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Synthesis and Deblocking Investigations of Phenol Blocked Aliphatic Isocyanates and Their Application in the Development of Epoxy-Polyurethane Films

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Phenol blocked hexamethylenediisocyanate adducts and polyisocyanates were synthesized and their structure was validated by FTIR, ^{1}H & ^{13}C NMR spectroscopy, TGA, DSC and CO_2 evolution techniques were used to evaluate the deblocking temperature of blocked isocyanates. Gel time studies of blocked isocyanates with terathane polyol and solubility study of blocked isocyanates with different polyols were conducted to demonstrate the structure-property correlation. Epoxy-polyurethane films were produced utilizing the blocked isocyanates reported in this work with epoxy resin and their structure was verified by ATR Spectroscopy. TGA, DSC, shore A hardness, tensile strength and flexural strength analysis were used to investigate the thermal and mechanical characteristics of these films. The findings of deblocking temperature and gel time revealed that unsubstituted phenol blocked isocyanates and polyisocyanates deblock at lower temperatures and cure for a shorter time period than substituted phenol blocked isocyanates. Thermal and mechanical characteristics of epoxy-polyurethane films based on blocked polyisocyanates are satisfactory.

Keywords: Blocked isocyanates, Deblocking, Epoxy, Polyurethane, Phenol.

INTRODUCTION

Blocked isocyanates are important industrial materials utilized in 1K polyurethane heat curable systems [1]. This material is utilized in a wide range 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 utilized as adhesives [8,9], sealants [10], elastomers [11], photographic films [12], electro photography [13], printing and copying applications. Wicks [14,15] documented industrial uses of blocked isocyanates. Blocked isocyanates are the products of the reaction between an isocyanate and a molecule containing an active hydrogen atom. Blocked isocyanates regenerate the reactive isocyanate functional groups and blocking agents at high temperatures. This regenerated isocyanate can then react with hydroxyl/amine functional polyol to create thermally more stable urethanes or ureas. Fig. 1 depicts the reaction process of 1K polyurethane heat curable systems.

Many of these applications rely on the deblocking temperature of blocked isocyanate. The selection of isocyanates and blocking agents are mostly determined by the deblocking temperature. In general, it is preferable to keep the deblocking temperature as low as possible for a variety of industrial applications [16]. It is dependent on the structure of the blocking agents as well as the isocyanates [17]. Several compounds having active hydrogen atoms such as phenols, oximes, amides, imides, imidazoles, amidines and related compounds, pyrazoles, 1,2,4-triazoles, hydroxamic acid esters, *N*-methylaniline and active methylene compounds have been described as blocking agents [18-24]. Among these blocking agents, phenols are the most commonly reported because they are inexpensive and allows the introduction of a greater number of substituent on the benzene ring [25]. It should be noted that the effect of blocking agents on deblocking temperature has been intensively investigated whereas, the effect of isocyanate structure has not really been extensively studied; even so, the structure of isocyanates, like that of blocking agents has been shown to have a substantial impact on the deblocking temperature.

The majority of the reported blocked isocyanates are however only based on aromatic isocyanates [26-28], may be due to the fact that aromatic isocyanates are less expensive than

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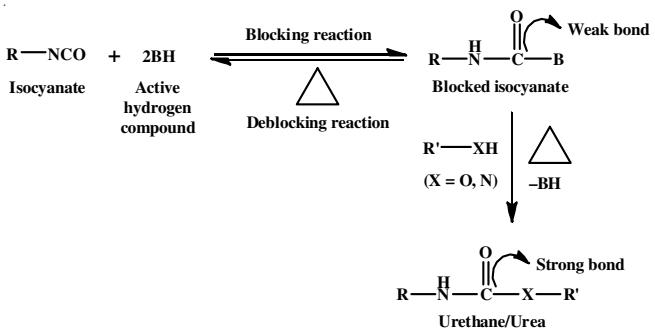


Fig. 1. 1K Polyurethane from blocked isocyanate

aliphatic isocyanates. However, aliphatic isocyanates are used in certain application areas especially in coatings because of excellent physical properties such as UV resistant and exterior durability [29]. They also exhibit exceptional light and weathering stability compare to the easy yellowing aromatic diisocyanates [30]. Yet, the research on deblocking studies of aliphatic isocyanates based blocked isocyanates are meager. Although, few researchers documented the synthesis of aliphatic isocyanate based blocked isocyanates and their applications [31-36]. However, blocking reaction is their major emphasis in these literatures and they were not examined how the different variables such as blocking agents, heating rate, analytical methods utilized and isocyanate structure impact the deblocking reaction.

Epoxy resin is known for its high mechanical strength and modulus, good adhesion property and dimensional stability [37-39]. However researchers prefer to use epoxy-polyurethane composite resins for better cost and performance ratio [40] and for its enhanced characteristics such as strong abrasion resistance, flexibility, elasticity and shock absorption as well as high environmental resilience [41]. It is also found that the epoxy resin is toughened by imidazole and caprolactum blocked isocyanates [34,39,42]. However, to our best of knowledge use of phenol blocked isocyanates in making epoxy-polyurethane films and effect of blocking agent and isocyanate structure on forming epoxy urethane blends is not reported.

With this view, we set out to synthesize a series of hexamethylene diisocyanate (HDI) based several substituted phenol blocked isocyanates and polyisocyanates and then to systematically investigate their deblocking reaction using different analytical techniques and to synthesis epoxy-polyurethane films using blocked isocyanates and to study thermal and mechanical properties of the epoxy-polyurethane films.

EXPERIMENTAL

Hexamethylenediisocyanate (HDI; TCI), poly(tetrahydrofuran)diol (Sigma), crystalline phenol (SRL), methyl-4-hydroxyphenol (Alfa Aesar), 4-methoxyphenol (Alfa Aesar), dibutyltindilaurate (DBTDL; TCI), polyethylene glycol (PEG) with the molecular weight of 4000 and 6000 (SRL), barium hydroxide (SRL), epoxyamine resin (Rotopolymers and chemicals) were used as received. Dimethylformamide (DMF; SRL), tetrahydrofuran (THF; SRL), diethylether (SRL) and hexane (SRL) were distilled before use.

Characterization: The ^{1}H & ^{13}C NMR spectra of synthesized compounds were recorded with Bruker AV III 300 MHz spectrophotometer using $CDCl_3$ as a solvent containing tetramethylsilane (TMS) as an internal standard. FTIR spectra were recorded with Bruker (FT-MID-IR) spectrophotometer by KBr pellet methods. Thermo Gravimetric Analysis (TGA) was carried out in a NETZSCH-STA 2500A thermal analyzer from 30 ºC to 550 ºC at a heating rate of 20 ºC/min under nitrogen atmosphere. Differential scanning calorimeter (DSC) was performed with DSC-250 of TA instruments; thermograms were recorded from 50 ºC to 300 ºC under nitrogen atmosphere at a heating rate of 10 ºC/min. Shalom oil bath with digital temperature controller was used for CO_2 evolution experiments at a heating rate of 5 ºC/min. The relative viscosities (η_r) of cured polymers were measured in THF at 30 ºC using an Ubbelohde viscometer. The hardness of the cured polymer films were measured by using Shore A hardness tester. Tensile and flexural strength of cured polymer films were recorded using universal testing machine (FSA UTM M-50). The contact angles of the films were measured using Contact Angle Meter (Kyowa Interface Science Co., Ltd. Model no. DMe-211 Plus).

