

Thermal Decomposition Behavior of Blocked Diisocyanates Derived from Mixture of Blocking Agents

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Abstract: To improve the performance and reduce raw material costs, blocked isocyanates were prepared with mixture of blocking agents in many industries. Three blocked isocyanates (adducts) namely ϵ -caprolactam/benzotriazole-blocked 4,4'-diphenylmethane diisocyanate (MDI), toluene-2,4-diisocyanate (TDI) and 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI) were synthesized. Six reference adducts were also prepared by blocking MDI, TDI, and H_{12} MDI with ϵ -caprolactam (ϵ -CL) or benzotriazole. The reactions were carried out in acetone medium and dibutyltin dilaurate (DBTDL) was used as a catalyst. The progress of the blocking reaction was monitored by IR spectroscopy. De-blocking temperatures (dissociation temperatures) of these adducts were studied using DSC and TGA and the results were correlated. As expected, the thermal analysis data showed that de-blocking temperature of blocked aromatic isocyanates was lower than that of the blocked aliphatic isocyanates. The low de-blocking temperature of blocked aromatic isocyanate could be due to electron withdrawing benzene ring present in the blocked isocyanates. It was also found that benzotriazole-blocked adducts de-blocked at higher temperature compared with ϵ -CL-blocked adducts.

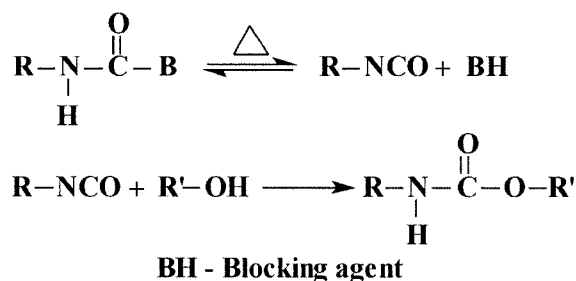
Keywords: blocked isocyanate, blocking agent, deblocking behavior, adducts, dissociation.

Introduction

Cross-linking reactions between isocyanates and hydroxyl functional resins are widely used in many applications, such as adhesive, coating, foam, and elastomeric materials due to the high reactivity of isocyanates group, which should be protected prior to use. For this purpose, blocked isocyanates or blocked polyisocyanates have been developed. The blocking and de-blocking reactions are presented in the Scheme I. Generally free isocyanates are generated when blocking agent, which has an active hydrogen to block the isocyanates, is split from the blocked isocyanates at elevated (i.e., deblocking) temperature and reacts with non-volatile ingredients having active hydrogen to form more stable urethane or urea bonds.^{1,2} This mechanism has led to increasing interest in the water-based polyurethane dispersion (PUD) since aromatic isocyanates are rarely used in the PUD preparation (especially, prepolymer mixing process) due to their extremely high reactivity with water molecules.³ There are many publications in water-based PUDs.^{4,5}

Blocked isocyanates or polyisocyanates seem to be very

important in view of technical and economic aspects. They are essentially insensitive to moisture and storage stability of the blocked isocyanates is generally high. There are a few reviews^{1,2,6,7} in which a large number of patents describe the application of the blocked isocyanates in industrial areas. While there are broad claims of applicability to virtually any type of heat-cured coating application, there are significant limitations to their applications. Perhaps two most important limitations are (1) the relatively high temperatures required for curing and (2) the evolution of undesirable volatile blocking agents such as phenol. For example, phenol, and oxime have been widely used to block isocyanates for the



Scheme I. Blocking, deblocking and cross-linking reaction of isocyanate group.

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urethane coil coating process where very high curing temperatures are normally used with many systems. The best results are obtained with oxime adducts, which give better gloss and faster cure than those obtained with phenol-blocked systems. Two of the most widely patented applications can be wire coatings⁸ and tire cord adhesives.⁹⁻¹³

