

Effect of Catalysts on Deblocking and Cure Reactions of Phenol-blocked Aliphatic Diisocyanate Adducts and Pre-polymers

Karthi Rajendran, Vennila Srinivasan, Sankar Govindarajan*

Department of Polymer Science, University of Madras, Guindy Campus, Chennai, Tamil Nadu, India

ABSTRACT

Effect of catalysis on deblocking and cure reactions of phenol-blocked aliphatic diisocyanate adducts and pre-polymers were investigated using CO₂ evolution method and cure time studies, respectively. Completion of cure reaction of blocked aliphatic diisocyanates and Terathane 2000 was confirmed by ATR spectroscopy. Tertiary amines and organotin compounds were used as catalysts for the deblocking and cure reactions, and the organotin catalyst demonstrated better catalytic activity. However, due to the synergistic effect, a combination of tertiary amine and organotin catalysts demonstrated superior catalytic activity than individual ones. The influence of catalyst concentration on the cure reaction was also investigated. The lowest deblocking temperature of 35°C was achieved in the case of unsubstituted phenol-blocked aliphatic diisocyanate pre-polymer in solution state using a mixture of DBTDL and DABCO, and the cure time was found to be 25 min as it is an important factor for thermal cure process need to be carried out at mild conditions.

Key words: Amine catalysis, Cure reaction, Deblocking, Organotin catalysis, Phenol-blocked aliphatic diisocyanate, Synergistic effect, Terathane 2000.

1. INTRODUCTION

Blocked isocyanates are essential industrial materials used in the production of 1K polyurethane heat curable systems [1]. This material is used in a variety of polyurethane applications, including powder coating [2], eco-friendly waterborne coating [3,4], coil coating [5,6], automotive coating [7], and wire insulating coating. They are also used as adhesives [8,9], sealants [10], elastomers [11], photographic films [12], electrophotography [13], and printing and copying applications. Wicks [14,15] described industrial applications of blocked isocyanates. Blocked isocyanates are the outcomes of an isocyanate reaction with a molecule containing an active hydrogen atom. At high temperatures, blocked isocyanates generate the reactive isocyanate functional groups and blocking agents. This regenerated isocyanate can then be combined with a hydroxyl/amine functional polyol to produce thermally more stable urethanes or ureas. The reaction process of 1K polyurethane heat curable systems is depicted in Figure 1.

Many of these applications rely on the temperature at which blocked isocyanate is deblocked. The choice of isocyanates and blocking agents used mainly depends on the deblocking temperature. In general, most of the industrial applications required the deblocking temperature as low as feasible for a wide range of industrial applications [16]. The deblocking temperature is depends on the structure of the blocking agents, as well as the isocyanates and the amount of catalysts used [17]. Solvents also have an effect on deblocking temperature as well [18-20], although they are rarely used in industrial processes.

Few studies have already documented catalytic effects on the deblocking and cure reactions of aromatic-based blocked isocyanates [21,22]. Moreover, according to the literature, tertiary amines and organotin compounds are normally employed as catalysts in these researches. The catalytic reactions of aromatic blocked isocyanate with mixed catalysts of organotin and tertiary amines exhibited extremely effective catalytic

activity for both deblocking and cure time experiments [22]. However, there is no research on the influence of catalyst on the deblocking and cure reaction of aliphatic blocked isocyanate. Therefore, in this study, the catalytic influence of tertiary amines, organotin compounds, and a combination of organotin-amine catalysts on the deblocking and cure reaction of a variety of phenol-blocked aliphatic diisocyanate adducts and pre-polymers was investigated.

2. EXPERIMENTAL

2.1. Materials

Hexamethylene diisocyanate (HDI) (TCI, Chennai, India), Terathane 2000 (Sigma, Chennai, India), crystalline phenol (SRL, Chennai, India), methyl-4-hydroxyphenol (Alfa Aesar, Chennai, India), 4-methoxyphenol (Alfa Aesar, Chennai, India), barium hydroxide (SRL, Chennai, India), dibutyltin dilaurate (DBTDL) (TCI, Chennai, India), dibutyltin diacetate (DBTDA) (Aldrich, Chennai, India), tributylamine (TBA) (TCI, Chennai, India), triethylamine (TEA) (SRL, Chennai, India), and 1,4-diazobicyclo(2,2,2)octane (DABCO) (Sigma, Chennai, India) were used as received. Dimethylformamide (DMF) (SRL, Chennai, India), tetrahydrofuran (THF) (SRL, Chennai, India), diethyl ether (SRL, Chennai, India), and hexane (SRL, Chennai, India) were distilled before use.

*Corresponding author:

E-mail: gsankarphd@gmail.com

ISSN NO: 2320-0898 (p); 2320-0928 (e)

DOI: 10.22607/IJACS.2022.1001007

Received: 22nd November 2021;

Revised: 22th December 2021;

Accepted: 25th December 2021

2.2. Measurements

FTIR spectra of synthesized and deblocking compounds were taken using KBr pellet approaches on a Thermo-Mattson Satellite model FTIR spectrophotometer (Thermo Scientific, Chennai, India). Shalom oil bath (Shalom Instruments, Bengaluru, India) with a digital temperature controller was employed for CO₂ evolution experiments. An ATR spectrum of cured product was recorded using Nicolet iS50 FTIR-ATR model spectrophotometer (Thermo Scientific, Chennai, India).

