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Catalysis of *N*-Methylaniline-Blocked Polyisocyanate-Hydroxyl-Terminated Polybutadiene Cure Reaction

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Catalysis of cure reaction between *N*-methylaniline-blocked polyisocyanate and hydroxyl-terminated polybutadiene was investigated using a variety of tertiary amine and organotin catalysts. The catalytic activity of amine and organotin compounds was determined from the cure-time results. It was found that the activity of the catalyst depends upon the steric constrain around the catalytic center. The organotin compounds showed higher catalytic activity than the amine catalysts. FTIR results obtained under isothermal condition revealed that DABCO selectively catalyze the urethane formation reaction, whereas DBTDL catalyze both the allophanate formation and urethane formation reactions during curing process. The synergistic effect of amine and organotin mixed catalysts on the cure reaction was also investigated.

Keywords: *N*-methylaniline-blocked polyisocyanate; hydroxyl-terminated polybutadiene; cure reaction; amine catalysis; tin catalysis; hot-stage FTIR; synergistic effect

1. Introduction

Polyurethanes are a very large and varied family of incredibly versatile and useful engineering materials. They can be prepared in different forms like elastomers, coatings, adhesives, binders, sealants and foams. Polyurethanes can be tailored by chemistry and processing to produce products in a vast array of applications. Commercially manufactured polyurethanes are prepared from diisocyanates or polyisocyanates and polyfunctional hydroxyl compounds.

Hydroxyl-terminated polybutadiene (HTPB) is a commonly used dihydroxyl compound in the polyurethane industry, because its high reactivity towards isocyanate, it makes it possible to produce sealants and waterproofing membranes with excellent hydrophobic properties. Resistance of HTPB in water is excellent and surpasses most other resins.

HTPB is referred to as a workhorse binder used in solid propellants (1) and in rocket motor case (2). The polybutadiene chain gives a higher energy value and good mechanical properties. HTPB is used to bind the fuel and oxidizer into a solid mass for solid rocket motors. Unsaturation in the HTPB backbone is responsive to oxidative crosslinking, thus, together with nitrous oxide as the oxidizer, it is used to power the rocket motor. Cured HTPB has tough, rubbery properties, which are prime requirements for modern propellants. The very efficient isocyanate-alcohol reaction (urethane formation reaction) is used for curing HTPB. The main problem associated with HTPB is the high reactivity of the primary hydroxyl groups to isocyanate group, and hence, suffers from a short pot-life. This problem may be overcome by the use of a blocked polyisocyanate crosslinker instead of isocyanate as such. The concept of blocked isocyanate can be better understood from Figure 1.

Blocked polyisocyanates have many advantages in the polyureathane industry. They permit the formulations of stable one package polyurethane systems. They eliminate the toxicity associated with isocyanates and moisture sensitivity is completely reduced.

Phenols are the important blocking agents for isocyanates and are widely used in industrial processes (3–6). Other documented blocking agents include oximes, amides, imides, imidazoles, amidines and related compounds, pyrazoles, 1,2,4-triazoles, hydroxamic acid esters, and active methylene compounds (3–11). The author has studied the thermal dissociation of phenol-blocked isocyanate crosslinkers (12–15) and investigated the effect of the catalysts on the cure reaction between phenol-blocked isocyanate with HTPB (16). Recently, we have reported thermal dissociation of *N*-methylaniline-blocked polyisocyanates (17) and we found that the *N*-methylaniline is the potent blocking agent for the isocyanates and hence, we intended to study the effect of catalysts on the cure reaction between *N*-methylaniline-blocked polyisocyanate with HTPB. A wide

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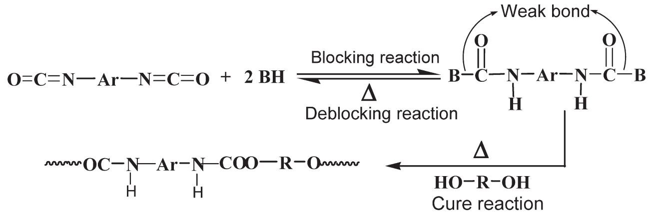


Where BH is the blocking agent.