General procedure for the preparation of blocked isocyanate adducts (BIA-1 to 3): In a typical synthesis, 5 g of blocking agent (0.0531 equiv.) was dissolved in 50 mL of dry THF and placed in a 250 mL of three-necked round bottom flask equipped with a condenser, nitrogen inlet and addition funnel and then dibutyltindilaurate (DBTDL) (0.1 g) was introduced as a catalyst and stirred for 30 min. Hexamethylenediisocyanate (HDI) (0.0531 equiv.) dissolved in 30 mL of dry THF and taken in an addition funnel and then HDI solution was added dropwise to the reaction mixture over a 45 min period with stirring under inert atmosphere. The reaction temperature was then raised to the reflux temperature and the process was monitored using FTIR spectroscopy until the -NCO stretching frequency at 2270 cm^{-1} completely disappeared. The adduct was precipitated by adding the reaction mixture to 400 mL of hexane, then the filtrate was filtered and washed with diethylether before drying under vacuum at room temperature.

Phenol blocked isocyanate adduct (BIA-1): FTIR (KBr, cm^{-1}): 3303 (urethane NH *str.*), 1711 (urethane C=O *str.*), 1536 (urethane NH bend.); ^{1}H NMR (DMSO-d_6, δ): 1.31-1.48 (alkyl CH_2), 2.97 (N-CH_2), 7.01-7.37 (aromatic protons), 7.64 (urethane NH); ^{13}C NMR (DMSO-d_6, δ): 24.70 (alkyl carbon), 28.09 (N-CH_2), 116.38-127.82 (aromatic carbons), 160.55 (urethane C=O).

4-Methoxyphenol blocked isocyanate adduct (BIA-2): FTIR (KBr, cm^{-1}): 3286 (urethane NH *str.*), 1703 (urethane C=O *str.*), 1510 (urethane NH bend.); ^{1}H NMR (DMSO-d_6, δ): 1.33-1.48 (alkyl CH_2), 3.04-3.06 (N-CH_2), 3.74 (OCH_3), 6.88-7.01 (aromatic protons), 7.53 (urethane NH); ^{13}C NMR (DMSO-d_6, δ): 24.61 (alkyl carbon), 27.87 (N-CH_2), 54.12 (O-CH_2), 112.92-153.36 (aromatic carbon), 154.97 (urethane C=O).

Methyl-4-hydroxybenzoate blocked isocyanate adduct (BIA-3): FTIR (KBr, cm^{-1}): 3303 (urethane NH *str.*), 1710 (urethane C=O *str.*), 1516 (urethane NH bend.); ^{1}H NMR (DMSO-d_6, δ): 1.24-1.50 (alkyl CH_2), 2.97-3.10 (N-CH_2), 3.79 (ester CH_3), 6.83-7.98 (aromatic protons); ^{13}C NMR (DMSO--d_6, δ): 25.84-26.01 (alkyl carbon), 29.05-29.96 (N-CH_2),

51.99 (ester-CH_3), 115.30-153.50 (aromatic carbon), 155.09 (urethane C=O), 165.63 (ester C=O).

General procedure for the preparation of blocked isocyanate pre-polymers (BPI-1 to 3): A two-step procedure was used to synthesize blocked isocyanate pre-polymers. In the first stage, HDI (2.1 equiv.) were placed in a 100 mL three necked round bottom flask equipped with a mechanical stirrer, nitrogen inlet and addition funnel. A polyol (poly(tetrahydrofuran)diol) [5 g (1 equiv.)] was introduced dropwise to the flask, over the course of 1 h. The temperature of the reaction was increased to 50 ºC for 2 h and then held at 70 ºC for 3 h. After 5 h, the temperature was lowered to 40 ºC to get the isocyanate terminated pre-polymer. The -NCO terminated pre-polymer was then blocked in the second stage by adding an equivalent quantity of (1 equiv.) blocking agent and 0.1 g of dibutyltindilaurate (DBTDL) as a catalyst to the reaction mixture, which was then mechanically agitated overnight at 40 ºC. The reaction was carried out until the -NCO group absorption peak at 2270 cm^{-1} in the FTIR dissipated. A waxy product of blocked polyisocyanates was obtained upon completion of the reaction.

Determination of deblocking temperature through CO_2 evolution method: In a typical experiment, 1 g of blocked isocyanate sample dissolved in 20 mL of DMF and 5 mL of water was introduced in a 25 mL two necked round bottom flask which was equipped with a CO_2 free nitrogen gas inlet which attached to the flask containing saturated solution of barium hydroxide. The reaction kettle was kept in a temperature regulated silicon oil bath. The temperature was then increased at a rate of 5 ºC/min. Blocked isocyanates undergo deblocking reactions at certain temperatures, regenerating isocyanates and blocking agents. The regenerated isocyanates reacted with water to produce carbamic acid, which released CO_2.The released CO_2 was reacted with a saturated solution of barium hydroxide to produce turbidity in the form of barium carbonate. Temperature at which turbidity develops is referred to as the deblocking temperature.

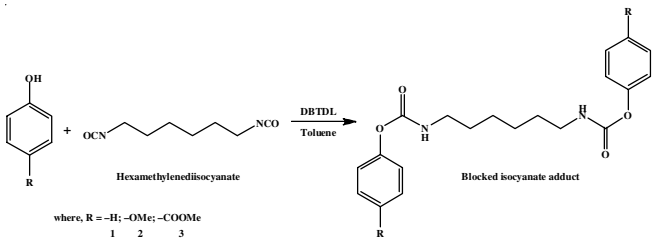
Solubility test: The solubility of blocked isocyanate adducts and pre-polymers was studied in this experiment using the different polyols. Blocked isocyanate was disseminated in each polyol individually in 25 mL beaker and heated on a temperature regulated oil bath at a heating rate of 5 ºC/min. The temperature at which the dispersed blocked isocyanate changes into clear solution was recorded as the dissolution temperature.

Gel time studies: In six 30 mm diameter beakers, 0.002 equiv. of terathane (2000) was taken separately. At each of these, 0.002 equiv. of blocked isocyanate was added and properly mixed, and the beakers were then put in an air circulated oven heated to 160 ºC. The beakers were inverted at regular intervals to monitor the flow behaviour of the mixture. The gel-time was measured from the time when the mixture stopped flowing. To confirm the correctness of the results gathered, each blocked isocyanate was subjected to a duplicate experiment.