Aminimides and nitrile carbonates have been used for cross-linking acrylic powders.^{13,14-16} Various blocked isocyanates are used for the cross-linking of paper to achieve wet strength and enhanced properties.¹⁷ Paper coatings¹⁸ and cross-linking of latex paper impregnates¹⁹ were also reported. Cotton fabric has been treated with blocked isocyanates for permanent press properties. Several patents^{20,21} cover the use of blocked isocyanates in fabric coatings, particularly for adhesion to nylon fabrics. ϵ -CL-blocked isocyanates are reported as being used in glass fiber coatings. Blocked isocyanates have also been used to increase the adhesion of polyamide coatings to leather. Blocked isocyanates are extensively used in the preparation of urethane elastomers.^{22,23} Synthesis of the copolymers blocked with butanone oxime and their cross-linking behaviors have been studied.²⁴ Prepolymers blocked with 4-nonylphenols are used with diimines for molding prepolymer sheets.²⁵ Heat-setting adhesives incorporating blocked isocyanates have been patented.²⁶ Benzophenone oxime blocked isocyanates are used for magnetic tape coatings.²⁷ A number of reports disclose that heterocyclic compounds such as triazoles, imidazolines, and imidazoles can also be used as blocking agents for isocyanates.²⁸⁻³²

Bayer has filed patents on the synthesis of polyisocyanates blocked with a mixture of blocking agents aimed to reduce raw material costs.³³ One of them is a pyrazole or substituted pyrazole. The other blocking agent is either a triazole or hydrazine derivative. Recently, combinations of blocking agents are used to achieve a two-stage cure or achieve high build coatings by imparting some cross-linking at a relatively low temperature and thus reduce the tendency of the film to flow when the higher temperature is reached. But there was no systematic investigation on these types of blocked isocyanates. In our group, aromatic blocked polyurethane dispersion (BPUD) based on MDI and TDI by "blocked isocyanate" technique has been developed and aromatic BPUD by blocking NCO groups with suitable blocking agents is studied.³⁴⁻³⁷

In the present investigation, therefore, we have prepared and studied the effects of mixture of blocking agents on the deblocking behavior of blocked isocyanates. ϵ -CL, due to its low price, relatively low toxicity and outstanding resistance to discoloration, is a good choice as a blocking agent in this study. Another blocking agent is benzotriazole. These blocking agents were selected because they represented adducts which were capable of decomposing over a wide range of temperature.

Experimental

Materials. All raw materials are laboratory grade chemicals and were used without further purification except acetone. The diisocyanates used were toluene-2,4-diisocyanate (TDI; Junsei Chem. Co.), 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI; Aldrich Chem. Co.) and 4,4'-diphenylmethane diisocyanate (MDI; Aldrich Chem. Co.). ϵ -caprolactam (ϵ -CL; Yakuri Pure Chem. Co.) and benzotriazole (Aldrich Chem. Co) were used as blocking agents for diisocyanates. Dibutyltin dilaurate (DBTDL; Aldrich Chem. Co) was used as reaction catalyst. Acetone (Carlo Erba Reagent) was used as reaction medium, which contains less than 0.2% water and was stored in a 4 Å molecular sieve to keep it dry. Structural formulae of used chemicals are shown in Table I.

Preparation of Blocked Isocyanates. A 500 mL 4-necked and rounded flask equipped with mechanical stirrer, nitrogen inlet, thermometer, and condenser was charged with blocking agent and acetone. The temperature of the reactants was raised to the reflux temperature of acetone. After blocking agent was dissolved in acetone completely, 0.1 g of DBTDL was added to fasten the reaction and diisocyanate was added slowly. During the reaction, isocyanate (NCO) peak of the diisocyanate was observed using FTIR in every two hours

Table I. Structural Formula of Used Chemicals

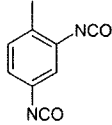
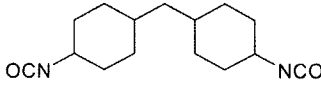
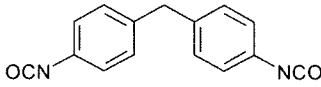
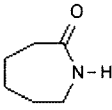
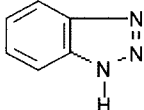
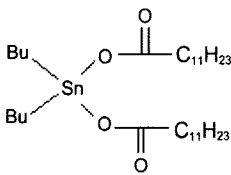
Chemicals	Abbreviation	Structural Formula
Toluene-2,4-diisocyanate	TDI	
4,4'-dicyclohexylmethane diisocyanate	H_{12} MDI	
4,4'-diphenylmethane diisocyanate	MDI	
ϵ -caprolactam	ϵ -CL	
Benzotriazole	-	
Dibutyltin dilaurate	DBTDL	