Fig. 1. Concept of blocked isocyanate.

spectrum of compounds are disclosed as catalysts for the reaction of isocyanate with alcohols (3). Though, several reports are available on the catalysis of isocyanate-alcohol reaction, the reports on the catalysis of blocked isocyanates-alcohol cure reactions are very meager (16, 18). The effect of catalyst on the cure reaction of *N*-methylaniline-blocked isocyanate with HTPB has not been reported. The aim of the present report is to study the catalytic activity of some amine and tin compounds and synergistic effect of amine and tin mixed compounds on *N*-methylaniline-blocked isocyanate-HTPB cure reaction.

2. Experimental

2.1 *Materials*

The preparative method for *N*-methylaniline-blocked polyisocyanate was described in our previous report (17). Hydroxyl terminated polybutadiene (HTPB) (average molecular weight = 2500) obtained from Vikram Sarabhai Space Center was used after drying for 2 h at 80°C *in vacuo*. Dibutyltindilaurate (DBTDL) (Aldrich), dibutyltindiacetate (DBTDA) (Aldrich), stannous-2-ethylhexanoate (Aldrich), diethylcyclohexylamine (DECHA) (Sigma), tributylamine (Fluka), tribenzylamine (Fluka), ethyl-2-pyridylaacetate (Sigma), *N,N*-dimethyl-p-toludene (Sigma) and 1,4-diazobicyclo(2,2,2)octane (DABCO) (Sigma) were used as received.

2.2 *Cure-Time Studies*

In a typical experiment, 2.5 g (0.002 equiv.) of HTPB was taken in a beaker with 30 mm diameter. To this, 0.002 equiv. of *N*-methylaniline-blocked polyisocyanate and 2×10^{-4} moles of catalysts were added and mixed thoroughly. Then, the beakers were placed in an air-circulated oven maintained at 160°C. The beakers were inverted at regular time intervals to observe the flow behavior of the mixture. The time at which the mixture ceased to flow was taken as the cure-time. A duplicate experiment was conducted for each blocked polyisocyanate to ensure the accuracy of the data collected.

2.3 *FTIR Studies*

The effect of DBTDL and DABCO on the cure reaction of *N*-methylaniline-blocked polyisocyanate with HTPB was followed using a Thermo Mattson FTIR spectrophotometer equipped with hot-stage accessories and programmable temperature controller. In a typical experiment, a thin film of blocked polyisocyanate, HTPB and catalyst mixture prepared according to the proceeding section was cast onto a NaCl disc and was covered with an uncoated disc. Both discs were separated by a 0.5 mm lead spacer and placed in a heated transmission cell (HT-32, model 0019-200, Thermo Electron Corp., Madison, WI). The heated transmission cell was connected to a microprocessor-based programmable temperature controller (Omega CT-3251), which provided a constant heating rate for isothermal experiments. The experiment was carried out isothermally at 125°C. Initially, the sample was heated from ambient to 100°C for which the time set was 6 min and then the temperature was raised to 125°C for which the time set was only 2 min. The program was performed in the heating device in such a way that once the desired temperature was reached, the experiment proceeded isothermally. Spectra were recorded for the zero time immediately when the sample reached 125°C and then recorded for every 5 min. In order to monitor the cure reaction of blocked polyisocyanates, the urea carbonyl stretching at $1685\,\mathrm{cm}^{-1}$ was chosen. As reaction time increased, the absorption of the urea carbonyl of the blocked isocyanate group decreased due to cleavage of the blocked isocyanate group. The peak area of the urea carbonyl in each spectrum was calculated with OMNIC software (Thermo Nicolet) and considered equivalent to the concentration factor at a particular time t. The changes in film thickness were compensated by normalizing the urea absorbance band at $1685\,\mathrm{cm}^{-1}$, to an absorbance band (reference band) which remains constant during the course of the reaction. For this study, the absorbance band at $1108\,\mathrm{cm}^{-1}$ was used as reference band. The normalized degree of conversion of the cure reaction was calculated using the following equation.

$$x = 1 - \left[\frac{(\text{Peak area at 1685/peak area at 1108})_t}{(\text{Peak area at 1685/peak area at 1108})_{t=0}}\right]$$