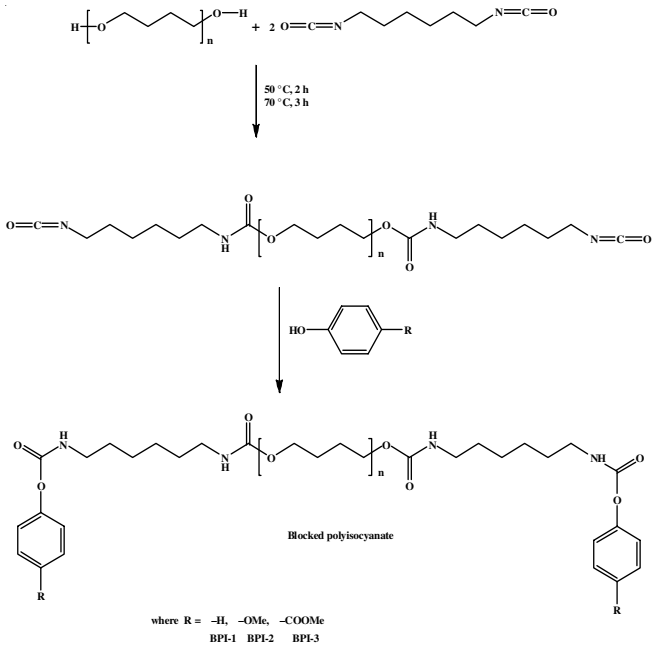
Preparation of epoxy-polyurethane films: Epoxy-polyurethane films produced using blocked isocyanates and epoxy resin. Epoxy resin (1 equiv.) and blocked isocyanate were added with 1 equivalent of hardener and mixed uniformly before being poured onto a wax coated petri-dish. The sample was then kept in vacuum desiccators for 15 min to remove air bubbles trapped during mixing. Afterwards, the sample was kept at room temperature for 24 h before being placed in an air circulated oven set to 160 ºC for 4 h to cure the film.

RESULTS AND DISCUSSION

Synthesis of phenol blocked isocyanates: Blocked diisocyanate adducts and polyisocyanates were prepared using an equivalent amount of blocking agent with -NCO terminated polyisocyanate or with hexamethylenediisocyanate (HDI). The -NCO terminated polyisocyanates prepared using HDI (2 equiv.) and poly(tetrahydrofuran)diol (1 equiv.). Absence of -NCO stretching absorption at 2270 cm^{-1} in FTIR spectrum was used to confirm the completion of the blocking reaction. **Schemes I** and **II** depict the chemical process for the preparation of blocked isocyanate adducts and polyisocyanates respectively and their detailed experimental conditions are shown in Table-1. The use of dibutyltindilaurate (DBTDL) as a catalyst is required for all the blocking reactions. Since the phenolic hydroxyl's relative reactivity, towards the -NCO group is 1000 times less than that of an aliphatic primary hydroxyl group, this is primarily attributable to the fact that phenols are poor nucleophiles due to their size and resonance stability. The reaction between methyl-4-hydroxybenzoate and isocyanates required an excess of blocking agent and higher reaction time. This might be



Scheme-I: Synthesis of blocked isocyanate adducts (BIA 1-3)



Scheme-II: Synthesis of blocked polyisocyanates (BPI 1-3)

TABLE-1
SYNTHESIS OF PHENOL BLOCKED HDI

Sample code	Blocking agent	Equivalents used	Reaction temperature (°C) and time (h)	Equivalent weight of blocked isocyanates (g/mol)
	Adducts			
BIA-1	Phenol	1.0	50 (7)	356.42
BIA-2	4-Methoxyphenol	1.0	50 (7)	416.48
BIA-3	Methyl-4-hydroxyphenol	1.3	50 (56)	472.50
	Pre-polymers			
BPI-1	Phenol	1.0	40-70 (15)	2524.62
BPI-2	4-Methoxyphenol	1.0	40-70 (15)	2584.68
BPI-3	Methyl-4-hydroxyphenol	1.3	40-70 (23)	2640.70

explained by the existence of an electron withdrawing (-COO) group at the *para* position, as suggested by earlier studies [21].

The FTIR spectra for all of the blocked isocyanates are extremely similar and show urethane -NH stretching absorption around 3300 cm^{-1}, urethane -NH bending absorption around 1535 cm^{-1}, urethane -C=O stretching absorption at 1730 cm^{-1} and C-O stretching absorption of the polyol around 1100 cm^{-1}. The disappearance of the absorption peak at 2270 cm^{-1} for all the compounds synthesized in this work, indicated that the phenol had entirely occluded the isocyanate groups. Fig. 2 depicts a typical FTIR spectrum of phenol blocked isocyanate adduct and polyisocyanate.

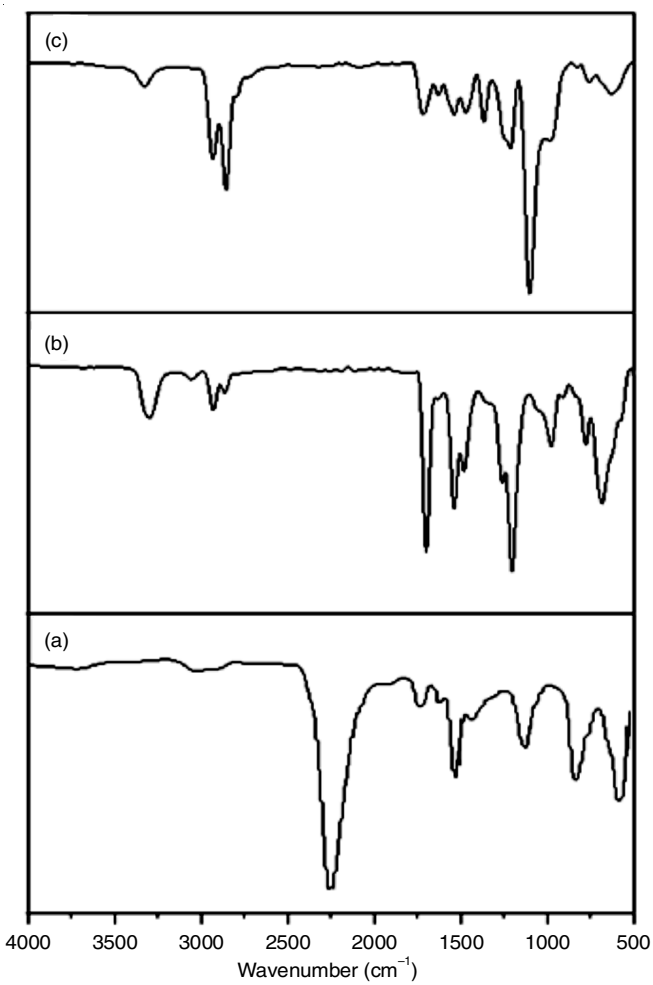


Fig. 2. FTIR spectrum of (a) HDI; (b) blocked isocyanate adducts (BIA-1) and (c) blocked isocyanate pre-polymers (BPI-1)

^{1}H and ^{13}C NMR spectra of phenol blocked isocyanate adducts are almost similar to one another, just as the FT-IR spectra. Figs. 3 and 4 show the typical ^{1}H and ^{13}C NMR spectra of phenol blocked isocyanate adducts. The aromatic protons appeared in the range of 7.07-7.39 ppm whereas, the methyl group from the HDI moiety exhibited in the range of 1.30-1.47 ppm and the -NCH_2 group appeared at 2.97-3.06 ppm. The existence of the urethane group was further confirmed by the peak at 7.61 ppm which is due -NH proton. The presence of a urethane carbonyl (-C=O) carbon confirmed by the signal appeared at 160 ppm in the ^{13}C NMR spectrum indicates that the isocyanates have been fully blocked by phenols. NMR analysis for blocked polyisocyanates cannot be performed as they are not soluble in NMR solvents. This is mostly caused by the cross-linking of the isocyanate functional group due to the presence of DBTDL catalyst.

