

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

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ABSTRACT

Cure characteristics of hydroxyl terminated polybutadiene (HTPB) prepolymer with a variety of blocked toluene diisocyanate (TDI) in the presence of triethylamine (TEA) and chloroacetic acid catalyst are reported. Phenol, thiophenol, p-chlorophenol, p-nitrophenol, p-cresol, resorcinol, naphthols, caprolactam and butylated-hydroxytoluene were used as blocking agents. Viscosity measurements have been carried out using a mixture of HTPB and blocked TDI in cyclohexanone in the presence of the catalysts at 50°C and 60°C using Haake rotational viscometer. Viscosity measurements have also been carried out with 50% solids such as ammonium sulphate along with HTPB and TDI adduct.

INTRODUCTION

Curing time of HTPB prepolymer can be varied by chemical capping of the isocyanato function in TDI with different organic reagents. The viscosity of the HTPB prepolymer does not change as long as the blocked TDI remains undissociated. The blocked TDI should be able to dissociate at a reasonably low temperature. Dyer and Newborn^[1] have shown that arylbiscarbamates dissociate to the corresponding isocyanates at 300°C, which is well above the temperature normally used with blocked isocyanate. Thermal dissociation of blocked TDI have been determined by Griffin and Willwerth^[2] and the lowest dissociation temperature were observed with negatively substituted phenol. Mukaiyama and Iwonami^[3] have shown that in a given series of

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substituted N-phenyl-benzylcarbamates, the rate of thermal dissociation increases with increasing electron attracting power of the substituent on the ring. Mukaiyama et al.^[4,5] have reported that while on heating the urethans dissociate into the components in the presence of either fatty acids or amines.

Blocked TDI helps to maintain the low viscosity and prolongs the processing time till the blocked TDI is completely dissociated and used up. After the required mixing time, the parent TDI gets regenerated through dissociation by organic base like triethylamine or acidic catalyst such as chloroacetic acid. Cure characteristics of HTPB with four differently blocked TDI adducts (A to D) under the influence of triethylamine catalyst have been reported in our previous paper^[6]. With the view to improve the working condition for HTPB urethane into rocket fuel, we have extended our work to six more blocked TDI (Table 1). Cure characteristics of HTPB with these adducts in the presence of triethylamine as well as chloroacetic acid catalyst have been carried out by using HAAKE rotational viscometer. To understand the influence of solids on the cure characteristics, ammonium sulphate was introduced to the extent of 50% to the HTPB-TDI (blocked) system and the viscosity measured. Ammonium sulphate was used in place of ammonium perchlorate from the point of view of environmental precaution in the lab.

The aim of this study is to identify a suitable blocked TDI for the HTPB/TDI binder system which would help to maintain low viscosity and release TDI at relatively low temperature.

EXPERIMENTAL

Materials

Hydroxy terminated polybutadiene (HTPB), Dioctyladipate (DOA) Toluene diisocyanate (TDI) (commercial 80:20 mixture of 2,4 and 2,6 isomer), TDI (2,4 isomer) and triethyl amine (BDH) and chloroacetic acid (Merck) were used as such. All phenols (BDH), cyclohexanone (Merck) and toluene (Merck) were purified by standard chemical methods before use.

Synthesis of blocked TDI

Blocked TDI adducts were prepared as per the reported procedure^[2] and purified by recrystallization. The TDI adducts were characterized by melting

point, IR, NMR spectra, and C, H and N analyses. (Table 1).

Table 1

S. No.	TDI adduct	Blocking agent for TDI	M. P. (°C)	% Nitrogen	
				Calcd.	Found
1	A	Phenol	138—139	7.73	7.61
2	B	Thiophenol	132—133	7.11	7.40
3	C	p-chlorophenol	128—129	6.50	6.34
4	D	p-nitrophenol	155—156	12.39	12.29
5	E	p-cresol	115—156	7.18	7.07
6	F	2-naphthol	315—317	6.06	6.08
7	G	Resorcinol	174—175	7.11	7.05
8	H	1-naphthol	310—312	6.06	6.02
9	I	Caprolactam	160—162	14.00	14.09
10	J	Butylated-hydroxy- toluene (BHT)	312—315	4.56	4.49

Viscosity measurements

A HAAKE viscometer model 'Roto visco RV 20' with measuring device M5, PG-242 programmer and NV sensor was used to measure the system viscosity. A solution of cyclohexanone (10 ml) containing HTPB (5g) and blocked TDI (1g) was loaded into the NV cup and the instrument was allowed to stabilize for 30 min. at the required temperature. 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 amount of sample was adjusted so that during the operation, the top surface of the cylinder was just covered. In absolute values of shear rate, this sensor provides a range from $D=27$ to 2700 1/s and in shear stress, a range from 17.8 Pa to 178 Pa.