Table II. Compositions of Blocked Isocyanates

Sample No.	Benzotriazole (mole)	ϵ -CL (mole)	H ₁₂ MDI (mole)	TDI (mole)	MDI (mole)
1	0.02	-	0.01	-	-
2	-	0.02	0.01	-	-
3	0.01	0.01	0.01	-	-
4	0.02	-	-	0.01	-
5	-	0.02	-	0.01	-
6	0.01	0.01	-	0.01	-
7	0.02	-	-	-	0.01
8	-	0.02	-	-	0.01
9	0.01	0.01	-	-	0.01

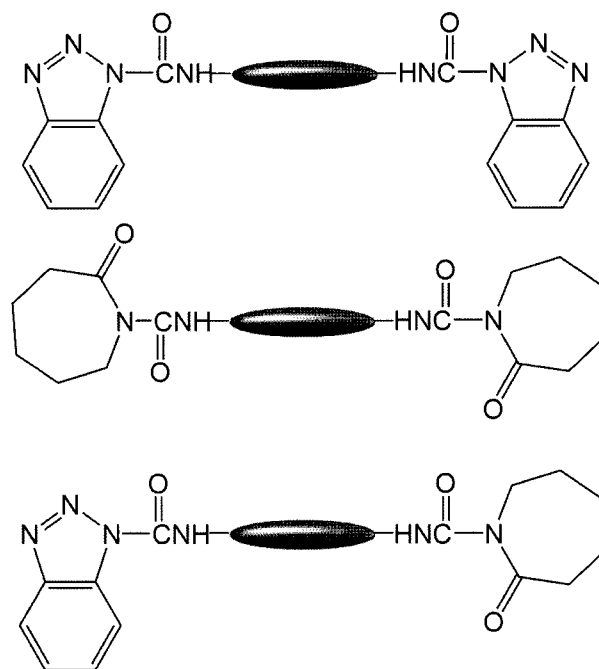
to monitor the reaction. The reaction was carried out until disappearance of -NCO peak in the FTIR spectrum. In the case of H₁₂MDI, the reaction was performed in a thermostat with agitation for 40 hrs at reflux temperature. To prepare blocked aromatic (MDI and TDI-based) diisocyanates, the same procedure was followed at the same reaction condition. In this case, the reaction time was 7 hrs. The compositions of the prepared blocked isocyanates are given in Table II.

The white precipitate of blocked aromatic diisocyanates that formed at the end of the reaction was purified by washing with acetone and water for 5 times. The products of the blocked aliphatic diisocyanate were washed several times with water for purification. The obtained powder products were dried in a vacuum oven for 24 hrs at 60 °C. For each diisocyanate (H₁₂MDI, MDI, and TDI), three different blocked isocyanates were prepared using ϵ -CL, benzotriazole, and mixture of both blocking agents as given in Table II. Totally 9 different blocked isocyanate samples were synthesized. Expected reaction products are shown in Figure 1. As can be seen in Table II, the samples, 1,2,4,5,7, and 8 were used as reference samples for the mixing effect of two blocking agents. In the case of mixed blocking agent samples, three types of blocked isocyanates in Figure 1 are believed to be obtained together.

Characterization. For the reference samples, elemental analyses were carried out with a Heraeus CHN RAPID analyzer.

FTIR spectrophotometer (BRUKER OPTIK GmbH, U.S.A.) was used to confirm the end point of reaction with 4 cm⁻¹ resolution. The disappearance of NCO peak at 2268 cm⁻¹ in FTIR spectrum was taken as the end point of the blocking reaction.

The deblocking temperature of blocked isocyanates was examined by modulated DSC (Model DSC Q10, T.A. Instruments Inc., U.S.A.) instrument. Sample weight was ca. 10 mg and the measuring temperature was from room temperature to 250 °C with a constant heating rate of 10 °C min⁻¹ under 60 mLmin⁻¹ N₂ gas flow rate. The initial

**Figure 1.** Expected structures of three different blocked isocyanate.

deblocking temperature was defined as the temperature where sudden heat flow increases.

Thermo-gravimetric analysis (TGA) was performed with a TGA analyzer (Model TGA Q50, T.A. Instruments Inc., U.S.A.). In the analysis, 10 mg of sample in a platinum sample pan was heated from room temperature to 500 °C with a 10 °C min⁻¹ heating rate under 60 mLmin⁻¹ N₂ gas flow rate.