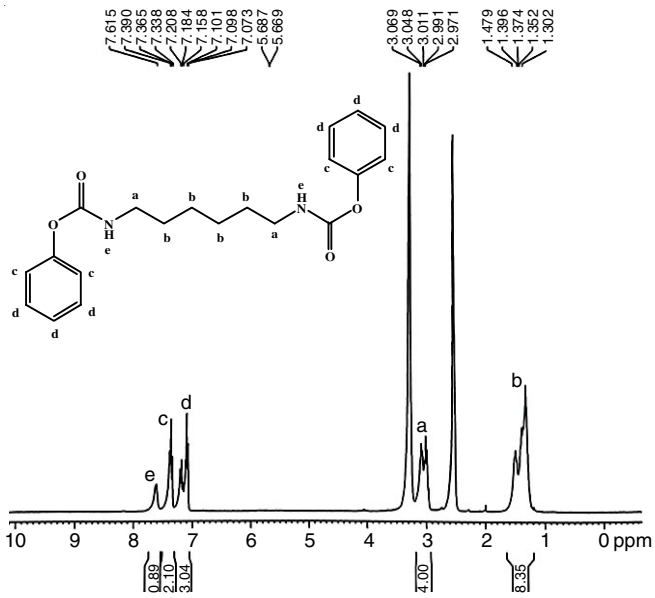


Fig. 3. ^{1}H NMR spectrum of phenol-blocked isocyanate adduct (BIA-1)

This DBTDL-induced cross-linking activity is consistent with the idea presented in the literature [43]. Blocking agent and catalyst were mixed and introduced via additional funnel without any solvent. Since polyisocyanate blocking reaction is a solvent-free and then added to the polyisocyanate pre-polymer which kept at reaction kettle. However, in case of blocked isocyanate adducts, catalyst was mixed with phenol

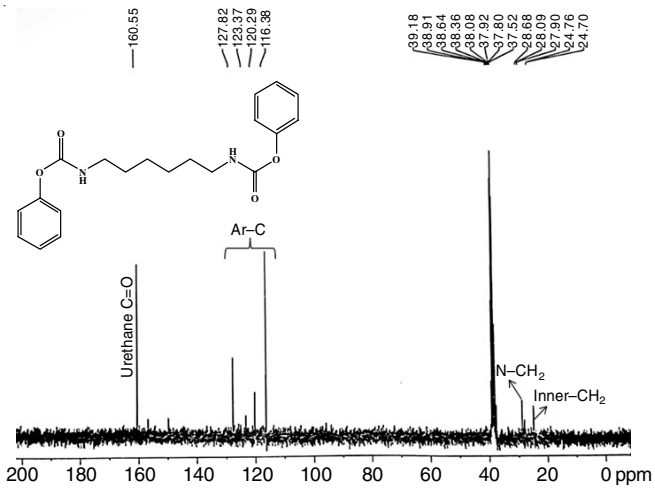
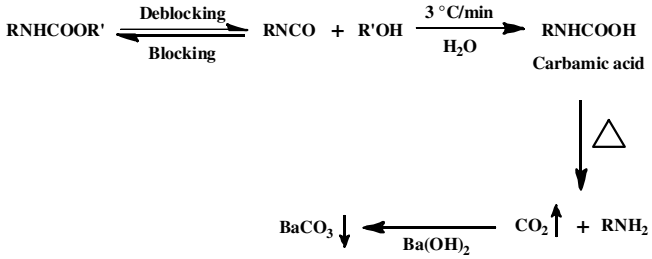


Fig. 4. ^{13}C NMR spectrum of phenol-blocked isocyanate adduct (BIA-1)

and solubilized in the solvent and taken in reaction kettle then isocyanate in dry solvent was added *via* additional funnel drop by drop in a controlled manner to avoid any cross-linking reaction.

Deblocking studies: Deblocking temperature of blocked isocyanates is critical for producing flawless heat cured polyurethanes in industrial applications. The bond formed between the isocyanate and the blocking agents in blocked isocyanates is labile and thermally unstable and the temperature at which the labile bond breaks termed the deblocking temperature. To investigate the impact of analytical methods and heating rate as well as isocyanate and blocking agent structures on deblocking temperature. This study used three distinct analytical methods: TGA, DSC and CO_2 evolution technique. The first enthalpy curve in DSC caused due to melting and the second endothermic transition was caused by the deblocking reaction and the deblocking temperature was determined using tangent of this transition. Deblocking temperature was defined as the temperature at which 5% weight loss occurred in TGA. However, for the CO_2 evolution technique, the temperature at which the turbidity produced as a result of the interaction between CO_2 and $Ba(OH)_2$ is considered as deblocking temperature. The CO_2 was released as a result of the breakdown of carbamic acid, which produced as a result of the interaction between the regeneration of the -NCO functional group and water. **Scheme-III** explains the deblocking response mechanism of this approach.



Scheme-III: Deblocking reaction mechanism of blocked isocyanates using CO_2 evolution method

The deblocking temperatures determined using all techniques are shown in Table-2 and the TGA and DSC thermograms of blocked isocyanates are shown in Figs. 5 and 6, respectively. The deblocking temperature determined by these three methods is consistent with each other methods with respect to the isocyanate and blocking agent structures. The CO_2 method gives lowest de-blocking temperature, which can be attributed as it was carried out at in the solution state whereas TGA and DSC methods were carried out in the solid state.

TABLE-2
DETERMINATION OF DEBLOCKING TEMPERATURE USING TGA, DSC AND CO_2 EVOLUTION METHOD

Sample code	Blocked isocyanates	Deblocking temperature (°C)		
		TGA	DSC	CO_2
BIA-1	Phenol	203.0	178.6	77.5
BIA-2	4-Methoxyphenol	258.6	227.2	125.0
BIA-3	Methyl-4-hydroxyphenol	251.1	184.3	106.5
BPI-1	Phenol	165.0	161.9	68.0
BPI-2	4-Methoxyphenol	208.0	222.6	116.0
BPI-3	Methyl-4-hydroxyphenol	203.6	143.7	94.5

