

CURE CHARACTERISTICS OF HYDROXYL TERMINATED POLYBUTADIENE PREPOLYMER WITH BLOCKED TOLUENE DIISOCYANATE-I

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ABSTRACT

Controlled release of TDI and hence the cure characteristics of several blocked TDI with HTPB are reported. The reactions were followed through viscosity measurements as a function of time and temperature under the catalytic influence of triethylamine. The effect of nature of substituents present on the end capping substrate, temperature, solvent, basicity of catalyst and kinetics thereon have been studied.

INTRODUCTION

The facile and instant reactivity of isocyanates with materials containing active hydrogens make them attractive as cross-linking or modifying agents for several of the plastic resins. In most of these applications it may be necessary to delay this cross-link reaction rate, if one desires a property modification of the final product. Several attempts have been made in this direction, with derivatives of isocyanate capable of undergoing thermal dissociation, to generate the isocyanate at an appropriate stage.

Isocyanates react with phenols to yield aryl-urethanes. It has been established^[1] that on heating, the aryl urethanes dissociate at 150 °C to give the parent isocyanate and phenol, thus providing an isocyanate generator, stable under normal conditions but an effective reactant at elevated temperatures. This reaction however, has a serious limitation for application as rocket propellant binder, since the thermal dissociation occurs *in masse* at 150 °C. In this case, considering the environmental hazard involved, it is preferred the cure reaction should occur at a temperature as close to ambient as possible. It is a complicated system since one has to ensure dissociation of blocked TDI at low temperature and follow the cure reaction as well. Hence understanding of both the rheological and kinetic changes during the reaction becomes important to evaluate the kinetics of such a system.

The viscosity of hydroxyl-terminated polybutadiene (HTPB) prepolymer does not change as long as the end TDI remains undissociated. It is known^[2] that the dissociation of the end capped TDI and of diurethano compounds in general depend on the substituents attached to the aromatic ring, basic strength of the catalyst and the

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polarity of the solvent or medium. Mukaiyama and Hoshino^[3] have reported that in the presence of catalytic amount of amine, capped isocyanates dissociate at lower temperatures and the rate of dissociation increases with the increase in basic strength of the amine. Richter and Macosko^[4] studied the reaction kinetics of polyurethane catalyzed by dibutyltindilaurate and proposed four limiting cases. Chern^[5] has reported curing kinetics of polyurethane reactions.

While literature details the effect of diisocyanate structure, more specifically on the properties like tensile strength, ultimate elongation and modulus etc.,^[6] as cited already, work on blocked TDI is very limited. The data on blocked TDI derivatives, the cure characteristics etc. are also very scanty. Hence emphasis was laid on hitherto unreported aspects of the TDI/HTPB system, particularly on the cure reaction when the TDI is blocked.

The aim of this project was to develop a suitable blocked toluene diisocyanate (TDI) that would dissociate under the influence of a catalyst to free TDI to cure HTPB prepolymer, present in our system at around 60 — 70 °C, at a slow pace. A success in this venture would enable casting big propellant grains. The adduct is stable to moist environment and safe to handle not being as toxic as TDI. This paper describes cure characteristics of HTPB and differently end capped TDI systems under the influence of amine catalysts.

EXPERIMENTAL

Materials

Hydroxyl-terminated polybutadiene (HTPB) resin (viscosity 6150 in mPa.s and molecular weight by end group analysis 2700) and TDI (commercial mixture of isomers containing 80% toluene 2,4-diisocyanate and 20% toluene 2,6-diisocyanate) were obtained from SHAR Centre, Sriharikota and stored in dry condition. Commercially available phenols, amines and solvents were purified by distillation.

Method

End-capped TDI's were prepared from phenol, thiophenol, p-chlorophenol and p-nitrophenol and TDI in toluene solution containing few drops of triethylamine catalyst as per the reported procedures^[7,8]. The adducts referred to as A, B, C and D to the four phenols above in that order were recrystallized and characterized by melting point, IR, NMR spectra and C, H, N analysis.

Instrumentation

Rheological properties were determined using a Haake viscometer 'Rotovisco RV 20' on a M 5 system attached to a PG 242 programmer and a plotter. The sample was loaded into a NV cup sensor system which consisted of a cup and a bell-shaped rotor. It is a coaxial cylinder sensor system with two gaps for shearing the samples on the inside and on the outside of the rotor under thermostatically controlled conditions.

