and the curing behavior with *HTPB*, were discussed for the first time.
3. Among the three adducts prepared, the benzimidazole-blocked TDI adduct shows low thermal stability and high solubility in the polyols.

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