Results and Discussion

As one can see the Table II, three blocked isocyanates from equimolar concentration of ϵ -CL and benzotriazole and six reference samples from single blocking agent were prepared using H₁₂MDI, MDI, and TDI. Benzotriazole and ϵ -CL are basic in nature. The reaction was carried out in acetone medium and the recipe is given in Table II. As the reaction was conducted in low boiling solvent, DBTDL was used to catalyze the reaction. The reaction was conducted at the reflux temperature of the solvent.

A representative FTIR spectrum of the blocked adducts and the reagents are presented in Figure 2. All the spectra of blocked adducts are identical and do not show absorption peak in the 2250-2270 cm⁻¹ range. This indicates that the NCO groups of the original H₁₂MDI, TDI, and MDI molecules are completely blocked with blocking agents. Strong absorptions at 1690-1725 cm⁻¹ (C=O stretching), 3200-3400 cm⁻¹ (N-H stretching), 1530-1560 cm⁻¹ (N-H bending) and 1210-1240 cm⁻¹ (the stretching vibration of the C=O group of urea combined with the N-H group)³⁸ confirm the

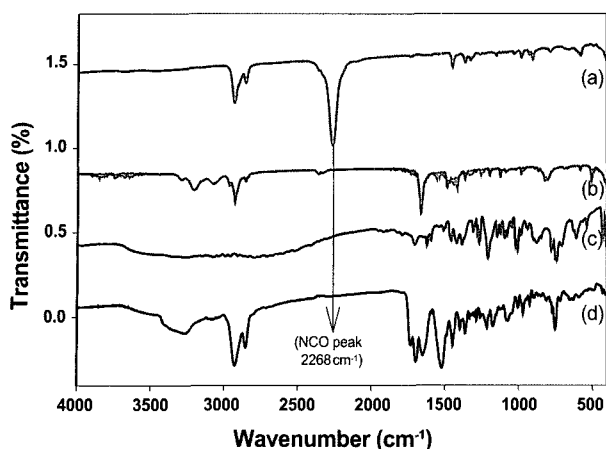


Figure 2. FTIR spectra of (a) pure H₁₂MDI, (b) ϵ -CL, (c) benzotriazole, and (d) ϵ -CL/benzotriazole blocked adduct.

formation of blocked H₁₂MDI, TDI, and MDI adducts.

The elemental analyses data for the blocked isocyanates are included in Table III. The results agree well with the calculated values, indicating that the compounds are relatively pure and confirm the formation of blocked adducts.

Deblocking Behavior of H₁₂MDI Based Blocked Isocyanate. DSC measures heat flow into or out of a sample over a specified temperature range. This technique was used because the compounds synthesized have different adduct structures and, thus, should exhibit significant difference in energy (endothermic) when they unblock. DSC curves of H₁₂MDI based adducts are depicted in Figure 3. As seen in Figure 3, all the curves show broad deblocking temperature range and especially for ϵ -CL/benzotriazole adduct. But the initial (onset) deblocking temperature of the ϵ -CL/benzotriazole adduct occurs in between ϵ -CL blocked adduct and benzotriazole blocked adduct. The single broad endotherm peaks are melting point of the blocked isocyanates. The melting points of ϵ -CL-, benzotriazole-, and ϵ -CL/benzotriazole-blocked H₁₂MDI adducts are observed at 208, 212, and 227°C, respectively and the melting points

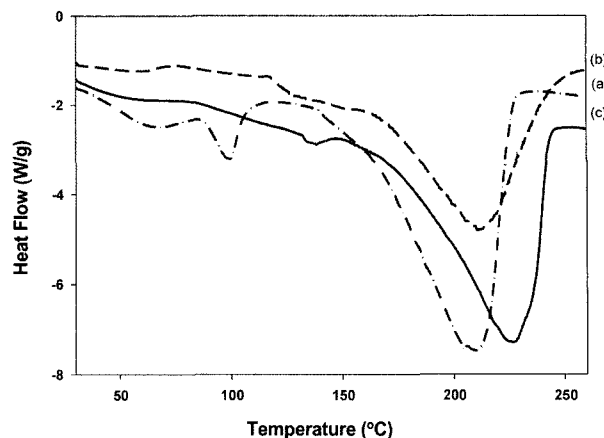


Figure 3. DSC curves of H₁₂MDI based blocked isocyanates: (a) ϵ -CL blocked adduct, (b) benzotriazole blocked adduct, and (c) ϵ -CL/benzotriazole blocked adduct.