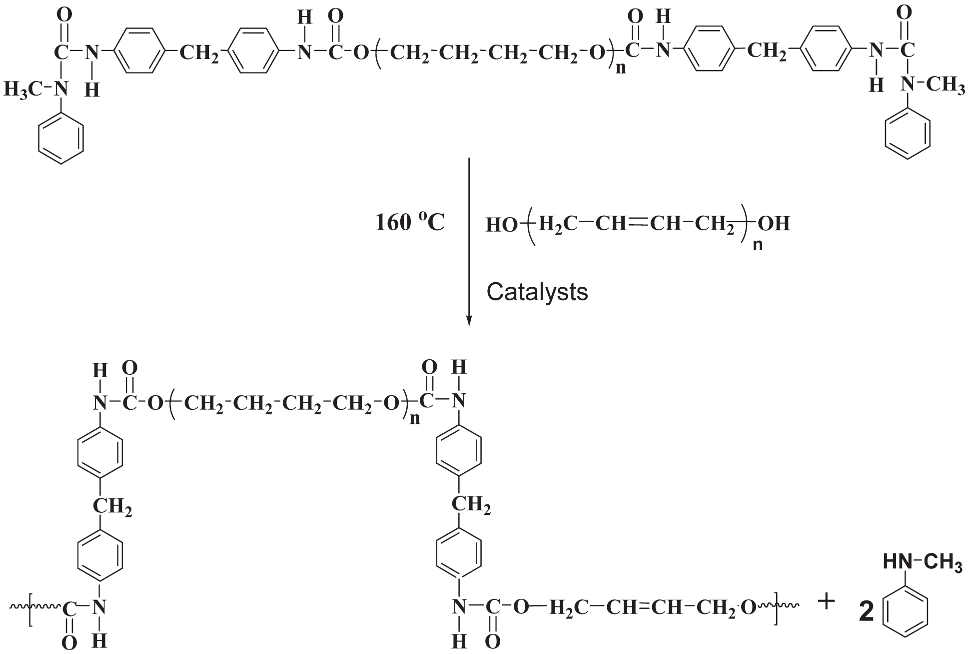
Where, t is the time of the cure reaction.

2.4 *Viscosity*

The relative viscosities (η_r) of the cured polymers were measured at a concentration of 0.1 g/dL in toluene at 30°C using an Ubbelohde viscometer.

3. Results and Discussions

The cure reaction of *N*-methylaniline-blocked polyisocyanate with HTPB is explained in Scheme 1. This cure reaction was catalyzed by two types of catalysts. The first type consists of six tertiary amines and the second type consists of three organotin compounds. Cure-time recorded for different



Sch. 1. Cure reaction of *N*-methylaniline-blocked polyisocyanate with HTPB.

amine catalyzed reactions are given in Table 1. Among six amines tried, DABCO showed highest catalytic activity. Considering a series containing DABCO, DECHA, tributyl amine and tribenzyl amine, the catalytic activity decreases with respect to increase in steric hindrance at the catalytic center. The lowest catalytic activity of ethyl-2-pyridyl acetate and *N,N*-dimethyl-p-toludene is due to low basicity of nitrogen atom.

Tertiary amine may abstract a proton from urea -NH or from -OH of HTPB. Since oxygen is more electronegative than nitrogen, the -OH proton is easily removable compared to -NH proton. Also the urea -NH proton of blocked isocyanate moiety is in association with the nitrogen atom of *N*-methylaniline via intra molecular hydrogen bonding (17). Thus, abstraction of a proton from -OH group of HTPB by tertiary amine is more favorable compared to abstraction from -NH group. Subsequently, the alkoxide anion formed will interact with the blocked isocyanate group. Accordingly, it is believed that the cure reaction proceeds through a addition-elimination (S_N2 type) mechanism and the proposed mechanism is given in Figure 2. According to this mechanism, the greater activity of DABCO is attributed to its less sterically hindered structures, making nitrogen more accessible to abstract the proton from hydroxyl group. The nitrogen atom is totally inaccessible in the tribenzylamine and hence showed very little catalytic activity.