2.3. Synthesis of Blocked Isocyanate Adducts and Polyisocyanates

2.3.1. Synthesis of blocked isocyanate adducts

Five grams of phenol and 0.1 g of DBTDL were dissolved in 50 mL of dry toluene and placed in a 250 mL three-necked round-bottomed flask with a magnetic stirrer and a nitrogen inlet. An equimolar quantity of HDI in 50 mL of dry toluene was taken in an addition funnel equipped with the reaction flask. The isocyanate solution was added dropwise to the round-bottomed flask under a nitrogen environment; the reaction was carried out overnight at 50°C. Hexane was used to precipitate the blocked isocyanate adduct, which was then filtered and dried in vacuum desiccators.

2.3.2. Synthesis of blocked polyisocyanates

Two equivalents of HDI were placed in a round-bottom flask connected with a mechanical stirrer. One equivalent of polyol was added dropwise to the flask using an addition funnel. The reaction temperature was originally kept at 50°C for 2 h, then increased to 70°C and continued for 3 h. The reaction mixture was then allowed to cool to 50°C. Finally, an equimolar amount of phenol and 0.1 g of DBTDL were added to the reaction mixture, which was allowed to continue overnight at 50°C.

2.4. Determination of Solution Deblocking Temperature through CO₂ Evolution Method

The CO₂ evolution technique was used to determine the deblocking temperature of phenol-blocked aliphatic diisocyanate adducts and pre-polymers in the presence of organotin catalysts, tertiary amine catalysts, or mixed amine and tin catalysts. In a typical experiment, 1 g of aliphatic blocked isocyanate sample dissolved in 20 mL of DMF and 5 mL of water was introduced into a 25 mL two-necked round-bottom flask, followed by the addition of 3×10^{-4} M catalyst with a CO₂-free nitrogen gas inlet attached to the flask containing saturated solution of barium hydroxide. The reaction kettle was immersed in a temperature-controlled silicon oil bath. The temperature was then raised at a rate of 5°C/min. At certain temperatures, aliphatic blocked isocyanates undergo deblocking reactions, regenerating isocyanates, and blocking agents. The regenerated isocyanates interact with water to form carbamic acid, which then exhaled CO₂. The exhaled CO₂ then reacted

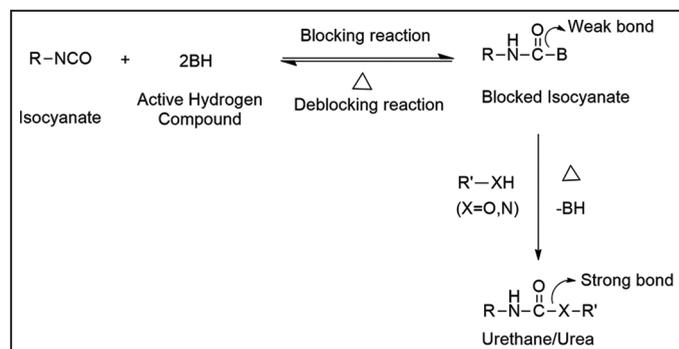


Figure 1: 1K Polyurethane from blocked isocyanate.

with a saturated solution of barium hydroxide to generate barium carbonate turbidity. The temperature at which turbidity forms is known as the deblocking temperature.

2.5. Gel Time Studies

0.002 equivalent of Terathane (2000) was taken individually in eleven 30 mm diameter beakers. At each of these, 0.002 equivalents of aliphatic blocked isocyanate and 2×10^{-4} moles of catalyst were added and thoroughly mixed before the beakers were placed in an air circulated oven heated to 160°C. To observe the flow behavior of the mixture, the beakers were inverted at regular intervals. The gel time was calculated from the point at which the mixture ceased to flow. Each aliphatic blocked isocyanate was subjected to a repeated experiment to ensure the accuracy of the results. Using the same procedure, the cure time of a phenol-blocked polyisocyanate-Terathane 2000 combination was determined.

3. RESULTS AND DISCUSSION

Completion of the reaction between phenol and HDI and polymeric isocyanates was confirmed by FTIR. Typical FTIR spectrum of phenol-blocked HDI adducts and polyisocyanate is shown in Figure 2.