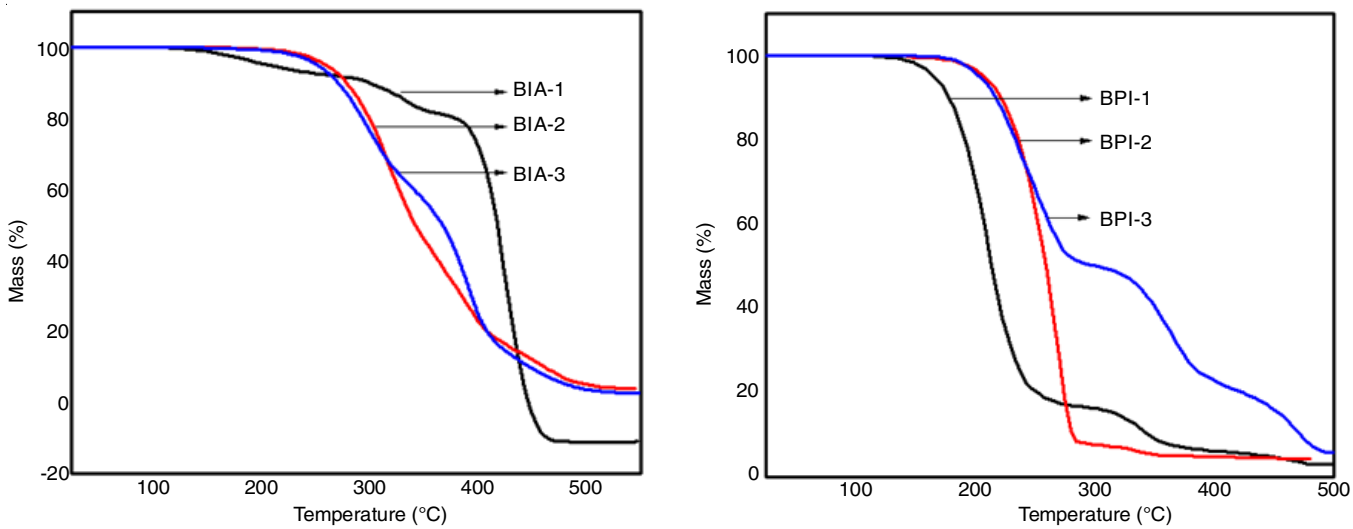


Fig. 5. TGA graphs for blocked isocyanate adducts (BIA 1-3) and pre-polymers (BPI 1-3)

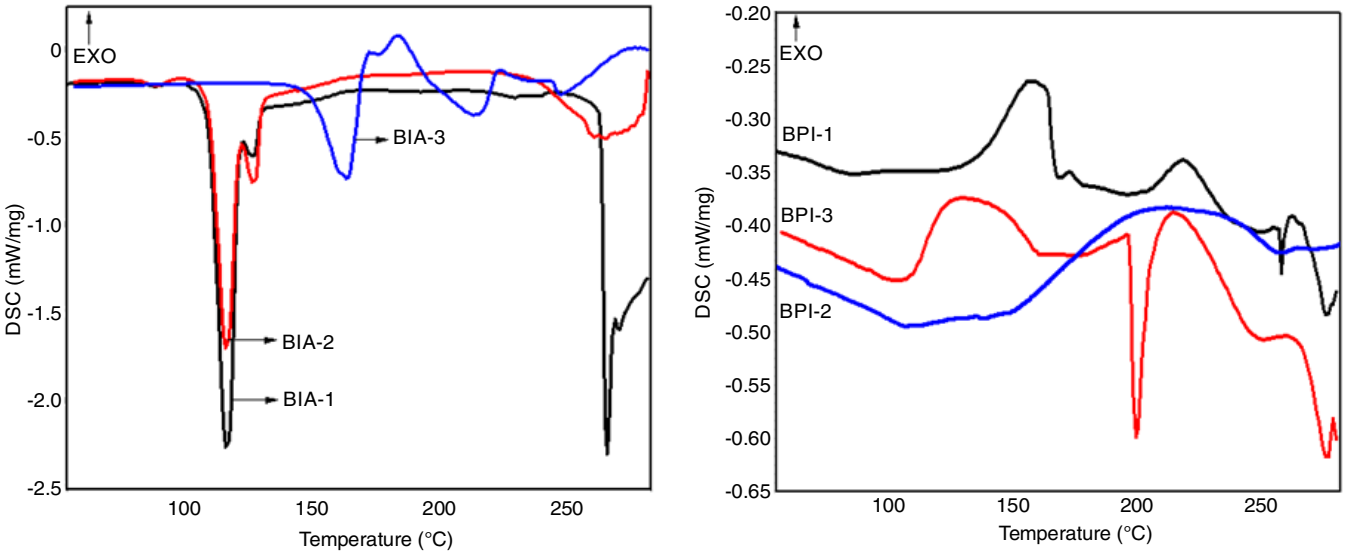
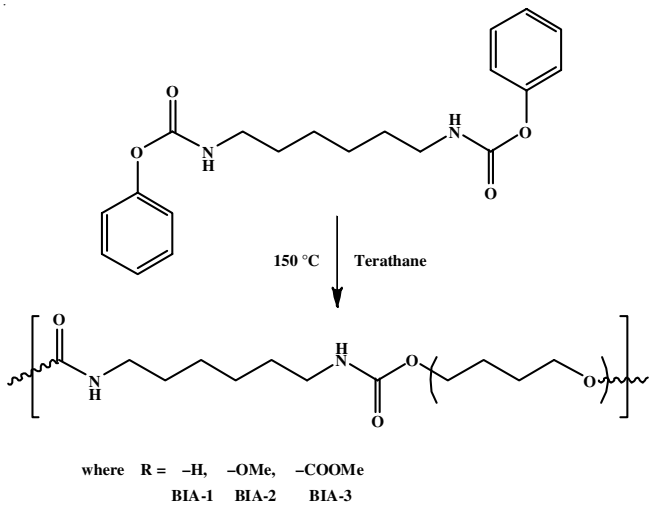


Fig. 6. DSC graphs for blocked isocyanate adducts (BIA 1-3) and pre-polymers (BPI 1-3)

By closely studying the data, it is discovered that the deblocking temperature is affected not only by the analytical methodologies utilized but also by the isocyanate and blocking agent structures. According to the findings of this investigation, the blocking agent can have a significant impact on the strength of the labile bond created during the blocking process and therefore the deblocking temperature. When compared to 4-methoxyphenol blocked isocyanates, phenol blocked diisocyanate adduct and polyisocyanate (BIA-1 & BPI-1) deblocks at lower temperatures in three methods. The presence of an electron donating substituent (-OMe) at the *para*-position increases the nucleophilicity of the phenolate ion and hence strengthens the labile bond. Electron withdrawing substituent like ester and nitro in phenolate ion decreases the stability of the labile bond formed and therefore they deblock at lower temperatures than phenol. However, methyl 4-hydroxybenzoate blocked isocyanate adducts and polyisocyanate has a high deblocking temperature. It is quite surprising to discover that the blocking agent with an electron withdrawing substitution deblocks at a higher temperature than unsubstituted phenol. This is mostly due to the creation of intramolecular hydrogen bonding between the carbonyl oxygen of the ester substituent and the -NH proton from the isocyanate moiety, making the transfer of hydrogen atoms from isocyanate N- to phenol O-challenging and the results are also consistent with findings of Sankar & Nasar [21].