were in the order: ϵ -CL-H₁₂MDI > benzotriazole-H₁₂MDI > ϵ -CL/benzotriazole-H₁₂MDI. It is understandable from the above explanation that the endotherm of ϵ -CL/benzotriazole blocked H₁₂MDI adduct is not in between the endotherms of ϵ -CL- and benzotriazole-blocked H₁₂MDI adducts, whereas the onset deblocking temperature of ϵ -CL/benzotriazole blocked H₁₂MDI adduct is in between the ϵ -CL- and benzotriazole-blocked H₁₂MDI adducts.

Thermogravimetric analysis (TGA) measures the changes in sample weight over a specified temperature range. Thus, TGA is unsuitable for compounds that do not exhibit volatility over the unblocking temperature range. The rate and extent of elimination reaction depend on several variables: the structure of isocyanate and blocking agents including substituents, solvents, the presence of catalysts, and temperature. It was recognized before that thermal dissociation of urethanes generally takes place in the following order:³⁹

n-Alkyl-NHCOO-n-Alkyl	approx. ca. 250°C
Aryl-NHCOO-n-Alkyl	approx. ca. 200°C
n-Alkyl-NHCOO-Aryl	approx. ca. 180°C
Aryl-NHCOO-Aryl	approx. ca. 120°C

Table III. Element Analysis Data of Various Blocked Isocyanates

Isocyanates	Blocking Agents	Element Analysis (%)					
		Calculated			Found		
		C	H	N	C	H	N
H ₁₂ MDI	ϵ -CL	66.39	9.02	11.47	66.30	8.98	11.40
H ₁₂ MDI	Benzotriazole	64.80	6.40	22.40	64.67	6.38	22.36
TDI	ϵ -CL	63.00	7.00	14.00	62.81	7.02	13.65
TDI	Benzotriazole	61.16	3.88	27.18	60.24	3.74	26.97
MDI	ϵ -CL	68.07	6.72	11.76	67.96	6.70	11.72
MDI	Benzotriazole	66.39	4.10	22.95	66.23	4.03	22.93

Figure 4 indicates TGA plots of blocked isocyanate adducts of H₁₂MDI. As observed in the Figure 4 and Table IV, the deblocking of ϵ -CL blocked adduct occurs over the temperature range of 155-230°C. The deblocking temperature range of benzotriazole blocked and ϵ -CL/benzotriazole blocked adducts are 160-250 and 170-250°C, respectively. It is confirmed from the results that the deblocking temperature of ϵ -CL blocked adduct is lower than that of benzotriazole blocked adduct and the deblocking temperature of ϵ -CL/benzotriazole blocked adduct should be in between. But it shows slightly higher deblocking temperature and also a single stage deblocking reaction. This may be due to the merging of the two deblocking temperature.

Deblocking Behavior of TDI Based Blocked Isocyanate. DSC curves of TDI based adducts are shown in Figure 5. As seen from the Figure 5, all the deblocking curves show sharp deblocking temperature range for all TDI based blocked adducts. The deblocking of ϵ -CL blocked adduct occurs at a temperature range of 150-180°C. The deblocking temperature of benzotriazole blocked and ϵ -CL/benzotriazole blocked adducts occurs at a temperature range of 175-210 and 175-200°C, respectively. The sharp endothermic peak at 168°C is the melting point of the ϵ -CL blocked TDI adduct and the broad endotherm at 207°C may be melting point of decomposed products.

The endotherm of the ϵ -CL/benzotriazole-blocked TDI adduct is not exactly matching with endotherms of ϵ -CL

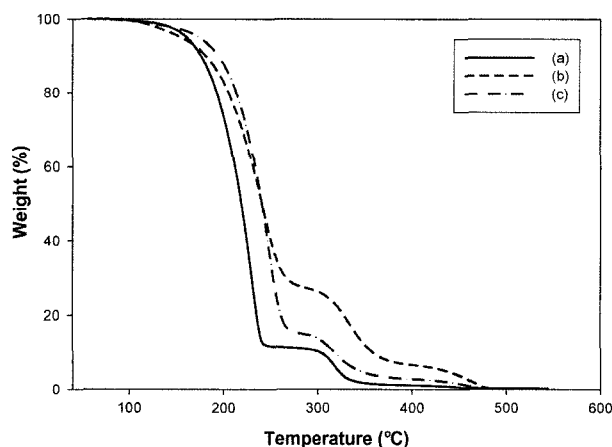


Figure 4. TGA curves of H₁₂MDI based blocked isocyanates: (a) ϵ -CL blocked adduct, (b) benzotriazole blocked adduct, and (c) ϵ -CL/benzotriazole blocked adduct.