3.1. Determination of Deblocking Temperature through CO₂ Evolution Method

The temperature at which aliphatic blocked isocyanates are deblocked is a crucial for creating efficient heat cured polyurethanes in industrial applications. In aliphatic blocked isocyanates, the bond formed between the isocyanate and the blocking agents is labile and thermally unstable, and the temperature at which the labile bond breaks is referred to as the deblocking temperature. The purpose of this research is to look into the effect of heating rate and catalyst, as well as isocyanate and blocking agent structures, on deblocking temperature employing the CO₂ evolution method. The deblocking process was first performed

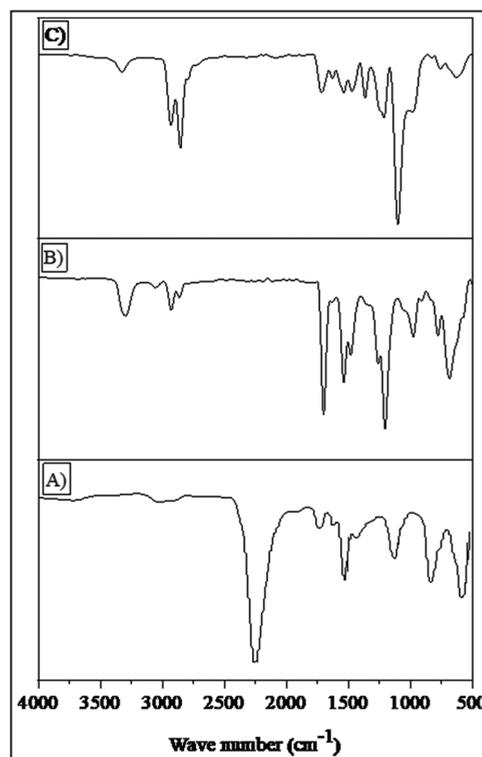


Figure 2: FTIR spectrum of A) HDI; B) Blocked isocyanate adducts (BIA-1) and C) Blocked isocyanate pre-polymers (BPI-1).

at three different heating rates: 3°C/min, 4°C/min, and 5°C/min. CO₂ was released as a result of the breakdown of carbamic acid formed by the interaction between the regeneration of the –NCO functional group and water. The turbidity was produced by the interaction of CO₂ and Ba(OH)₂. The temperature at which turbidity was produced is taken as the deblocking temperature for that particular blocked isocyanate. Deblocking temperatures determined by this method are shown in Table 1. To demonstrate the regeneration of isocyanate in the CO₂ evolution technique, the experiment was carried out for the BIA-1 without water and FTIR was recorded at different time intervals, as shown in Figure 3. We observed that the isocyanate was regenerated

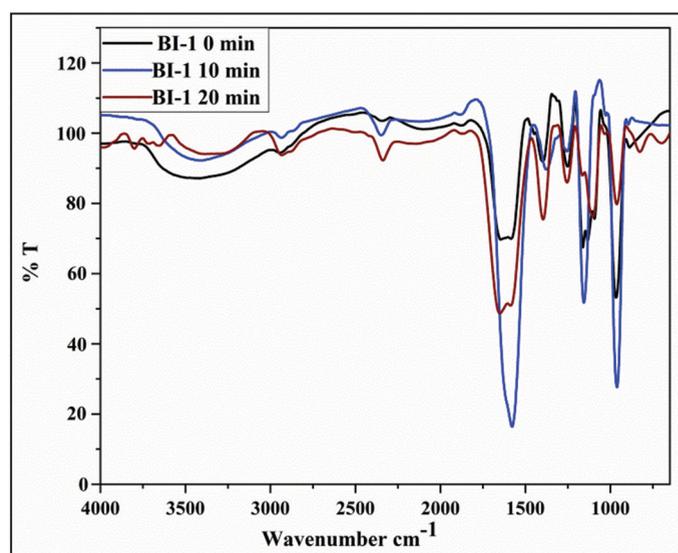


Figure 3: FTIR spectrum of BIA-1 taken without water in CO₂ method.

Table 1: Determination of deblocking temperature of aliphatic blocked isocyanate adducts and pre-polymers with different heating rate using CO₂ evolution method.

Blocked isocyanate	Blocking agent	Deblocking temperature (°C)		
		3°C/min	4°C/min	5°C/min
BIA-1	Phenol	71	75	77.5
BIA-2	4-Methoxyphenol	118	121.5	125
BIA-3	Methyl-4-hydroxybenzoate	101	103	106.5
BPI-1	Phenol	64	66.5	68
BPI-2	4-Methoxyphenol	107	110.5	116
BPI-3	Methyl-4-hydroxybenzoate	89.5	92	94.5

Table 2: Catalysis of cure reaction of phenol-blocked isocyanate adducts and pre-polymer with Terathane 2000.

Blocked isocyanate	Blocking agent	Cure time (Min.)					
		None	DBTDL	DBTDA	DABCO	TBA	TEA
BIA-1	Phenol	360	90	120	105	300	285
BIA-2	4-Methoxyphenol	420	150	180	165	375	360
BIA-3	Methyl-4-hydroxybenzoate	390	120	150	140	345	330
BPI-1	Phenol	300	75	105	90	270	260
BPI-2	4-Methoxyphenol	390	120	145	135	345	330
BPI-3	Methyl-4-hydroxybenzoate	330	90	125	105	285	270

during the technique, thus we plan to investigate the deblocking reaction using this technique.

