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ORIGINAL RESEARCH ARTICLE

Synthesis and curing studies of blocked isocyanate based prepolymer

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ABSTRACT

Prepolymers containing isocyanates must be prevented from curing when exposed to moisture, which can be achieved by blocking the isocyanate groups with a suitable agent. The study carefully examines several blocking agents, including methyl ethyl ketoxime (MEKO), caprolactam, and phenol, and concludes that methyl ethyl ketoxime is the best choice. Spectroscopic and thermal analyses, as well as oven curing studies, are conducted with various blocking agents and isocyanate prepolymer to castor oil ratios, revealing MEKO to be the most effective blocking agent which gets unblocked at higher temperatures.

Keywords: isocyanate; prepolymer; blocking agents; MEKO; caprolactam

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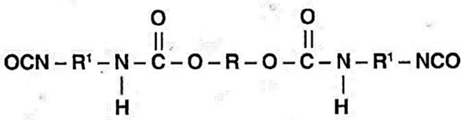
1. Introduction

Isocyanate is a very important raw material in the manufacturing of polyurethanes. One of the common methods of polyurethane synthesis is via the prepolymer route. The polyols, polymers consisting of multiple hydroxyl groups, are reacted with appropriate isocyanates (in excess) to yield an intermediate polyurethane precursor, which in turn, when reacted with a chain extender or crosslinker, yields polyurethane. Polyurethane precursors are termed isocyanate-terminated polyurethane prepolymers. The typical isocyanate-terminated prepolymer may be represented in **Figure 1**. Working with isocyanate-terminated prepolymers is highly challenging because of the reactivity of isocyanate with moisture, which leads to premature curing.

Blocking of the prepolymer helps to control the reactivity of isocyanates, allowing for easier handling and storage.

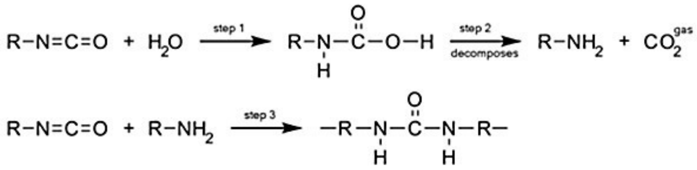


$$\mathrm{OCN-R'-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-R-O-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-R'-NCO}$$

Figure 1. Structure of isocyanate-terminated prepolymer.

Isocyanate-terminated pre-polymers are synthesized by the reaction between an excess of polymeric isocyanates like MDI or TDI and polyol at a temperature between 60 °C–90 °C in the presence or without a gelling catalyst, such as dibutyltin dilaurate. By varying the stoichiometric ratio of poly isocyanates with respect to polyol, a prepolymer with the desired isocyanate content and average molecular weight can be synthesized. The isocyanate content of the prepared prepolymer typically varies from 5 to 25 wt%.

Isocyanates are well known for their electrophilic nature of reaction. They have a strong affinity for electron-rich species such as alcohols, amines, water, etc. When isocyanates react with alcohols, a fascinating chemical transformation takes place. The oxygen atom in the alcohol molecule acts as a nucleophile and attacks the carbon atom of the isocyanate group. This leads to the formation of a new bond between carbon and oxygen, resulting in the creation of a urethane linkage. Isocyanates also react vigorously with water to form carbon dioxide and amine (intermediate products), and they further react with isocyanate to yield urea (**Scheme 1**). This property of isocyanates makes the storage of NCO-terminated prepolymers challenging and results in viscosity buildup issues, thereby creating processing difficulties. A possible solution for this problem is restricting the activity of the NCO group, i.e., capping or blocking the terminal NCO group with blocking agents.



$$R{-}N{=}C{=}O + H_2O \xrightarrow{\text{step 1}} R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H \xrightarrow[\text{decomposes}]{\text{step 2}} R{-}NH_2 + CO_2^{\text{gas}}$$

$$R{-}N{=}C{=}O + R{-}NH_2 \xrightarrow{\text{step 3}} {-}R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{N}{-}R{-}$$

Scheme 1. Reaction of –NCO– with water.