Preliminary experiments on the viscosity measurements were carried out with

an Ubbelohde viscometer. A 10% solution of HTPB in methyl ethyl ketone (MEK) was found to be suitable for these experiments. In a standard flask, MEK solution (50ml) containing HTPB (10g) was prepared and in a second standard flask MEK solution (50 ml) containing end capped TDI (2 g) was also prepared. The two solutions were mixed and maintained at 40 °C under dry condition. Triethylamine (0.1 ml) was added as catalyst at a noted time (t_0). Viscosity of the solution was calculated at various known intervals of time. The experiments were repeated at temperatures 40, 50, 60 and 70 °C for all the capped TDI. The results are listed in Table 1.

A more accurate curing study of HTPB prepolymer with blocked TDI were made using the Haake Rotovisco RV 20. A clear solution of cyclohexanone (10 ml) containing blocked TDI (1 g) was added to HTPB (5 g) and stirred well. This solution was loaded into the NV cup of the Haake viscometer at a set temperature of 50 °C and the instrument was allowed to stabilize for 30 min. One drop (0.02 ml) of triethylamine was added into the cup to initiate the dissociation of the blocked TDI and the time was noted as t_0 . The rheograms (plot of shear stress vs. shear rate) were recorded every 30 minutes over a period of 6 hours. The curves shifted upward with time, due to increase in viscosity of the solution. The viscosity ' η ' of the solution at different time intervals were calculated from the rheograms. A plot of relative viscosity ' η / η_0 ' vs. time is shown in Fig. 1a (' η_0 ' is the viscosity of the mix at time t_0 and ' η ' is the viscosity at time t).

The cure characteristics of HTPB prepolymer with blocked TDI were compared with the data obtained from HTPB (5 g) and free TDI (0.5 g) under the same experimental condition. Viscosity change of HTPB prepolymer was also studied by taking adduct C with higher concentration of triethylamine at 50 °C as shown in Fig. 1b.

Table 1 Viscosity data of cure reaction of HTPB with TDI adducts in methylethylketone in the presence of catalytic amount of triethylamine at various temperatures (using Ubbelohde viscometer)

Time (h)	Viscosity ' η ' mPa. s															
	40 °C				50 °C				60 °C				70 °C			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
0	1.30	1.14	1.20	1.36	1.29	1.12	1.18	1.34	1.26	1.11	1.16	1.32	1.20	1.10	1.15	1.30
1	1.31	1.14	1.20	1.50	1.46	1.14	1.23	1.56	2.32	1.23	1.26	1.64	1.66	1.36	1.50	1.64
2	1.36	1.14	1.23	1.53	1.50	1.17	1.31	1.94	2.93	1.25	1.50	2.46	2.26	1.39	1.78	2.46
3	1.37	1.15	1.34	1.78	1.51	1.18	1.47	4.42	3.44	1.31	2.00	7.92	3.87	1.45	2.68	8.60
4	1.38	1.16	1.47	1.86	1.52	1.23	1.56	6.55	4.20	1.32	2.32	11.47	10.39	1.49	3.61	9.15
5	1.40	1.18	1.48	2.46	1.61	1.28	1.64	12.70	7.94	1.34	2.79	*	*	1.77	5.47	16.11
6	1.44	1.20	1.50	3.22	1.83	1.31	1.88	*	*	1.36	7.54	*	1.92	8.62	*	*

A- Phenol TDI adduct, B- Thiophenol TDI adduct, C- p-Chlorophenol TDI adduct, D- p-nitrophenol TDI adduct, * gel formation.

Kinetic studies

Cyclohexylamine (50 ml, 0.05 M) in cyclohexanone and adduct A (50 ml, 0.05M) in cyclohexanone were mixed at time t_0 in a round bottom flask and maintained at 30 °C in a thermostat. The solution (5 ml) was pipetted out at regular

intervals of time and titrated against standard HCl (0.025N) using bromophenol blue indicator. From the titre value the strength of the unreacted amine was calculated, at time $t_{\min}$ to determine the percentage adduct dissociated in that time interval. A plot of percentage adduct dissociated vs. time is given in Fig. 2.

RESULTS AND DISCUSSION

Table 1 shows that the viscosity change at certain temperature for adduct A to be relatively slow compared to adducts C and D. Viscosity change increases in the order $A < C < D$. It is observed that the adduct B which is expected to dissociate faster than adduct A is actually slower. The viscosity change at 40 °C became quite significant with the increase in temperature. At higher temperatures the solution gels up after a few hours preventing viscosity measurements.