The blocking agent can have a significant effect on the strength of the labile bond formed during the blocking process and hence the deblocking temperature. In comparison to 4-Methoxyphenol-blocked isocyanates, phenol-blocked diisocyanate adduct and polyisocyanate (BIA-1 and BPI-1) deblock at lower temperatures. The inclusion of an electron-donating substituent (-OMe) at the *para* position improves the phenolate ion's nucleophilicity and so strengthens the labile bond. Electron-withdrawing substituents in phenolate ion, such as ester and nitro, reduce the stability of the labile bond produced and hence deblock at lower temperatures than phenol. Methyl 4-hydroxybenzoate-based blocked isocyanate adducts and polyisocyanate, on the other hand, have a high deblocking temperature compare to phenol-based blocked isocyanates. Unexpectedly, the blocking agent with an electron-withdrawing substitution deblocks at a higher temperature than unsubstituted phenol. This is primarily due to the formation of intramolecular hydrogen bonding between the carbonyl oxygen of the ester substituent and the -NH proton from the isocyanate moiety, which makes the transfer of hydrogen atoms from isocyanate N- to phenol O- hard, and the results are also consistent with Sankar *et al.* findings [23]. Similarly, when different heating rates are used, similar results are seen. The heating rate of 3°C/min produces the lowest deblocking temperature when compared to the other heating rates (Table 1).

3.2. Cure Time Studies

This study established the structure–property correlation of aliphatic blocked isocyanates. All of the aliphatic blocked isocyanates and polyisocyanates gel times were measured by reacting them with Terathane-2000 (polyol) at 160°C. The blocked isocyanate had a longer cure time than the unblocked isocyanate, a long cure time is essential for a single component system to be practicable. At higher temperatures, the isocyanate functionality of the aliphatic blocked isocyanate adducts and pre-polymer was regenerated, and the reaction mixture was cured, as indicated in Schemes 1 and 2.

During the reaction, the viscous flow of the reaction mixture was stopped at a point known as gel time. Table 2 illustrates the durations required to cure the Terathane 2000 with aliphatic blocked isocyanates and then confirmed the cure reaction between blocked isocyanates with polyol with ATR analysis. The -C=O (str) absorption peak of blocked isocyanate at 1704 cm⁻¹ shifted to 1719 cm⁻¹ which corresponds to the -C=O (str) of cured polyurethane, in the ATR, confirming the successful formation of cured polyurethane with Terathane 2000, as illustrated in Figure 4.

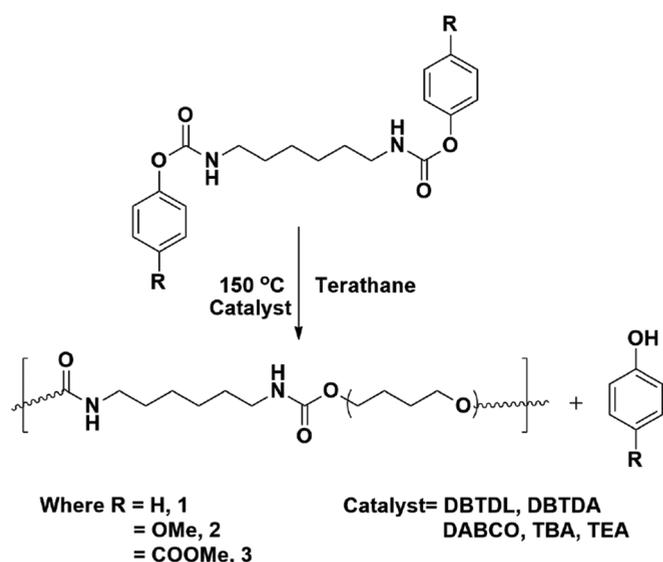
The cure time trend and the deblocking temperature trend were determined to be identical. Furthermore, the impact of an aliphatic blocked isocyanate substituent on the cure process was proportional to the rate of deblocking. The relative viscosity (η_r) of cured polymer as

measured by an Ubbelohde viscometer is shown in Table 2. The values of η_r were determined to be equal, indicating that the cure response was uniform across all experiments.

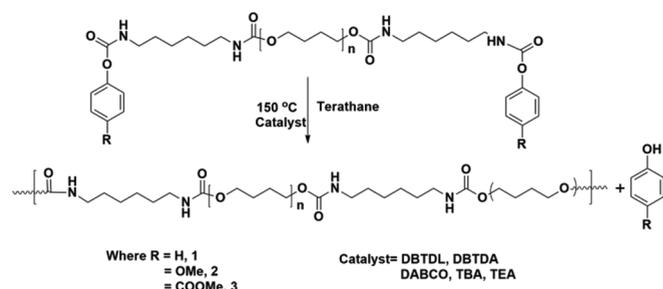
3.3. Effect of Catalysts on Deblocking and Cure Reaction

Two categories of catalysts were used for the deblocking and curing processes of all aliphatic blocked isocyanates and polyisocyanates. The first one of those is comprised of three tertiary amines, whereas the second is consisted of two organotin compounds. Both collected data were evaluated and found to follow good correlation, as shown in Tables 3-6.