Blocking agents are compounds that inhibit the activity of isocyanates temporarily, thus preventing reactions with other compounds until desired conditions are achieved. Blocking of the isocyanate group also helps in increasing the shelf life of the prepolymer. By carefully controlling temperature, pH levels, or exposing blocked isocyanate prepolymers to certain catalysts, these blocked functional groups can be deblocked and reactivated for subsequent reactions when needed. Commonly identified isocyanate (NCO)) blocking agents comprise phenol, alcohols, ε-caprolactam Nonylphenol, amides, pyrazoles, methyl ethyl ketoxime (MEKO), imidazole, etc.

The terminal isocyanate functional group in the synthesized prepolymer is masked with a suitable blocking agent, which subsequently results in a compound that is preferably inert at room temperature. However, blocked prepolymers are generated at elevated temperatures. The mechanism of the blocking/unblocking process is given in **Figure 2**[1].

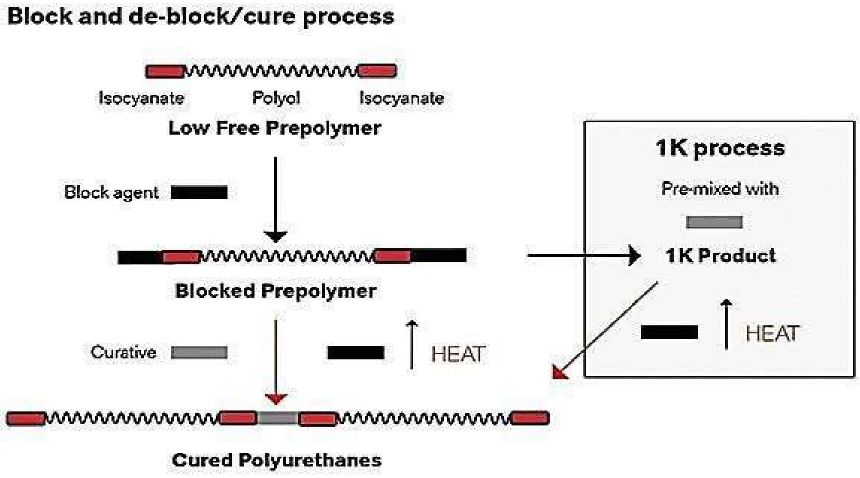


Figure 2. Blocking and deblocking process[1].

Aromatic blocked isocyanates undergo de-blocking at comparatively lower temperatures than aliphatic blocked isocyanates owing to the steric and electronic effects[2]. The chemical functional group of the blocking agent affects the de-blocking temperature. Electron-contributing groups fortify the bond, while electron-recessing substituents decrease the bond, resulting in a low de-block temperature. The de-blocking temperature is heavily impacted by the chemical functional group of the blocking agent. It is imperative to note that electron-contributing groups reinforce the bond, whereas electron-recessing substituents weaken the bond, leading to a lower de-block temperature.

Mühlebach[3] found that pyrazoles are a novel class of blocking agents that can be fine-tuned for reactivity and have good adhesion properties. Lee et al.[2] studied the thermal decomposition behavior of blocked diisocyanates derived from a mixture of blocking agents and found that the de-blocking temperature of blocked aromatic isocyanates was lower than that of blocked aliphatic isocyanates. Wicks and Wicks[4] provided an overview of the challenges of blocked isocyanates in coatings, including the structures of the isocyanate and blocking agent, the thermal stability of the isocyanate-blocking agent bond, the polarity of the reaction media, the nucleophilicity of the blocking agent vs. the co-reactant, the ability of the blocking agent to diffuse out of the film, and catalysis. Kalaimani et al.[5] found that phenols with higher acidity were more effective blocking agents, resulting in lower de-blocking temperatures. Mühlebach[3] proposed pyrazoles as a novel class of blocking agents that have good reactivity, latency, and adhesion properties. Lee et al.[2] found that the de-blocking temperature of blocked aromatic isocyanates was lower than that of blocked aliphatic isocyanates. Zhang et al.[6] investigated the use of sodium bisulfite as a blocking agent and found that it effectively blocked isocyanates and resulted in a lower de-blocking temperature compared to other blocking agents.