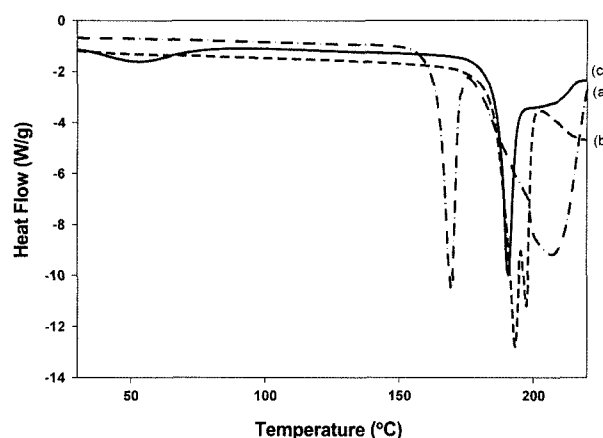


Figure 5. DSC curves of TDI based blocked isocyanates: (a) ϵ -CL blocked adduct, (b) benzotriazole blocked adduct, and (c) ϵ -CL/benzotriazole blocked adduct.

blocked and benzotriazole blocked TDI adducts. Since the reactivity of the benzotriazole with TDI is higher than the ϵ -CL, the endotherm of the resulting reaction mixture is showing more of the property of benzotriazole blocked TDI. As the reactivity of benzotriazole is higher compared to ϵ -CL, the percentage amount of resultant benzotriazole blocked TDI product is more. So it deblocks as like benzotriazole blocked TDI and near to benzotriazole blocked TDI. In addition, it is understandable that the percentage formation of the adducts may be in the order: Benzotriazole - TDI > ϵ -CL /benzotriazole-TDI > ϵ -CL -TDI. This phenomenon is observed in all the three types of blocked isocyanates.

The two peaks observed in benzotriazole blocked TDI may be the melting endotherm of this adduct. In this adduct, the first endotherm is due to the melting of the pure adduct and the second endotherm corresponds to the melting of the decomposed products. More detailed study is under progress to evaluate these adducts further.

Figure 6 represents that TGA plots of blocked isocyanate adducts of TDI. As noted from the Figure 6 and Table IV, the deblocking temperature range of ϵ -CL blocked adduct is about 140-200°C. The deblocking temperature range of benzotriazole blocked and ϵ -CL/benzotriazole blocked adducts are 150-210 and 150-200°C, respectively. These results confirmed that the deblocking temperature of ϵ -CL blocked adduct is lower than that of benzotriazole blocked

Table IV. Deblocking Temperature Range (°C) of Various Blocked Isocyanates by DSC and TGA Techniques

Isocyanates Blocking Agents	H ₁₂ MDI		TDI		MDI	
	DSC	TGA	DSC	TGA	DSC	TGA
ϵ -CL	broad	155-230	150-180	140-200	155-180	150-210
Benzotriazole	broad	160-250	175-210	150-210	215-240	190-220
ϵ -CL/Benzotriazole	broad	170-250	175-200	150-200	200-220	150-220

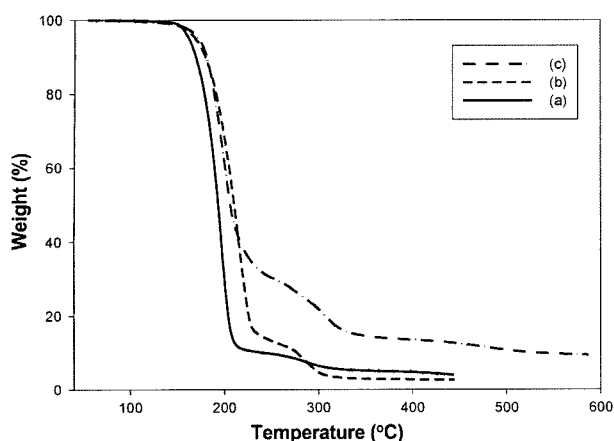


Figure 6. TGA curves of TDI based blocked isocyanates: (a) ϵ -CL blocked adduct, (b) benzotriazole blocked adduct, and (c) ϵ -CL/benzotriazole blocked adduct.

adduct and as expected the deblocking temperature of ϵ -CL/benzotriazole blocked adduct is in between the two of them. It also confirms that all the blocked adducts show the single stage deblocking reaction (single decomposition point). As mentioned before, the single stage decomposition temperature of ϵ -CL/benzotriazole blocked adduct may be due to the merging of the two deblocking temperature.