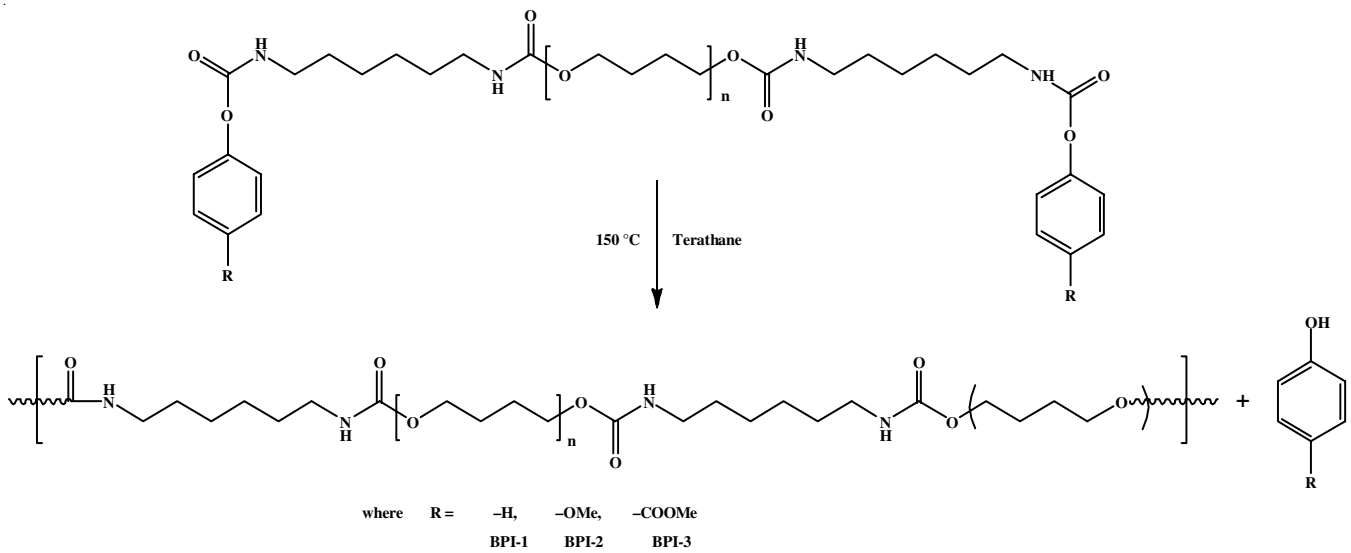
Gel time studies: The structure-property relationship of blocked isocyanates was established in this investigation. The gel time of all the blocked isocyanates was determined by reacting them with poly(tetrahydrofuran)diol at 160 ºC. When compared to unblocked isocyanate, the blocked isocyanate had a longer pot life; a long pot life is required for a single component system to be practical. The isocyanate functionality of the blocked isocyanate adducts and pre-polymer was regenerated at higher temperatures and the reaction mixture was cured as shown in **Schemes IV** and **V**. During the reaction, the viscous flow of the reaction mixture was stopped at a certain period



Scheme-IV: Cure reaction of blocked isocyanate (BI) adducts with poly(tetrahydrofuran)diol

known as gel time. Table-3 shows the time frames necessary to cure the poly(tetrahydrofuran)diol with blocked isocyanates. The cure time trend was discovered to be similar to the deblocking temperature trend. Furthermore, the influence of blocked isocyanate substituent on cure reaction was commensurate with the rate of deblocking reaction. Table-3 shows the relative viscosity (η_r) of cured polymer obtained using an Ubbelohde viscometer. The values of η_r were discovered to be equivalent, indicating the uniform cure response in all studies.

Solubility analysis: The solubility of blocked isocyanate is critical for effective curing with the hydroxyl coreactant. The findings of testing on the solubility of blocked isocyanate adduct and pre-polymers in three different polyols can be seen in Table-4. Because the blocked isocyanates are derived from aliphatic diisocyanate, all of the adducts and pre-polymers are readily soluble in all three polyols at about 65 ºC. Poly(tetrahydrofuran)diol was the most soluble of the three polyols tested.



Scheme-V: Cure reaction of blocked isocyanate pre-polymers with poly(tetrahydrofuran)diol

TABLE-3
RELATIVE VISCOSITY AND CURE TIME STUDIES OF PHENOL BLOCKED HDI

Sample code	Blocked isocyanates	Cure time (min)	Relative viscosity (η_r)
BIA-1	Phenol	360	1.04
BIA-2	4-Methoxyphenol	420	1.03
BIA-3	Methyl-4-hydroxyphenol	390	1.03
BPI-1	Phenol	300	1.02
BPI-2	4-Methoxyphenol	390	1.04
BPI-3	Methyl-4-hydroxyphenol	330	1.03

TABLE-4
DISSOLUTION TEMPERATURE OF THE PHENOL BLOCKED HDI IN POLYOLS

Sample code	Blocked isocyanates	Dissolution temperature (°C)		
		PTD	PEG 4000	PEG 6000
BIA-1	Phenol	50	65	65
BIA-2	4-Methoxyphenol	50	65	65
BIA-3	Methyl-4-hydroxyphenol	60	70	65
BPI-1	Phenol	50	65	65
BPI-2	4-Methoxyphenol	50	65	65
BPI-3	Methyl-4-hydroxyphenol	55	65	65

PTD = Poly(tetrahydrofuran)diol

Preparation of epoxy-polyurethane film: Epoxyamine resin cured with several blocked isocyanates at 160 ºC to produce epoxy-polyurethane films. The formulation of each blocked isocyanate (BI) based epoxy-polyurethane films are shown in Table-5.The cure reaction between blocked isocyanates and epoxy resin was confirmed using AT-IR, TGA and DSC studies. A typical AT-IR spectra of a blocked isocyanate based epoxy-polyurethane films are shown in Fig. 7. Appearance of new peak at 1650 cm^{-1} corresponds to the urea carbonyl group of epoxy-polyurethane film confirmed the reaction between epoxyamine resin and regenerated isocyanate. Fig. 8 depicts the DSC thermal analysis for the epoxyamine resin with blocked isocyanates and Table-6 shows the temperature at which change in endothermic peak occurred. The inclusion of aliphatic blocked

TABLE-5
FORMULATION FOR THE PREPARATION OF BLOCKED ISOCYANATE BASED EPOXY-POLYURETHANE FILM

Polyamine (equiv)	Epoxy resin (equiv)	Content of blocked isocyanate (equiv)
1	1.00	–
1	0.95	0.05
1	0.85	0.15

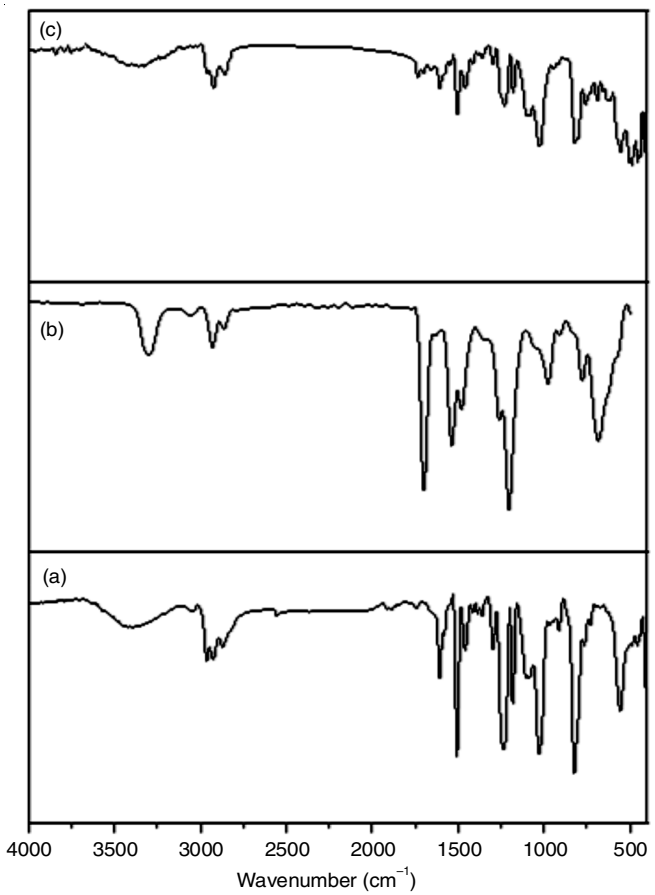


Fig. 7. AT-IR spectrum of (a) epoxy; (b) BIA-1 based epoxy-polyurethane films and (c) BPI-1 based epoxy-polyurethane films