Jana et al.[7] synthesized polyurethanes by blocking and deblocking diisocyanates using 3-(-4-bromo-phenyl)-H-pyrazole as the blocking agent. Spectroscopic techniques confirmed the structure of the blocked TDI and the resulting polyurethanes. The deblocking and polyurethane formation were performed under solvent-free conditions. The study found that the TGA thermogram showed that blocked TDI was stable up to 166 °C, and the polyurethanes were stable up to 200 °C and 240 °C. The DSC thermogram showed that the blocked TDI deblocks at 240 °C. The polyurethane from polyethylene glycol had a better yield than the polyurethane from polypropylene glycol, with the gel time increasing as the molecular weight of the polyol increased. Libni et al.[8] studied the catalysis of the reaction between ε-caprolactam-blocked polyisocyanate and a diol in the presence of non-tin catalysts. They used bismuth neodecanoate, calcium (II) 2-ethylhexanoate, zinc (II) 2-ethylhexanoate, tin (II) 2-ethylhexanoate, and DABCO as catalysts. They found that all the catalysts except for DABCO exhibited catalytic activity. However, bismuth neodecanoate acted differently from the other catalysts. It catalyzed the cure reaction, piloting the formation of polyurethane at the initial stage, but was found to support the degradation of urethane groups at future stages.

Petrak et al.[9] investigated the deblocking of blocked isocyanates in the presence of amino-type resins. They studied the deblocking of phenyl isocyanate blocked with pyrazole and oxime in the presence of different urea compounds and catalysts. Zirconium (IV) dionate was found to be a promising catalyst for industrial applications as it lowered the deblocking temperature from 144 °C to 100 °C. Kalaimani et al.[5] studied the preparation of blocked poly isocyanates using easily cleavable phenols such as 2-chloro-4-nitrophenol, 2,4-dichlorophenol, and 2-chloro-4-ester phenol as blocking agents. The deblocking and cure studies were conducted without a solvent. The forward and reverse reaction rates were proportional to the acidity of the blocking agent, except for 2-chloro-4-nitrophenol, which deblocked the isocyanate slowly despite its high acidity.

In this study, blocked isocyanate-terminated prepolymers were synthesized using MEKO and caprolactam blocking agents and characterized. The curing of the prepolymer with castor oil as the curing agent was also evaluated using differential scanning calorimetry.

2. Experimental

2.1. Materials

Polyester polyol with a viscosity of 2–9 Pas at 30 °C and a hydroxyl value of 40–60 mg of KOH/g has been developed at VSSC, Trivandrum. Toluene diisocyanate (TDI) with 98% purity, castor oil, and blocking agents, methyl ethyl ketoxime and caprolactam, were procured from M/s Chemporium and M/s Sigma Aldrich. DBTDL, a catalyst with a tin content of 18%–18.6%, was obtained from M/s Alfa Aesar.

2.2. Methods

2.2.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were taken by means of a Thermo Scientific iS50 Nicolet FTIR Spectrometer (spectral range: 15 to 27,000 cm^{-1}).

2.2.2. Differential scanning calorimetry (DSC) (instrument: 2920 DSC V2.4F)

Differential scanning calorimetry (DSC) tests were performed by mixing approximately 5 mg of blocked prepolymer and curing agent in different ratios in aluminum crucibles under an inert nitrogen atmosphere.

2.2.3. Thermogravimetric analysis (TGA) (instrument: 2960 SDT V3.0F)

The thermal stability of the samples is tested in a thermogravimetric analyzer, which records the change in weight of the sample with respect to temperature.

2.2.4. Isocyanate content

A known quantity of sample is reacted with an excess of n-butyl amine in toluene. The solution is then mixed with IPA and titrated with hydrochloric acid using a bromophenol blue indicator to determine the endpoint. A blank determination is also conducted.

$$\text{NCO content} = \frac{(B - V)xNx42}{Wx10} \tag{1}$$

where:

B—volume of the HCl consumed by blank,
V—volume of HCl consumed by sample,
N—normality of HCl,
W—weight of sample in g.

3. Synthesis of blocked isocyanate prepolymer

The preparation of blocked isocyanates requires two steps:

Step 1: Preparation of an isocyanate-terminated prepolymer.

Step 2: Block the NCO groups in the prepolymer using a suitable blocking agent.