Deblocking Behavior of MDI Based Blocked Isocyanate. DSC curves of MDI based adducts are presented in Figure 7. It can be seen from the Figure 7 that the deblocking curves show sharp deblocking temperature range for all MDI based blocked adducts. The deblocking of ϵ -CL blocked adduct occurs at a temperature range of 155-180°C. The deblocking temperature range of benzotriazole blocked and ϵ -CL/benzotriazole blocked adducts are 215-240 and 200-220°C, respectively. It is noticed from the DSC results that the deblocking temperature of ϵ -CL blocked adduct is

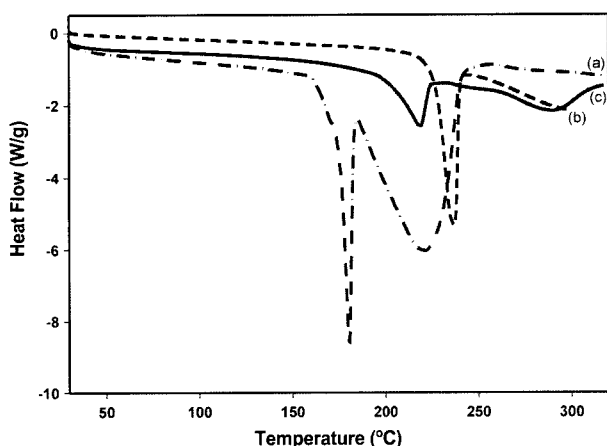


Figure 7. DSC curves of MDI based blocked isocyanates: (a) ϵ -CL blocked adduct, (b) benzotriazole blocked adduct, and (c) ϵ -CL/benzotriazole blocked adduct.

lower compared to benzotriazole blocked adduct and as expected the deblocking temperature of ϵ -CL/benzotriazole blocked adduct is in between the two of them. The deblocking temperature of ϵ -CL blocked MDI and benzotriazole blocked MDI are similar to the reported values.⁴⁰ It is also noticed that the sharp endothermic peak at 180°C is the melting point of the ϵ -CL blocked MDI adduct and the broad endotherm at 222°C may be melting point of decomposed products.

Figure 8 shows that TGA plots of blocked isocyanate adducts of MDI. As given in the Figure 8 and Table IV, the deblocking of ϵ -CL blocked adduct occurs over the temperature range of 150-210°C. The deblocking temperature range of benzotriazole blocked and ϵ -CL/benzotriazole blocked adducts are 190-220 and 150-220°C, respectively. It is determined from the results that the deblocking temperature of ϵ -CL blocked adduct is lower than that of benzotriazole blocked adduct and as expected the deblocking temperature of ϵ -CL/benzotriazole blocked adduct is in between to two of them. It also confirms that all the blocked adducts show the single stage deblocking reaction except ϵ -CL/benzotriazole blocked adduct. In the ϵ -CL/benzotriazole blocked adduct, the first stage dissociation extends upto 300°C. The deblocking temperature of ϵ -CL/benzotriazole blocked adduct is lower than that of benzotriazole blocked adduct that is in between to ϵ -CL blocked and benzotriazole blocked adducts.

Explanation for Deblocking Temperature Difference for Each Blocked Isocyanate. Table IV shows the deblocking temperature range of blocked isocyanates based on the DSC and TGA results.