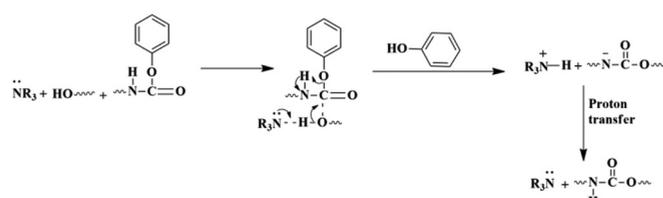
The amine catalyzed reaction was accelerated by three distinct tertiary amines, such as DABCO, TEA, and TBA, and the curing reaction mechanism is depicted in Scheme 3. Tertiary amine readily extracts a proton from polyol -OH rather than urethane -NH proton in the



Scheme 1: Possible mechanism for cure reaction of phenol-blocked diisocyanate adducts.



Scheme 2: Possible mechanism for cure reaction of phenol-blocked isocyanate pre-polymers.



Scheme 3: Possible mechanism for tertiary amine catalyzed cure reaction of phenol-blocked aliphatic isocyanate with polyol.

first step because oxygen has more electronegativity than nitrogen. Furthermore, the urethane group of aliphatic blocked isocyanates is bonded by intramolecular hydrogen bonding between the protons of the -NH moiety and the oxygen atom of the C=O moiety [23]. As a result, tertiary amine proton abstraction from the polyol's -OH group is preferred to abstraction from the -NH group. Following that, the produced alkoxide anion will interact with the aliphatic blocked isocyanate group to regenerate the blocking agent, catalyst, and eventually the polyurethane cured product. DABCO has stronger catalytic activity in this mechanism than other tertiary amines. The catalytic activity of a series including DABCO, TEA, and TBA declined as the steric constraints at the catalytic center grow. Because of the low basicity of the nitrogen atom, TEA and TBA have the lowest catalytic activity.

The cure reaction of all aliphatic blocked isocyanates with Terathane 2000 was catalyzed by organotin compounds such as DBTDL and DBTDA, as shown in Scheme 4. This method may entail the production of a ternary complex by interaction between Sn, oxygen from alcohol, and nitrogen from the urethane -NH group. Few studies have reported the production of ternary complexes such as those found in the urethane formation process [24,25].

In the proposed investigation, this type of interaction results in the formation of cured products as well as the regeneration of catalysts and blocking agents. The acetate and laureate anion in DBTDA and DBTDL are replaced by oxygen in polyol and nitrogen in the blocked isocyanate moiety during the process. Because of structural considerations, the laureate anion is a better leaving group than the acetate anion, is more readily replaced, and hence has higher catalytic activity than DBTDA. Within the catalyst concentration variations, the cure time decreased as the catalyst concentrations rose, as shown in Table 7.

Figures 5 and 6 show the ATR spectra of cured blocked isocyanates and polyisocyanates without and with DBTDL catalyst, respectively.

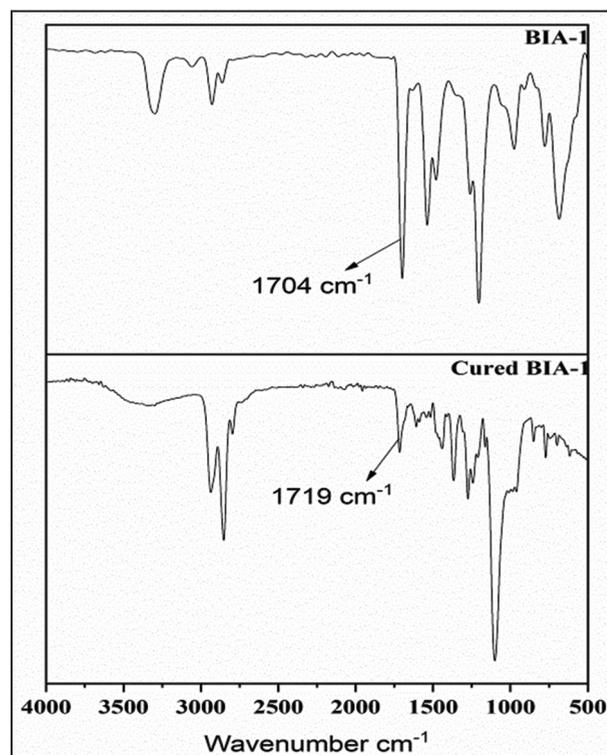


Figure 4: FTIR-ATR spectra of phenol-blocked isocyanate adduct and their DBTDL catalyzed cure reaction product.

Table 3: Synergistic effect on the cure reaction of aliphatic blocked isocyanate adducts and pre-polymer with Terathane 2000.

Blocked isocyanate	Cure time (Min.)						
	None	DBTDL+DABCO	DBTDL+TBA	DBTDL+TEA	DBTDA+DABCO	DBTDA+TBA	DBTDA+TEA
BIA-1	330	35	80	75	45	100	90
BIA-2	420	60	125	120	75	135	135
BIA-3	375	45	95	90	55	120	110
BPI-1	300	25	65	60	35	85	75
BPI-2	390	50	110	105	60	125	120
BPI-3	330	35	75	75	50	95	90

Table 4: Determination of catalyzed deblocking temperature of phenol-blocked aliphatic isocyanate adducts and pre-polymer using CO₂ evolution method.