3.1. Prepolymer preparation

The synthesis of NCO-terminated prepolymers is conducted in a round-bottom flask equipped with a heating mantle, a mechanical stirrer, nitrogen purging, and a degassing unit. NCO-terminated prepolymers with NCO content in the range of 4%–6% are prepared by reacting adipate-based polyester polyol with toluene diisocyanate (TDI) in excess in a round bottom flask. Reactions are conducted in an inert nitrogen atmosphere to prevent undesirable side reactions. The mixture is heated to a temperature range of 75–80 °C for 2 h and then degassed for 1 h to remove any residual moisture or volatiles. The synthesized NCO content of isocyanate-terminated prepolymers is 5%–6%.

3.2. Blocking of prepolymer

Studies were conducted using two blocking agents in the present work: methyl ethyl ketoxime (MEKO) and caprolactam. For synthesizing blocked prepolymer, 500 g of prepolymer is mixed with a stoichiometric equivalent amount of MEKO/caprolactam (ratio 1:1). The mixture is heated for two hours at 75 °C under vacuum, and the reduction in NCO content is noted. The NCO content has reduced from 5.58% to 0.17%, which indicates that effective blocking of terminated NCO has occurred.

4. Curing with castor oil

4.1. Without gelling catalyst

The MEKO/caprolactam-blocked prepolymer is mixed with castor oil with an isocyanate index of 1:1.2. The blocked prepolymer-castor oil mixture is thoroughly hand-mixed for 20 min and transferred to a petri dish. The mixture is heated to 180 °C under vacuum. The curing of the sample is checked visually.

The blocked prepolymer sample, both MEKO-blocked and caprolactam-blocked prepolymers, is analyzed for FTIR, DSC, and TGA.

4.2. With gelling catalyst

Dibutyl tin dilaurate is the gelling catalyst used. MEKO/caprolactam-blocked prepolymer is mixed with castor oil with an isocyanate index of 1.2, and to this, 0.2 g of DBTDL is added and mixed thoroughly for 20 min. It is then transferred to a petri dish. The mixture is heated at 180 °C under vacuum, and curing is done.

Blocked prepolymers are analyzed for DSC.

5. Results and discussion

5.1. NCO content

The NCO content of polyester based prepolymer is found to be 5.58%. NC decrease of NCO content after blocking is depicted in **Table 1**.

Table 1. NCO content of synthesized blocked isocyanate prepolymer.

Blocking agent used	NCO content before blocking	NCO content after blocking
MEKO	5.58%	0.17%–2%
Caprolactam	5.58%	0.18%–2%

The NCO content of both MEKO and caprolactam-blocked isocyanate was reduced drastically upon blocking. The NCO content got reduced by more than 90% in both cases. This shows both MEKO and caprolactam are good candidates to be used as blocking agents for isocyanate-terminated prepolymers. At least three sets of experiments were conducted to ensure repeatability in each case.

However, it is to be noted that a decrease in percentage NCO after blocking cannot be the sole criteria for the selection of a blocking agent. The deblocking temperature is also to be investigated to arrive at an economical and viable option.

5.2. Fourier transform infra-red spectroscopy

FTIR was done to confirm whether deblocking of NCO happened with MEKO and caprolactam. **Figure 3** shows the FTIR spectra of the isocyanate-terminated prepolymer. The characteristic peak at 2271 cm^{-1} indicates the presence of the NCO group. **Figures 4** and **5** show the FTIR spectra of MEKO and caprolactam-blocked prepolymers. In FTIR analysis of caprolactam-blocked prepolymers (**Figure 4**), the absence of the of the NCO characteristic peak at 2271 cm^{-1} indicates that the methyl ethyl ketoxime has effectively blocked the

NCO group of polyester-based prepolymers. Similarly, from **Figure 5**, the absence of the of the NCO characteristic peak at 2271 $\mathrm{cm^{-1}}$ indicates that MEKO also effectively blocked the NCO group of the polyester-based prepolymer.

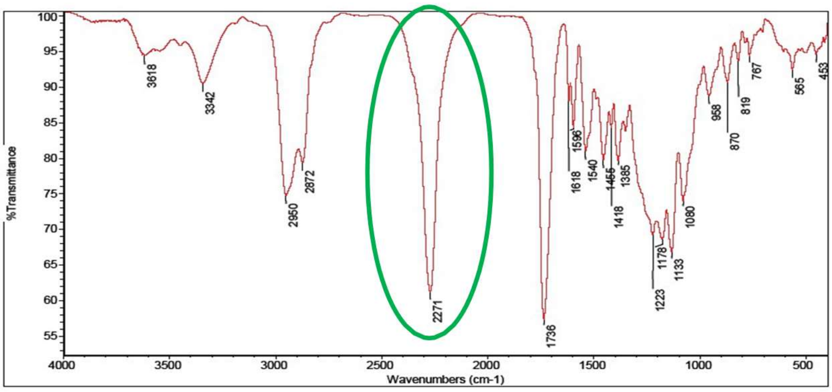


Figure 3. FTIR of isocyanate terminated prepolymer.