From this table, benzotriazole based blocked isocyanates show higher deblocking temperature than ϵ -CL based blocked adducts in all the cases. Benzotriazole has three nitrogen atoms and each nitrogen atom has unshared electron pair. This unshared electron pair makes benzotriazole more nucleophilic than ϵ -CL, so the negative charge density

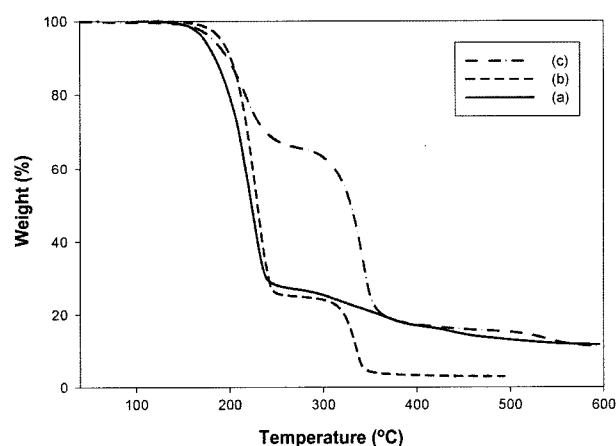
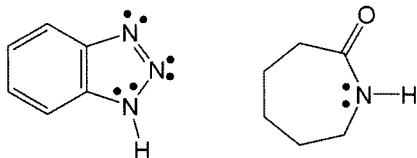


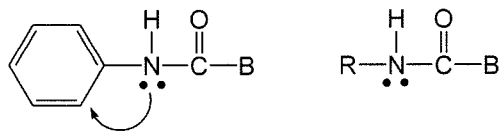
Figure 8. TGA curves of MDI based blocked isocyanates: (a) ϵ -CL blocked adduct, (b) benzotriazole blocked adduct, and (c) ϵ -CL/benzotriazole blocked adduct.

of benzotriazole is higher than that of ϵ -CL. Therefore, deblocking temperature of benzotriazole is higher than that of ϵ -CL. Electron pair position of benzotriazole and ϵ -CL blocking agents are shown below.



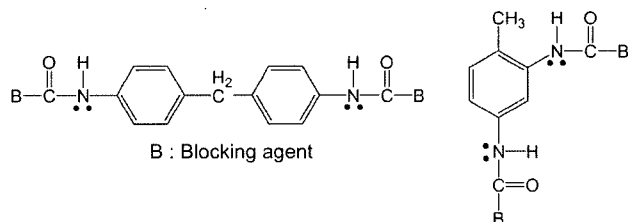
Unshared Electron Pairs Position of Blocking Agents

In general, dissociation temperatures of blocked aromatic isocyanates are always lower than blocked aliphatic isocyanates.⁴¹ As seen in the Table IV, H₁₂MDI based adducts dissociate at higher deblocking temperature range than aromatic diisocyanates (TDI and MDI) based adducts. Benzene ring of aromatic isocyanate attracts the electron pair of nitrogen atom and increases the positive charge density of nitrogen atom. Hence, there is a repulsion force between nitrogen atom and hydrogen atom. The electron withdrawing nature of aromatic isocyanate is the main reason for its lower deblocking temperature than aliphatic isocyanate. This is explained by the following scheme (where R and B are aliphatic and blocking groups).



Effect of Isocyanate Structure on the Deblocking Temperature

Among the aromatic diisocyanates based blocked isocyanates, TDI based blocked isocyanates show lower deblocking temperature than MDI based blocked adducts. The steric effect and electron withdrawing nature of the benzene ring are the main reasons for the lower deblocking temperature of the TDI based blocked isocyanate than that of MDI based blocked adducts. But there is no such effect in the MDI based adducts. The steric effect of TDI based blocked isocyanate is shown as follows.



Steric effect comparison of MDI and TDI based blocked isocyanates

Conclusions

Benzotriazole-, ϵ -CL-, and ϵ -CL/benzotriazole-blocked TDI, MDI, and H₁₂MDI adducts were successfully prepared and characterized. The structure-property relationship of the adducts was established by determination of dissociation temperatures using DSC and TGA techniques. It was found that the thermal stability of the adducts in terms of diisocyanates were in the following order: H₁₂MDI > MDI > TDI. Among the blocking agents, benzotriazole blocked adducts due to its higher negative charge density dissociate at higher temperature than the ϵ -CL blocked adduct. These blocked isocyanate adducts can be used as potential crosslinkers in one-package coating material. The combination of ϵ -caprolactam and benzotriazole as blocking agents gives formulators the flexibility to develop coatings to respond to a number of needs. This chemistry is continuing to evolve and exciting new developments in blocked isocyanate chemistry can be anticipated.

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