Blocked isocyanate	Deblocking temperature (°C)					
	None	DBTDL	DBTDA	DABCO	TBA	TEA
BIA-1	75	60	65	63	73	70
BIA-2	121.5	79	87	83	109.5	105
BIA-3	103	67	71	69	89	88
BPI-1	66.5	49	55	52	63	62
BPI-2	110.5	68	76	72	98	94
BPI-3	92	55	62	58	82	78

Table 5: Determination of deblocking temperature of aliphatic blocked isocyanate adducts and pre-polymer in the presence of organotin and amines mixed catalyst.

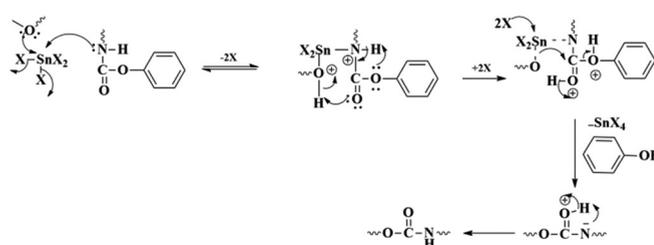
Blocked isocyanate	Deblocking temperature (°C)						
	None	DBTDL+DABCO	DBTDL+TBA	DBTDL+TEA	DBTDA+DABCO	DBTDA+TBA	DBTDA+TEA
BIA-1	75	45	58.5	56	55	63	63
BIA-2	121.5	68	75	73.5	71	78	76
BIA-3	103	61	65	63	65	69.5	69
BPI-1	66.5	35	45	44	45	55	53
BPI-2	110.5	60	68	65	63	70	68
BPI-3	92	47	62	51	54	62	61

Table 6: Effect of catalyst concentration on cure reaction of phenol-blocked isocyanate with Terathane 2000 in the presence of DBTDL.

DBTDL concentration [M]	Cure time (Min)	Relative viscosity (η_r)
1×10^{-4}	130	1.04
3×10^{-4}	80	1.05
4×10^{-4}	72	1.04

Both catalyzed and uncatalyzed spectra reveal a modest increase in -C=O (str) in comparison to the equivalent blocked isocyanate and polyisocyanates, confirming the curation of blocked isocyanate and polyisocyanates with Terathane.

Many studies have found that tertiary amines and organotin compounds work synergistically in the urethane production process [18,26,27]. In the current investigation, equimolar quantities of DBTDA or DBTDL are combined with different tertiary amines such as DABCO, TEA,

**Scheme 4:** Possible mechanism for organotin catalyzed cure reaction of phenol-blocked aliphatic isocyanate with polyol.

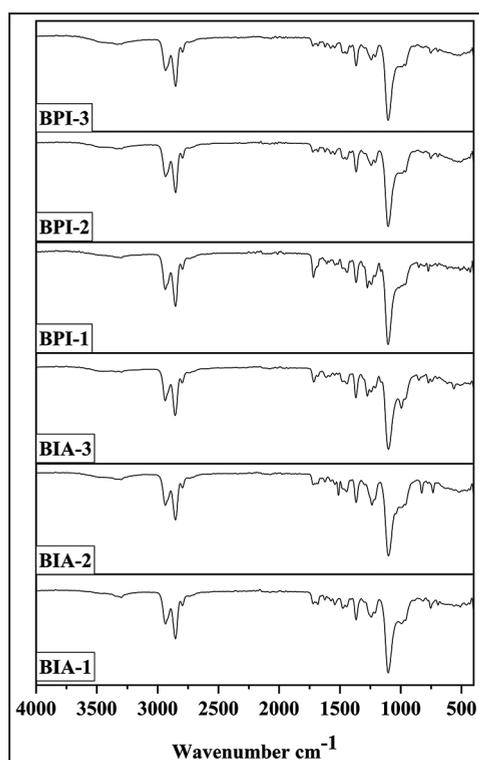
and TBA to pave way for the synergistic impact on the cure reaction of aliphatic blocked isocyanate with Terathane 2000 (Polyol), and the findings are described in Table 4. As a conclusion, the DABCO/DBTDL mixed catalyst had a significant synergistic impact in all of the blocked isocyanates and the phenol-blocked diisocyanate adducts and pre-polymers, yielding completely cured products possible in a short as 35 and 25 min, respectively.

Table 7: Relative viscosities of catalyzed cure products using Ubbelohde viscometer.