Table 1. Catalysis of cure reaction of *N*-methylaniline-blocked polyisocyanate with HTPB at 160°C

Catalyst [2×10^{-4} M]	Cure time (minutes)	η_r
Nil	315	1.490
DABCO	110	1.495
DECHA	260	1.480
Tributylamine	280	1.475
Tribenzylamine	310	1.480
Ethyl-2-pyridylacetate	300	1.485
N,N-dimethyl-p-toludene	310	1.486
DBTDL	80	1.485
DBTDA	130	1.479
Stannous-2-ethylhexanoate	190	1.480

The cure reaction mechanisms proposed here could be substantiated with FTIR results. FTIR spectra recorded separately for blocked polyisocyanate and blocked polyisocyanate-HTPB mixture at 125°C are given in Figure 3. The spectra of blocked polyisocyanate showed an absorption band at 2270 cm^{-1} range due to regenerated -NCO group. Whereas, the blocked polyisocyanate-HTPB mixture does not showed any peak for -NCO group. This observation strongly supports the proposed addition-elimination mechanisms.

Cure-time recorded for *N*-methylaniline-blocked polyisocyanate with HTPB catalyzed by different organotin compounds are also given in Table 1. It is found that the catalytic activity decreases in the following order: DBTDL > DBTDA > stannous-2-ethylhexanoate.

The mechanism (Fig. 4) may involve the formation of a ternary complex through interaction between Sn, oxygen of alcohol and nitrogen of urea -NH group. Formation of such a ternary complex in urethane formation reaction has already been described by Kresta and co-workers (19) and followed by Tan and co-workers (20). In the present study, this type of interaction leads to regeneration of catalyst and

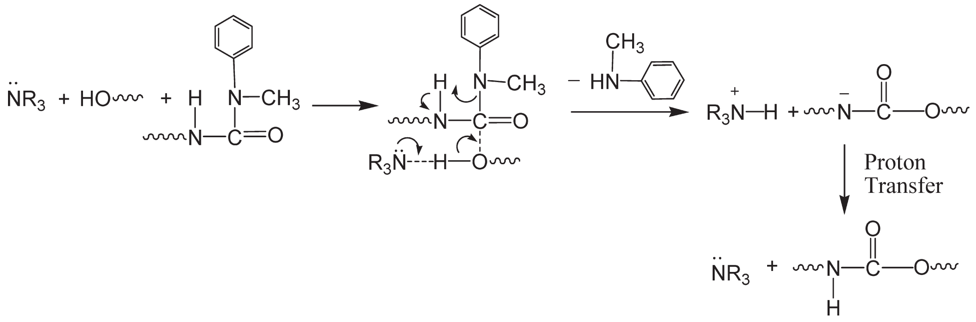


Fig. 2. Possible mechanism for amine catalyzed cure reaction of *N*-methylaniline-blocked polyisocyanate with polyol.

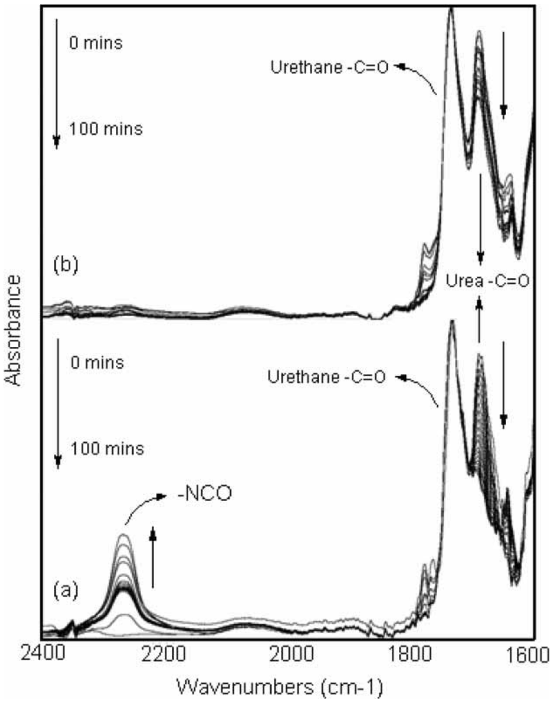


Fig. 3. FTIR spectra of (a) *N*-methylaniline-blocked polyisocyanate and (b) *N*-methylaniline-blocked polyisocyanate-HTPB mixture recorded at 125°C for different time intervals.