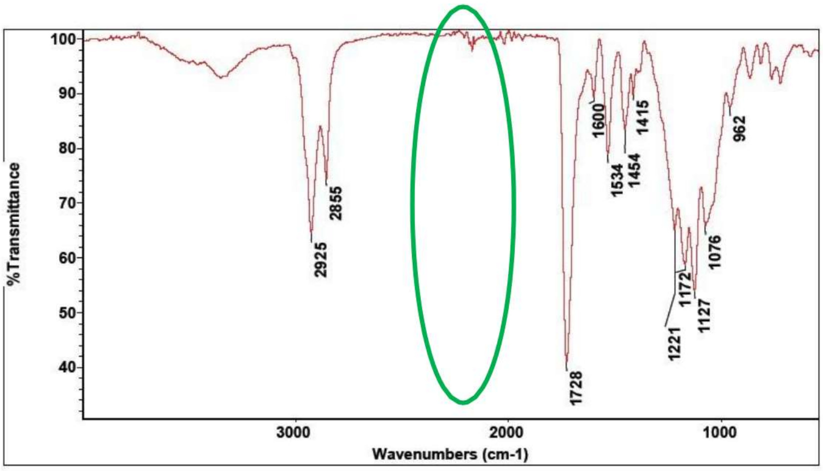


Figure 4. FTIR spectra of caprolactam based blocked prepolymer.

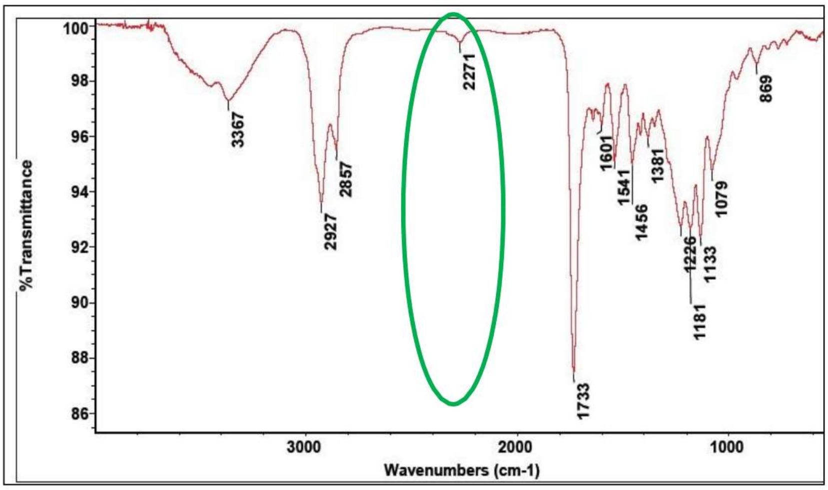


Figure 5. FTIR of MEKO blocked prepolymer.

In addition to the FTIR studies on the blocked prepolymer and base prepolymer, additional studies were carried out using FTIR to identify the deblocking temperature.

The sample is isothermally heated, and the FTIR spectrum is analyzed for the NCO peak at 2271 $\mathrm{cm^{-1}}$. It is observed that deblocking of MEKO starts at around 125 ℃ and complete deblocking occurs at 200 ℃. The FTIR plot (isothermal) carried out is as given in **Figure 6**.