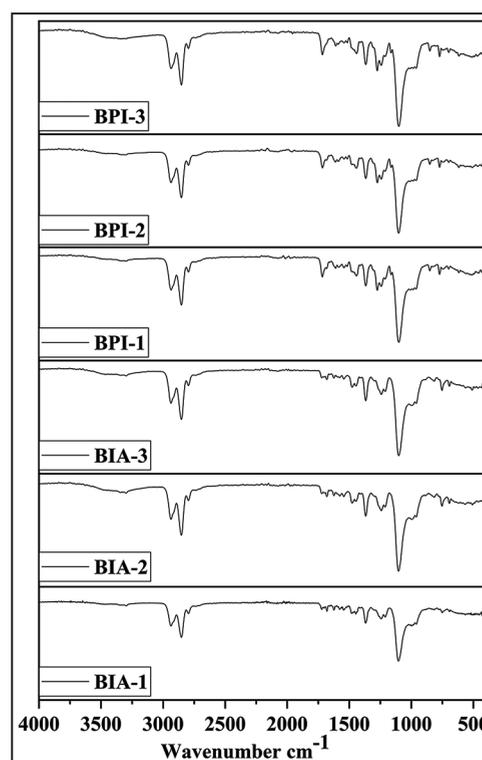
Blocked isocyanate	Blocking agent	Relative viscosity (η_r)					
		None	DBTDL	DBTDA	DABCO	TBA	TEA
BIA-1	Phenol	1.04	1.04	1.03	1.03	1.04	1.03
BIA-2	4-Methoxyphenol	1.03	1.02	1.03	1.04	1.03	1.03
BIA-3	Methyl-4-hydroxybenzoate	1.03	1.02	1.02	1.03	1.03	1.03
BPI-1	Phenol	1.02	1.03	1.02	1.02	1.03	1.04
BPI-2	4-Methoxyphenol	1.04	1.02	1.02	1.03	1.03	1.04
BPI-3	Methyl-4-hydroxybenzoate	1.03	1.04	1.03	1.02	1.02	1.03

Table 8: Relative viscosity of organotin and amine mixed catalyzed cure products using Ubbelohde viscometer.

Blocked isocyanate	Relative viscosity (η_r)					
	DBTDL+DABCO	DBTDL+TBA	DBTDL+TEA	DBTDA+DABCO	DBTDA+TBA	DBTDA+TEA
BIA-1	1.02	1.04	1.03	1.03	1.04	1.03
BIA-2	1.04	1.03	1.03	1.02	1.04	1.03
BIA-3	1.04	1.03	1.02	1.02	1.03	1.03
BPI-1	1.03	1.03	1.04	1.03	1.03	1.04
BPI-2	1.02	1.03	1.03	1.04	1.03	1.02
BPI-3	1.03	1.02	1.04	1.04	1.02	1.03

**Figure 5:** FTIR-ATR spectra of cured product made from blocked isocyanates and polyisocyanates with Terathane without catalyst.

The curing performance of phenol-blocked polyisocyanate is much higher in this investigation, that is, the cure time is significantly lower (90 min) in the presence of DABCO compared to the uncatalyzed reaction (300 min), and this performance is still high in the presence of DBTDL with cure time of 75 min (Table 2). Furthermore, it was discovered that the DABCO/DBTDL mixed catalyst (Table 3)

**Figure 6:** FTIR-ATR spectra of cured product made from blocked isocyanates and polyisocyanates with Terathane with DBTDL catalyst.

improves the curing efficiency of phenol-blocked polyisocyanates much more with cure time of 25 min. Similar tendencies were seen in the deblocking investigations; this value is lowest for the DABCO/DBTDL mixed catalyzed reaction (Table 5), and the value of the DBTDL catalyzed reaction is lower than that of the DABCO catalyzed reaction (Table 4). To check the consistency of the cure reaction, the

relative viscosities (η_r) of catalyzed cured products were evaluated using an Ubbelohde viscometer, as shown in Tables 2 and 8. The values of η_r were determined to be consistent, indicating a homogeneous curative response across all experiments. The findings are congruent with those of phenol-blocked aromatic polyisocyanates [22].

4. CONCLUSION

The catalyzed deblocking and cure process of the phenol-blocked aliphatic diisocyanate adducts and polyisocyanates were investigated. The deblocking temperature was determined using CO₂ evolution method and the cure reaction of blocked isocyanates was performed at 160°C with Terathane 2000 (polyol). Results of catalyzed deblocking and cure time indicated consistent results. Organotin catalyst's outperformed amine in terms of catalytic activity. Because of the synergistic effect, the combined catalysts demonstrated significantly higher catalytic activity than individual catalysts.