blocking agent. The cure-time results obtained are consistent with the mechanism given in Figure 4. During the course of the reaction, the acetate anion in DBTDA and laureate anion in DBTDL are replaced by the oxygen of HTPB and nitrogen of blocked isocyanate moiety. Since laureate anion is a better leaving group than the acetate anion due to structural reasons, the laureate anion is easily replaceable and hence showed higher catalytic activity than DBTDA. The lower activity of stannous-2-ethylhexanoate than of DBTDA and DBTDL may be due to more electronegative character of the Sn^{2+} ion than the Sn^{4+} ion.

The conversion (disappearance of carbonyl group of blocked isocyanate moiety) data plotted against time for the uncatalyzed, DABCO and DBTDL catalyzed cure reactions are given in Figure 5. Both the cure-time results and the conversion curves clearly indicate that the organotin compound is more efficient than the amine. Contour maps were derived from FTIR spectra recorded for different time intervals at 125°C for uncatalyzed, DABCO and DBTDL catalyzed cure reactions and the carbonyl region of the map of uncatalyzed and DABCO catalyzed reaction showed two kinds of carbonyl peaks at 1690 cm^{-1} and 1700 to 1725 cm^{-1} range due to urea carbonyl (blocked isocyanate moiety) and urethane carbonyl, respectively. Whereas, the map of DBTDL catalyzed reaction show an additional peak at 1647 cm^{-1} which is due to the formation of allophanate group. From these results, it can be concluded that the DBTDL catalyze crosslinking reaction such as allophanate formation during the cure process and DABCO is found to catalyze only cure reaction (urethane formation). Considering industrial application of blocked isocyanates, their cure-time with co-reactant is very important. Cure-time can be reduced by increasing the cure temperature and the use of efficient catalyst. Amount of catalyst will

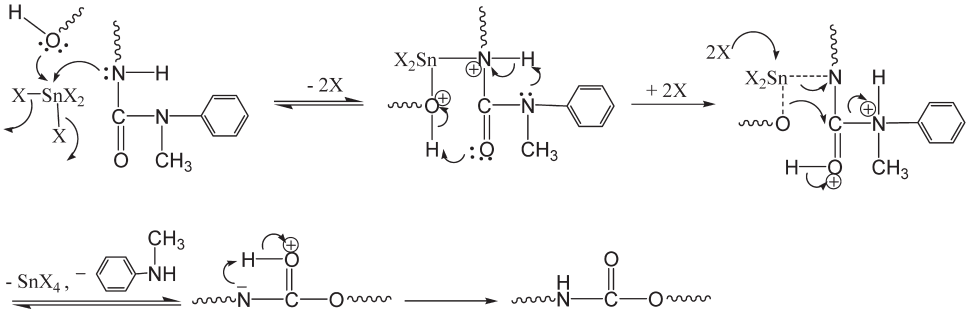


Fig. 4. Possible mechanism for a organotin catalyzed cure reaction of *N*-methylaniline-blocked polyisocyanate with polyol.

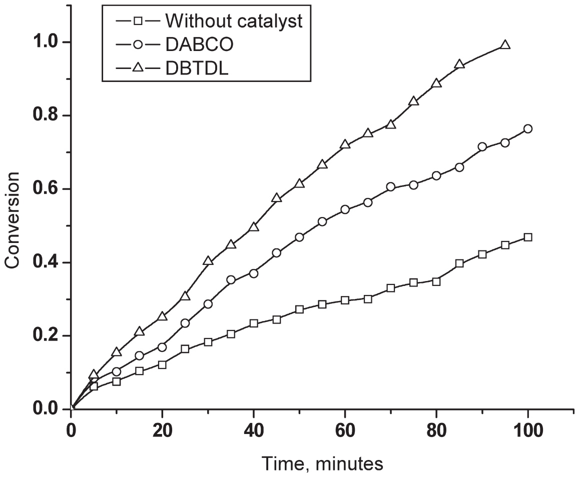


Fig. 5. Conversion curves of cure reaction of *N*-methylaniline-blocked polyisocyanate with HTPB at 125°C.