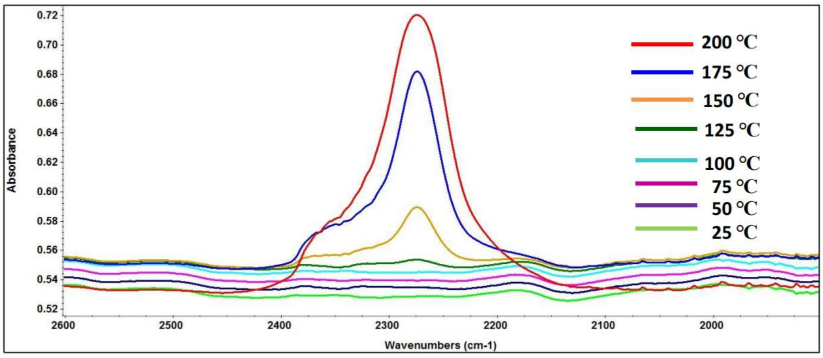


Figure 6. Deblocking of MEKO blocked prepolymer via FTIR temperature studies.

5.3. Differential scanning calorimetry

Curing studies of blocked prepolymers were done with and without catalysts using the DSC technique. The curing agent used is castor oil.

Studies carried out on MEKO-blocked prepolymers show that deblocking starts at 123.6 °C (**Figure 7**). At this temperature, the blocked NCO group is released and starts reacting with the hydroxyl group in castor oil. As the reaction of the isocyanate and hydroxyl groups is highly exothermic, the temperature is increased up to 184.9 °C and when the reaction is complete, the temperature is reduced.

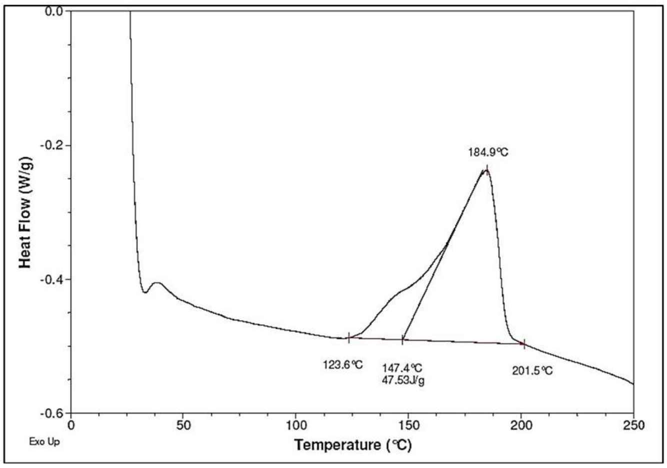


Figure 7. Deblocking of MEKO blocked prepolymer without DBTDL.

The use of DBTDL as catalyst in deblocking reaction shows difference in DSC pattern. When DBTDL is used, the deblocking temperature got reduced from 123.6 °C to 119.8 °C in MEKO blocked prepolymer (**Figure 8**).

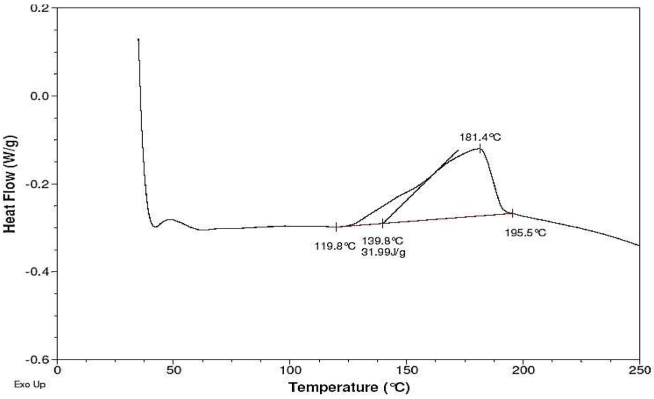


Figure 8. Deblocking of MEKO blocked prepolymer with DBTDL.

Similarly, DSC studies were carried out in caprolactam-blocked prepolymers as well. **Figure 9** shows that deblocking of NCO has not happened until 250 °C. But the deblocking may occur above 250 °C but due to instrumental constraints, studies were not conducted beyond 250 °C. Additionally, heating beyond 250 °C is not advisable for the polyurethane prepolymer, as degradation may be initiated. The use of DBTDL as a catalyst did not show any characteristic difference in the DSC pattern (**Figure 10**).