5. REFERENCES

- H. R. Moein, (2009) Synthesis and properties of novel polyurethane-urea insulating coatings from hydroxyl-terminated pre-polymers and blocked isocyanate curing agent, *Journal of Applied Polymer Science*, **112**: 3714-3720.
- G. Frizelle, (1972) *Blocked Polyurethane Powder Coating Compositions*, US Patent No. US3857818A.
- R. A. Chowdhury, C. M. Clarkson, S. Shrestha, S. M. El Awad Azrak, (2020) High-performance waterborne polyurethane coating based on a blocked isocyanate with cellulose nanocrystals (CNC) as the polyol, *ACS Applied Polymer Materials*, **2**: 385-393.
- J. Jorge, B. Debkumar, N. A. John, (2005) *Blocked Isocyanate and Their Use in Coating Compositions*, WO Patent No. WO2006029141A1.
- M. T. Li, R. S. Yang, L. Y. Yu, (2013) Properties of epoxy cathodic electro deposition coating by amino siloxane, *Advanced Materials Research*, **648**: 15-17.
- R. L. Briggs, (1995) The use of blocked isocyanates in automotive OEM clearcoats, *SAE Transactions, Journal of Materials and Manufacturing*, **104**: 753-758.
- M. Schink, G. Rix, J. Kirwin, (1995) *Wire Coating Composition and Process for Producing the Same*, US Patent No. US5854334A.
- M. S. Rolph, A. L. J. Markowska, C. N. Warriner, R. K. O'Reilly, (2016) Blocked isocyanates: From analytical and experimental considerations to non-polyurethane applications, *Polymer Chemistry*, **7**: 7351-7364.
- K. B. Bandlish, (1989) *Sealant Compositions or Coating Mixtures Containing Functional Silane or Siloxane adhesion Promoters Nonreactive with Blocked Isocyanates*, US Patent No. US4847319A.
- J. Mazanek, C. Thiebes, J. Meixner, O. Fleck, H. Muller, (2003) *Blocked Polyisocyanates*, US Patent No. US7074852B2.
- K. M. Zia, S. Anjum, M. Zuber, M. Mujahid, T. Jamil, (2014) Synthesis and molecular characterization of chitosan based polyurethane elastomers using aromatic diisocyanate, *International Journal of Biological Macromolecules*, **66**: 26-32.
- M. F. Molaire, (2006) *Blocked Polyisocyanates Incorporating Planar Electron-Deficient Tetracobonylbisimide Moieties*, US Patent No. US7579127B2.
- L. G. Snow, (2003) *Processes for Preparing Printable and Printed Articles*, EP Patent No. EP1699843B1.
- Z. W. Jr. Wicks, (1981) New developments in the field of blocked isocyanates, *Progress in Organic Coatings*, **9**: 3-28.
- D. A. Wicks, Z. W. Jr. Wicks, (2001) Blocked isocyanates III: Part B. Uses and applications of blocked isocyanates, *Progress in Organic Coatings*, **41**: 1-83.
- G. Sankar, N. Yan, (2015) Synthesis and deblocking studies of low temperature heat-curable blocked polymeric methylene diphenyldiisocyanates, *Journal of Macromolecular Science Part A Pure and Applied Chemistry*, **52**: 47-55.
- D. A. Wicks, Z. W. Jr. Wicks, (2001) Multistep chemistry in thin film; the challenges of blocked isocyanates, *Progress in Organic Coatings*, **43**: 131-140.
- H. Kothandaraman, A. S. Nasar, (1993) The thermal dissociation of phenol-blocked toluene diisocyanate crosslinkers, *Polymer*, **34**: 610-615.
- S. Mohanty, N. Krishnamurti, (1998) Synthesis and thermal deblocking of blocked diisocyanate adducts, *European Polymer Journal*, **34**: 77-83.
- H. Kothandaraman, A. S. Nasar, R. Kamal Lakshmi, (1994) Synthesis and thermal dissociation of phenol-and naphthol-blocked diisocyanates, *Journal of Applied Polymer Science*, **53**: 31-38.
- A. M. Issam, G. Sankar, (2011) Catalysis of secondary alcohol blocked isocyanate-hydroxyl terminated polybutadiene cure reaction, *Polymer Science Series B*, **53**: 52-56.
- S. Kalaimani, A. S. Nasar, (2017) Catalysis of deblocking and cure reaction of easily cleavable phenol blocked polyisocyanates with poly (tetrahydrofurancarboxylate) diol, *European Polymer Journal*, **91**: 221-231.
- G. Sankar, A. S. Nasar, (2007) Amine-blocked polyisocyanates. I. Synthesis of novel N-methylaniline-blocked polyisocyanates and deblocking studies using hot-stage fourier transform infrared spectroscopy, *Journal of Polymer Science Part A Polymer Chemistry*, **45**: 1557-1570.
- K. Wongkamolsesh, J. E. Kresta, (1985) Reaction injection moulding, *ACS Symposium Series*, **270**: 111-121.
- S. G. Luo, H. M. Tan, J. G. Zhang, Y. J. Wu, F. K. Pei, X. H. Meng, (1997) Catalytic mechanisms of triphenyl bismuth, dibutyltindilaurate, and their combination in polyurethane-forming reaction, *Journal of Applied Polymer Science*, **65**: 1217-1225.
- H. W. Wolf, (1956) *Catalytic Activity in One-Shot Urethane Foam*, Technical Bulletin, Wilmington: DuPont, p30-65.
- I. S. Bechara, (1981) The mechanism of tin-amine synergism in the catalysis of isocyanate reaction with alcohols, *ACS Symposium Series*, **172**: 393-402.

*Bibliographical Sketch



Dr. G. Sankar is an Assistant Professor at the University of Madras in Chennai, India, in the Department of Polymer Science. His research focuses on the development of novel non-conventional Blocked Isocyanates for room temperature curing systems for 1K polyurethanes, as well as the development of polymeric magnetic nanocomposites using environmentally hazardous waste and renewable resources to remove toxic effluents from industrial wastes and drug delivery applications. He has 15 peer-reviewed publications and one international patent.