The plots (Fig. 1a) clearly show that the viscosity build up with TDI adducts is less compared to free TDI. For a given mix time, the viscosity of TDI adduct/HTPB mixture is lower indicating slower cure rate. The difference in viscosity build-up may be explained on the basis of the rate of dissociation of TDI adducts under a given experimental condition. The plots also show that the viscosity increase is slow at the beginning and increases with time, which may be due to the enhanced rate of dissociation of TDI adducts with time.

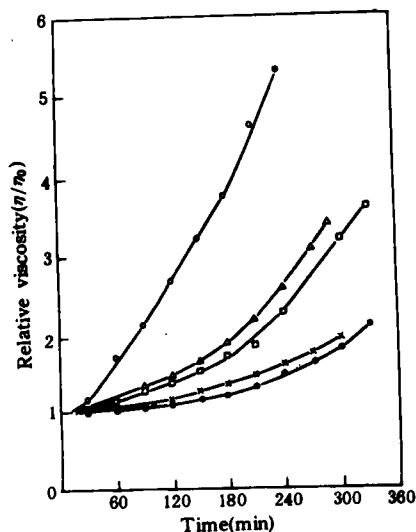


Fig. 1a Relative viscosity η/η_0 vs. time (min) for HTPB/TDI adducts in cyclohexanone with triethylamine catalyst at 50 °C (●) adduct A (×) adduct B (□) adduct C (○) adduct D (Δ) free TDI

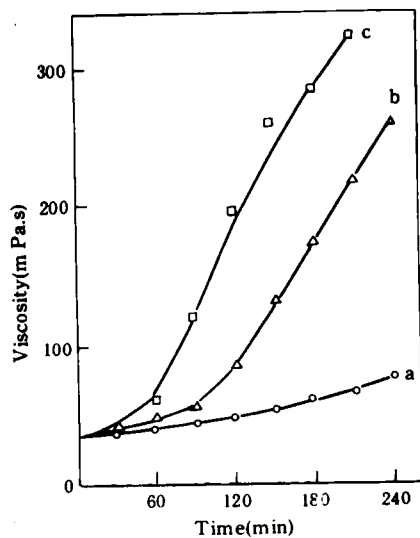


Fig. 1b Viscosity vs. time curve for HTPB/TDI adduct C in cyclohexanone with triethylamine (a- 0.02ml, b- 0.2ml, c- 2ml) at 50 °C

In the case of adduct D, the viscosity change was found to be faster than in free TDI/HTPB mixture, which may be explained as due to the very fast dissociation of adduct D even at 30 °C in the presence of catalytic amount of amine. Triethylamine added to catalyse the dissociation of the adduct enhances the cure reaction between HTPB and free TDI as well and hence an undefinable situation is created. Higher catalyst concentration (Fig. 1b) for adduct C/HTPB

system resulted in rapid viscosity change, showing there by the direct dependency of the cure reaction on catalyst concentration.

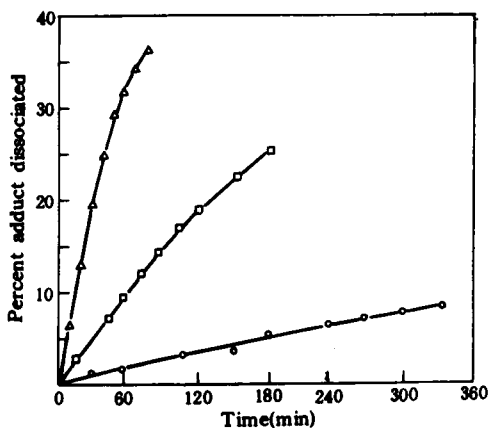


Fig. 2 A percentage dissociation vs. time plot for TDI adducts (0.025M) in cyclohexylamine (0.025M) and in cyclohexanone solvent at 30 °C (○) adduct A; (Δ) adduct B; (□) adduct C

The results in Fig. 2 also show that electron withdrawing substituents at p-position enhanced the rate of dissociation, which is obviously due to the higher acidity of the corresponding phenols through strong -I effect.

The effect of temperature on the dissociation of blocked TDI in cyclohexylamine and cyclohexanone solvent is shown in Fig. 3a,b for adduct A and adduct C at 30, 40, 50 and 60 °C. Rate of dissociation is faster at higher temperatures.