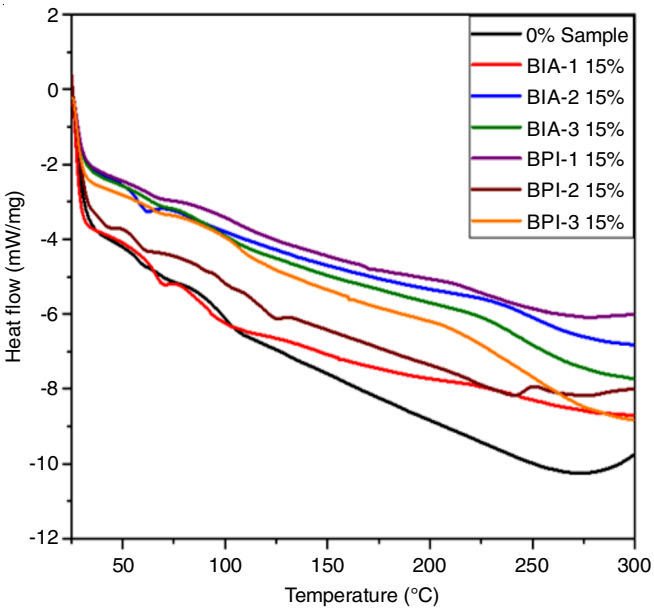


Fig. 8. DSC thermograms of epoxy and blocked isocyanate (BI) based epoxy-polyurethane films

TABLE-6
THERMAL STABILITY OF 15 wt.% CONTENT OF BLOCKED ISOCYANATE BASED EPOXY-POLYURETHANE FILMS

Sample code	TGA		DSC
	Temp. (°C)	Remaining mass (%)	T_g (°C)
Pure	331.2	14.3	96.0
BIA-1	317.9	13.0	85.6
BIA-2	321.3	10.0	80.2
BIA-3	321.0	10.2	86.1
BPI-1	324.0	12.1	94.6
BPI-2	326.1	10.2	93.7
BPI-3	318.0	12.6	94.3

isocyanates in the epoxy films lowered the endothermic glass transition temperature (T_g) from 960 ºC to 80.2 ºC, indicating that the flexible polyurethane was incorporated to epoxy film. TG analysis shows that thermal stability of epoxy-polyurethane is almost similar to epoxy films. TGA data is given in Table-6 and TGA curves are shown in Fig. 9.

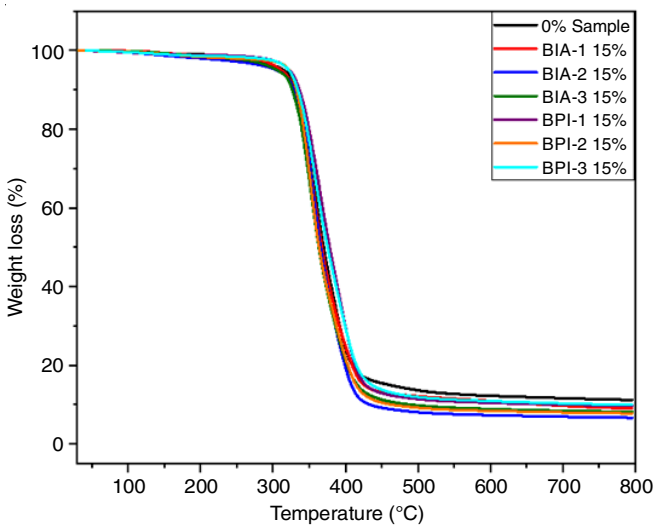


Fig. 9. TG curves of epoxy and blocked isocyanate (BI) based epoxy-polyurethane films

Contact angle analysis: The contact angle value of epoxy film was 59.2º. The result shows that hydrophobicity slightly increases for the epoxy-polyurethane films synthesized from blocked isocyanates adducts as well as polyisocyanates compared to epoxy films. Fig. 10 shows the images of water droplets to measure contact angles of epoxy and polyurethanes.

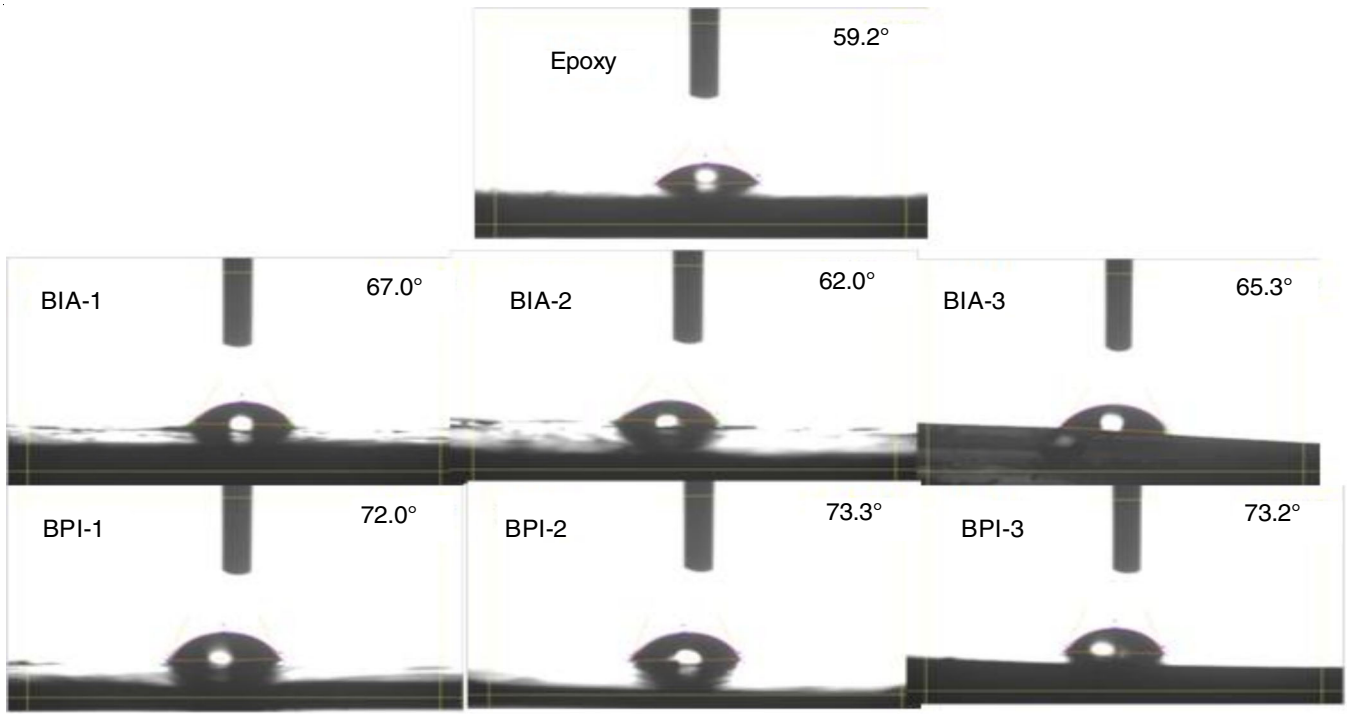


Fig. 10. Contact angle measurements for epoxy and blocked isocyanate (BI) based epoxy-polyurethane films