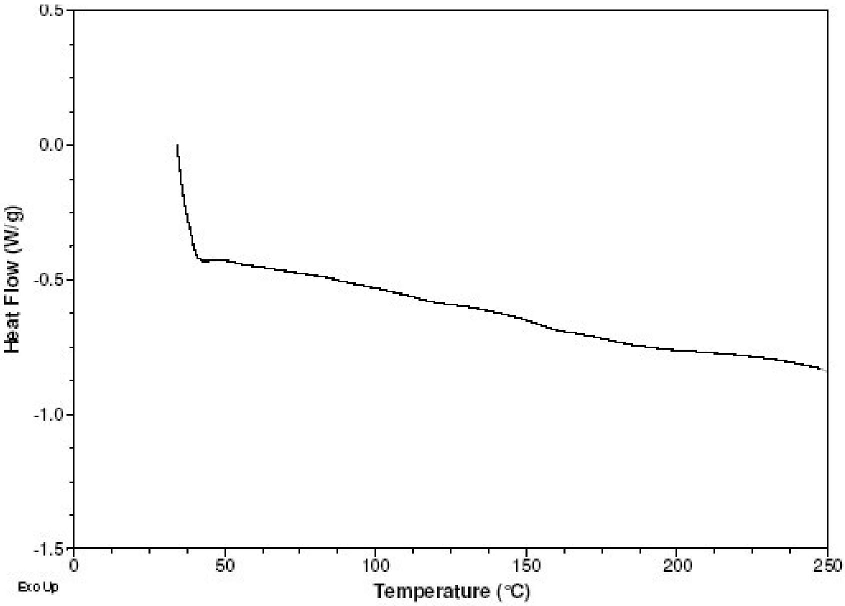


Figure 9. Deblocking of caprolactam blocked prepolymer.

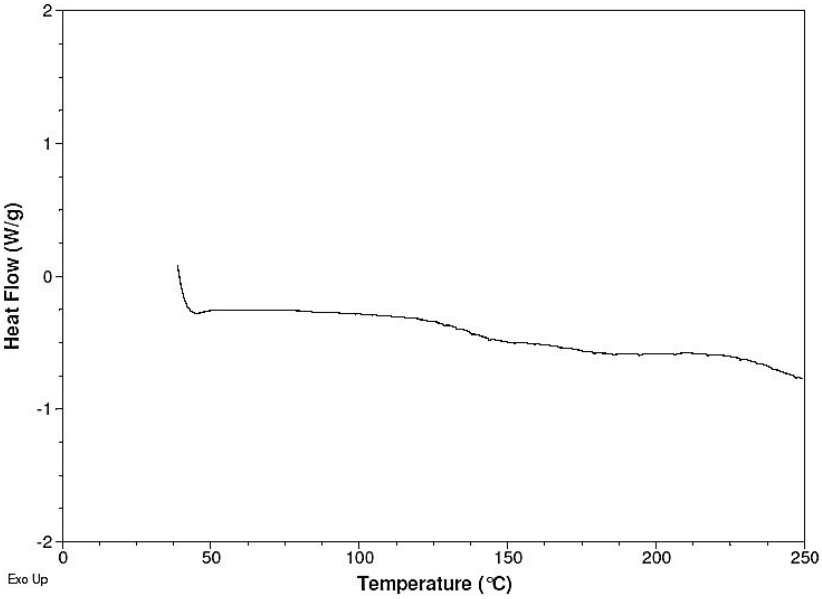


Figure 10. Deblocking of caprolactam blocked prepolymer with DBTDL.

5.4. Thermogravimetric analysis

TGA analysis was carried out for polyester prepolymers, MEKO-blocked prepolymers, and caprolactam blocked prepolymers. Samples were heated up to 900 °C with a heating rate of 10 °C/min under an atmosphere of air. TGA studies were done to study the deblocking temperature of MEKO and caprolactam. Thermogravimetric analysis of polyester polyol, MEKO-blocked prepolymer, and caprolactam-blocked prepolymer is given in **Figure 11**.