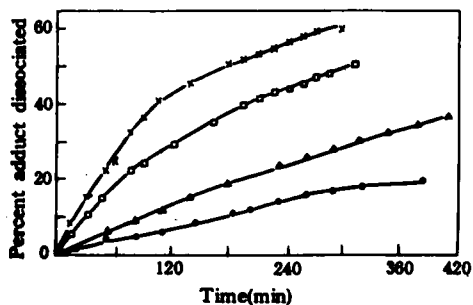


Fig. 3a A percentage dissociation vs. time plot for phenol-TDI adduct (0.025M), in cyclohexylamine (0.05M) and cyclohexanone solvent at (a) 30 °C (b) 40 °C (c) 50 °C and (d) 60 °C

The amount of adducts dissociated under different experimental conditions were determined by reaction of released TDI with excess of amine to form urea. The unreacted amine was estimated to get percentage dissociation of adduct indirectly. The percentage dissociation of adducts increased in the order $A \leq C \leq B \leq D$. Adduct D dissociated instantaneously. Taking the reactivity of adduct A as 1, the reactivity of other adducts come out as $C=5.37$, $B=17.78$ and $D=55.56$ times. The trend is in line with the electron withdrawing ability of the groups present in the blocking agent with D having a p-nitro and B a thiophenol while C is only p-chloro as against A being simple phenol.

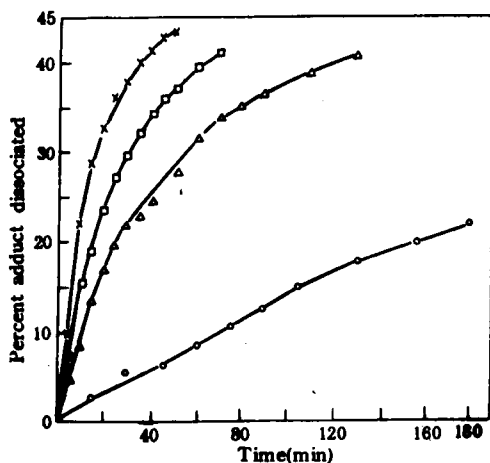


Fig. 3b A percentage dissociation vs. time for p-chlorophenol-TDI adduct (0.025M) in cyclohexylamine (0.025M) and cyclohexanone solvent (○) 30 °C (Δ) 40 °C; (□) 50 °C

Fig. 4a,b shows the percentage dissociation vs. time plot for adduct A and C in cyclohexanone with the increase in concentration of cyclohexylamine at 30 °C. The rate of dissociation increases with the increase in concentration of amine.

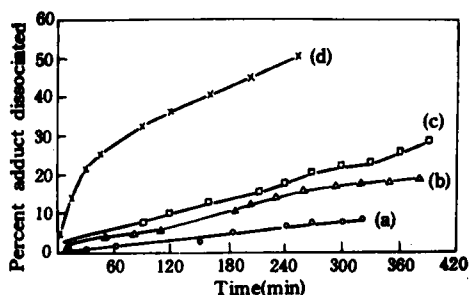


Fig. 4a A percentage dissociation vs. time plot for phenol-TDI adduct (0.025M) in cyclohexanone solvent at 30 °C and in cyclohexylamine (a) 0.025M (b) 0.05M (c) 0.1M (d) 0.25M

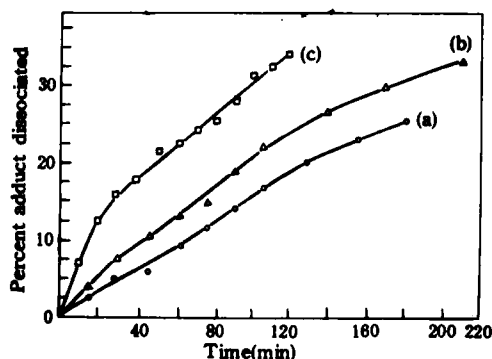


Fig. 4b A percentage dissociation vs. time plot for p-chlorophenol-TDI adduct (0.025M) in cyclohexanone solvent at 30 °C and in cyclohexylamine (a) 0.025M (b) 0.05M (c) 0.1M

The percentage dissociation of TDI adducts in amines (Fig. 5) decrease in the following order : di-n-butyl > n-hexyl, cyclohexyl > benzyl > dibenzyl. Phenol TDI adduct dissociates rapidly in di-n-butylamine (41% in 60 min at 50 °C), moderately in cyclohexylamine (9% in 60 min at 50 °C) and slowly in dibenzylamine (3% in 60 min at 50 °C). Similar results have been reported by Mukaiyama and others^[9] for thermal dissociation of urethanes in amines and the authors have proposed a base catalysed mechanism in which the process of deprotonation of urethanes by a base is a predominant factor. Their results show that, in amines the rates of dissociation increases as the basicities of the amines increase.