Table 2. Effect of catalyst concentration on cure reaction of *N*-methylaniline-blocked polyisocyanate with HTPB at 160°C

DBTDL [M]	Cure time (minutes)	η_r
1×10^{-4}	115	1.495
3×10^{-4}	73	1.490
4×10^{-4}	65	1.480

also affect the cure-time. The effect of catalyst (DBTDL) concentration on cure-time was studied and found that the cure process was completed with in 65 minutes at a catalyst concentration of 4×10^{-4} M (Table 2). This data was converted into graphical representations and it was found that there is no linear relationship between catalyst concentration and cure-time.

Wolf (21) showed that tertiary amines and tin carboxylates are synergistic in the urethane formation reaction. Bechara (22) also reported the enhanced activity of DBTDL/DABCO mixed catalysts towards the phenylisocyanate-butanol reaction. The author reported the synergistic effect of number of combination of tin/amine mixed catalysts towards phenol-blocked diisocyanate-alcohol cure reaction (12). In this present study, the mixed catalysts, in equimolar concentration, showed a synergistic effect, and the results are given in Table 3. It was found that the time taken for cure process employed with amine and tin mixed compounds are lower than the time taken with any one of the individual compounds (Table 1). Tribenzyl amine, ethyl-2-pyridyl acetate and *N,N*-dimetahyl-p-toludene, by themselves were very inefficient; however, when used in combination with tin compounds, they exhibited significant catalytic activity. Among the 18 combinations tried, the DABCO/DBTDL combination showed the highest catalytic activity. In this case, a fully cured product was obtained within 20 min and this low cure time is very attractive in an industrial application point of view. More studies are needed to understand the mechanism of cure reaction catalyzed by these mixed catalysts.

The relative viscosities (η_r) of the cured polymers obtained by the uncatalyzed and catalyzed reactions were determined by the use of an Ubbelohde viscometer to ensure the constancy of the cure reaction. It was found that the values of η_r are identical, confirming a uniform cure reaction in all the experiments.

Table 3. Synergistic effect of amine and tin catalysts on the cure reaction of *N*-methylaniline-blocked polyisocyanate with HTPB at 160°C

Amine catalyst [2×10^{-4} M]	Tin catalyst [2×10^{-4} M]	Cure time (minutes)	η_r
DABCO	DBTDL	20	1.495
DECHA	DBTDL	35	1.480
Tributylamine	DBTDL	55	1.475
Tribenzylamine	DBTDL	70	1.495
Ethyl-2-pyridylacetate	DBTDL	105	1.480
N,N-dimethyl-p-toludene	DBTDL	155	1.475
DABCO	DBTDA	30	1.480
DECHA	DBTDA	40	1.485
Tributylamine	DBTDA	50	1.486
Tribenzylamine	DBTDA	75	1.480
Ethyl-2-pyridylacetate	DBTDA	130	1.495
N,N-dimethyl-p-toludene	DBTDA	185	1.490
DABCO	Stannous-2-ethylhexanoate	45	1.480
DECHA	Stannous-2-ethylhexanoate	70	1.495
Tributylamine	Stannous-2-ethylhexanoate	100	1.490
Tribenzylamine	Stannous-2-ethylhexanoate	130	1.480
Ethyl-2-pyridylacetate	Stannous-2-ethylhexanoate	190	1.495
N,N-dimethyl-p-toludene	Stannous-2-ethylhexanoate	220	1.490

4. Conclusions

Catalysis of *N*-meathylaniline-blocked polyisocyanate-HTPB cure reaction was studied and the cure-times determined at 160°C were reported. Supporting with FTIR results, addition-elimination mechanisms were proposed for the cure reaction. The FTIR results indicated that DBTDL catalyze crosslinking reaction such as allophanate formation during the cure process whereas DABCO was found to catalyze only the cure reaction (urethane formation). Due to synergistic effect, it was found that DABCO/DBTDL mixed catalyst system was very efficient for the cure reaction.

5. Acknowledgment

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