TABLE-7
MECHANICAL PROPERTIES OF BLOCKED ISOCYANATE BASED EPOXY-POLYURETHANE FILM

Sample code	0.05 eq of Blocked isocyanate			0.15 eq of Blocked isocyanate		
	Tensile strength (MPa)	Flexural strength (MPa)	Shore A hardness	Tensile strength (MPa)	Flexural strength (MPa)	Shore A hardness
Pure	29.6	2.436	96	29.6	2.436	96
BIA-1	13.6	1.254	93	9.1	0.802	92
BIA-2	11.2	1.000	91	7.1	0.700	91
BIA-3	10.9	1.750	93	7.1	1.320	92
BPI-1	15.3	1.410	92	10.5	0.929	94
BPI-2	19.0	2.056	93	15.1	1.209	95
BPI-3	17.4	1.000	94	14.1	0.752	94

Mechanical property: Mechanical characteristics of new epoxy-polyurethane films were carried out, to assess the commercial viability of low temperature heat curing systems. The tensile and flexural strength of epoxy-polyurethane films are given in Table-7. Tensile and flexural strength of epoxy-polyurethane with different blocked isocyanate content are shown in Figs. 11-13. Due to the presence of the soft hexamethylene and terathane segment in blocked isocyanates, the integration of blocked isocyanate content leads to slightly decrease in mechanical strength as expected. Blocked polyisocyanates based epoxy films have higher mechanical strength than blocked isocyanate adducts. Among the blocked isocyanates used, BPI-2 found to have better tensile and flexural strength. The hardness of blocked isocyanate based epoxy film is tested by shore A hardness and the findings show that the films hardness ranging from 95 to 91 (Table-7), which are close to pure epoxy film.

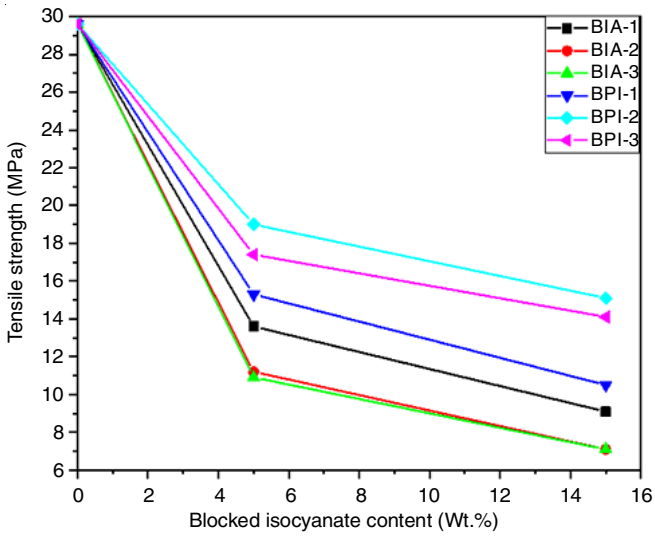


Fig. 11. Tensile strength of blocked isocyanate (BI) based epoxy-polyurethane films

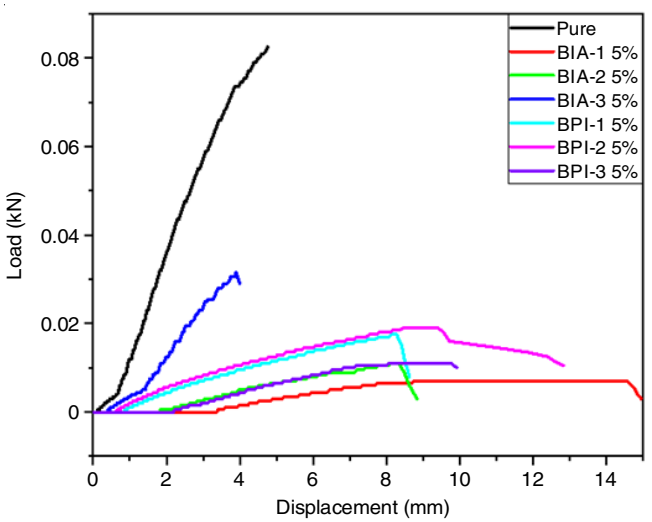


Fig. 12. Flexural strength of 5 wt% content of blocked isocyanate (BI) based epoxy-polyurethane films

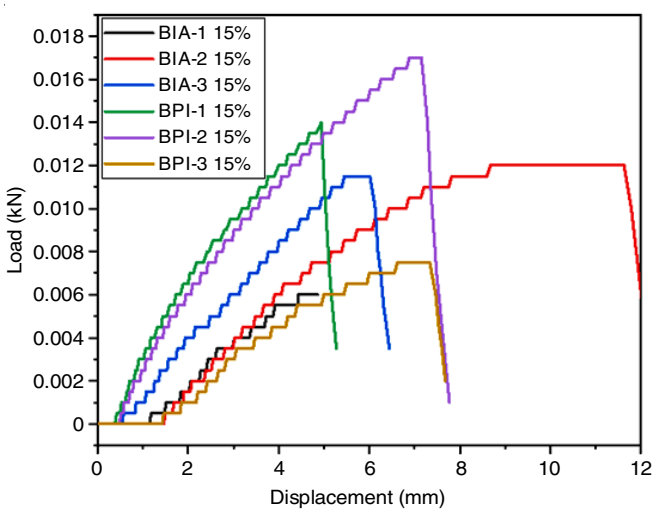


Fig. 13. Flexural strength of 15 wt% content of blocked isocyanate (BI) based epoxy-polyurethane films

Conclusion

In present study, phenol blocked aliphatic isocyanate adducts and polyisocyanates were prepared and the structure was confirmed using FTIR, ^{1}H & ^{13}C NMR spectroscopy. Deblocking temperatures, curing performance and solubility behavior of blocked isocyanates were investigated. The deblocking temperatures of blocked isocyanates were determined by TGA, DSC and CO_2 evolution methods. Epoxy-polyurethane films were produced using these blocked isocyanates and characterized by AT-IR, contact angle measurement, DSC and TGA. Thermal stability of epoxy-polyurethane is almost close to epoxy films, whereas, hydrophobic property is better for epoxy-polyurethane than epoxy films. Mechanical properties of blocked polyisocyanates based films are found to be better compare to blocked isocyanate adducts. The blocked isocyanates

reported here are potential curing agents for heat curable epoxy-polyurethane films.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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