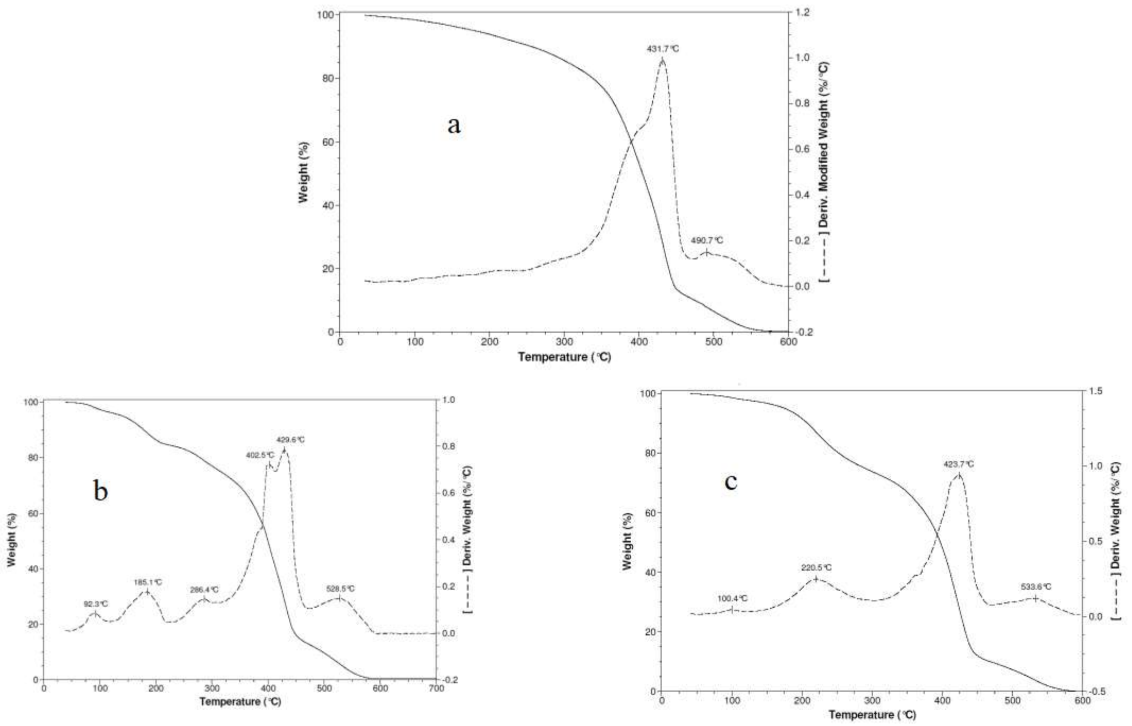


Figure 11. (a) thermogravimetric analysis of polyester prepolymer; **(b)** MEKO blocked prepolymer; and **(c)** caprolactam blocked prepolymer.

It was observed that first decomposition is observed in the range of 92 °C–100 °C for both the blocked prepolymers. This may be the release of moisture trapped in the system. However, the moisture peak is not visible in the unblocked sample, which confirms again that moisture available in the system is reacting with isocyanate present in the system.

Further decomposition of the unblocked prepolymer occurs beyond 430 °C. With respect to the blocked prepolymers, MEKO blocked and caprolactam blocked, the deblocking temperature was observed at 185 °C and 220 °C respectively. This emphasizes the observations noticed during FTIR and DSC analysis that MEKO has a higher deblocking temperature.

6. Conclusion

The synthesis of NCO-terminated prepolymers and the blocking studies of NCO-terminal groups were done using methyl ethyl ketoxime and caprolactam as blocking agents and castor oil as curing agent. FTIR and NCO content analysis confirm the blocking capability of MEKO and caprolactam. NCO content analysis shows that there is a considerable reduction in NCO from 5.58% to 0.17%–0.18% which was further confirmed through FTIR analysis.

Curing studies through DSC confirmed that the deblocking temperature (123.6 °C) of MEKO-blocked prepolymers is lower than that of caprolactam-blocked prepolymers. This was confirmed via thermogravimetric analysis as well. The catalytic effect of DBTDL in the deblocking reaction was also established through DSC studies, as the addition of DBTDL reduced the deblocking temperature in MEKO-terminated prepolymers from 123.6 °C to 119.3 °C. The blocking of isocyanate-terminated prepolymers with MEKO and caprolactam helps in the prolonged storage of the isocyanate-terminated prepolymers.

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Conflict of interest

The authors declare no conflict of interest.

Abbreviations

DABCO:	Diazobicyclo octane
DBTDL:	Dibutyl tin dilaurate
DSC:	Differential scanning calorimetry
FTIR:	Fourier transform infra-red
IPA:	Isopropyl alcohol
MDI:	4,4’mthylene diphenyl diisocyanate
MEKO:	Methyl ethyl ketoxime
TDI:	Toluene diioscyanate
TGA:	Thermogravimetric analysis

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