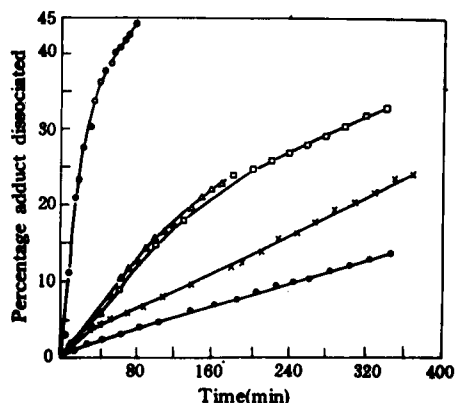


Fig. 5 A percentage dissociation vs. time plot for phenol-TDI adduct (0.025M) catalysed by amines (0.025M) in cyclohexanone solvent at 50 °C (○) di-n-butylamine; (Δ) hexylamine; (□) cyclohexylamine; (×) benzylamine; (●) di-benzylamine

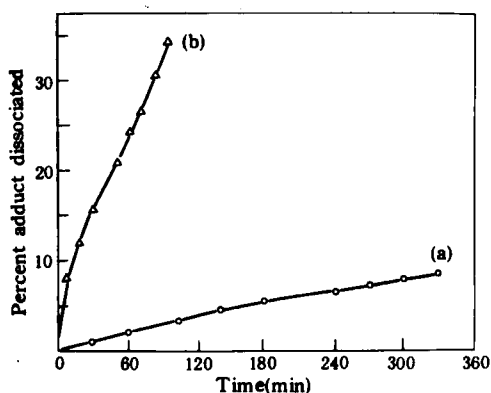


Fig. 6 A percent dissociation vs. time plot for phenol TDI adduct (0.025M) in cyclohexylamine (0.025M) at 30 °C and in solvent (a) cyclohexanone and (b) nitrobenzene.

In nitrobenzene as solvent the dissociation of equimolar amount of adduct A and cyclohexylamine at 30 °C is found to be much faster than in cyclohexanone solvent as shown in Fig. 6. Mukaiyama and others^[9] have reported that the dissociation is also affected by the nature of solvents, since interaction by solvent during dissociation may stabilize the formation of phenoxy ion and facilitate the cleavage of the C = O bond in the activated state.

The relative dissociation of TDI adducts due to factors such as nature of the adduct, temperature, catalyst concentration, its basicity and effect of solvents are compared in Table 2. The reported values are based on the assumed value of 1 for adduct A at a concentration of 0.025M in cyclohexanone.

Table 2 Relative dissociation of TDI adducts in 60 min [assuming phenol TDI adduct (0.025M) in cyclohexylamine (0.025M) and in cyclohexanone solvent at 30 °C having reactivity 1]

TDI adduct	Amine	Adduct: Amine mol. ratio	Temperature (° C)	Percentage dissociation	Relative dissociation	
Solvent- Cyclohexan one						
A	Cyclohexylamine	1 : 1	30	1.80	1	effect of substituent
C	"	1 : 1	30	9.66	5.37	
B	"	1 : 1	30	32.00	17.78	
D	"	1 : 1	30	100	55.56	
A	"	1 : 2	30	4.50	2.50	effect of increase in amine concentration
A	"	1 : 4	30	5.24	2.91	
A	"	1 : 10	30	27.50	15.28	
A	"	1 : 2	40	7.00	3.89	effect of temperature
A	"	1 : 2	50	17.14	9.52	
A	"	1 : 2	60	25.02	13.90	
A	Dibenzyl	1 : 1	50	3.50	1.94	
A	Benzyl	1 : 1	50	5.65	3.14	effect of increase in basicity of the amine
A	Cyclohexyl	1 : 1	50	9.28	5.16	
A	Hexyl	1 : 1	50	10.61	5.89	
A	Di-n-butyl	1 : 1	50	41.13	22.85	
Solvent-Nitrobenzene						
A	Cyclohexylamine	1 : 1	30	24.42	13.57	effect of solvent (dielectric constant)

CONCLUSION

With a fair understanding of the influence of the medium, basicity, temperature etc., it will be possible to choose an end capped TDI for HTPB/TDI system such that the TDI adduct would release TDI at the required time and at a required rate so that the viscosity increase becomes a controllable factor.

Keywords:

Blocked TDI; HTPB; Cure characteristics; Toluene diisocyanate

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