After selecting the shear rate ranges, the t_1 , the hold time period was set at $t_1=8$ min, the program time $t_2=0.8$ min. The t_2 value defines the time to ramp up the speed from zero to the maximum set value and back to zero. Flow curves were recorded for continuously increasing shear rates (up curve) and for continuously decreasing the shear rates (down curve). t_3 is the hold time at maximum shear rate before the program cycle is reversed. The given calculation factors A and M of the sensor system are used to determine shear rate, shear stress and viscosity values from the recorder curve.

A - shear rate factor = 1.78 Pa

M - shear stress factor = 27s^{-1}

$$\text{Viscosity} = \frac{A \times \eta_0 \tau}{M \times \eta_0 D} = \text{Pa. s.}$$

The viscosity increases have been compared with other adducts by taking relative viscosity η/η_0 (η is the viscosity at time t and η_0 is the viscosity at t_0).

RESULTS AND DISCUSSION

It is observed that as the time of mixing increased, the curve shifted to higher shear stress values corresponding to higher viscosity for a given shear rate, due to the cure reaction. A mixture of HTPB : DOA : TDI in the ratio 16 : 3 : 1 is normally used in propellant systems. The viscosity buildup during propellant mixing could be understood by measuring the viscosity of a mixture of HTPB/DOA/TDI at regular intervals of time. A plot of viscosity versus time for such a system showed that the viscosity at 50°C increased from 75 mPa. s to 475 mPa. s in 4h. Relative (η/η_0) measurement showed that in one hour the viscosity became double, in two hours it became three and a half hour times, four and a half hour times (3h) and six and a half hour times (4h).

Viscosity data of four systems A, B, C and D in cyclohexanone medium catalyzed by triethylamine at 50°C have been reported in our earlier paper^[6]. A plot of the relative viscosity vs. time showed that the viscosity build-up was slower with TDI adducts compared to free TDI. For a specific monitoring time after mixing, the viscosity variation for the adduct-HTPB system was lower, thus indicating, slower cure rate. The difference in viscosity buildup may be explained on the basis of rate of dissociation of these adducts. The percentage dissociation of the adducts increased, in the order $A < C < B < D$. This trend is in line with the electron withdrawing capacity of the substituents present at the para position on the blocking agents with enhanced rate of dissociation, arising through the higher acidity of the corresponding phenols by strong-I effect.

In an earlier paper, we have also reported the kinetics of dissociation of blocked 2,4-diisocyanatotoluene (TDI) in amines. The second order rate constant for the TDI adducts increased in the order $A < C < B < D$. These kinetic data give support to our studies on the cure characteristics of TDI adducts.

The relative viscosity versus time for E to J in cyclohexanone solvent catalyzed by triethylamine at 60°C are plotted in Fig. 1. It is evident that the viscosity increases for the adducts in the order $H < F < J < I < G < E$. The difference in viscosity buildup may be explained on the basis of differences in reactivity of the blocking reagent. TDI adducts E, F, G and H after dissociation in the presence of triethylamine, release naphthols, cresol and resorcinol into the propellant system which are solids and are hence less harmful compared to corrosive liquids such as phenol or thiophenol released during the dissociation of adduct A and B. Also the fact that the released mass

is a solid, provide less negative impact on the properties of the mass. Such solid blocking agents may be used for slowing down the cure reaction without disturbing the physical and mechanical properties of the propellant.

Caprolactam adduct of TDI (I) was also quite successful in slowing down the curing process of HTPB prepolymer. An advantage in using adduct I is that the caprolactam released after the dissociation of adduct I may possibly take part in the polymerization reaction as well. Butylated-hydroxytoluene TDI adduct (J) dissociates in the presence of triethylamine to give TDI and butylate-hydroxytoluene (BHT).

BHT is used in propellant as antioxidant and hence if this reagent is used as blocking agent, the presence of additional reagent in the propellant after dissociation of the adducts will be avoided.

Cure characteristics for all these systems have also been carried out in the presence of chloroacetic acid. Relative viscosity versus time was plotted graphically for HTPB/TDI adducts in cyclohexanone with chloroacetic acid catalyst at 60°C. The plots are shown in Fig. 2 and 3 for adducts A to I.

Solid loading experiments

In solid rocket propellants, binder (HTPB), plasticizer (DOA) and

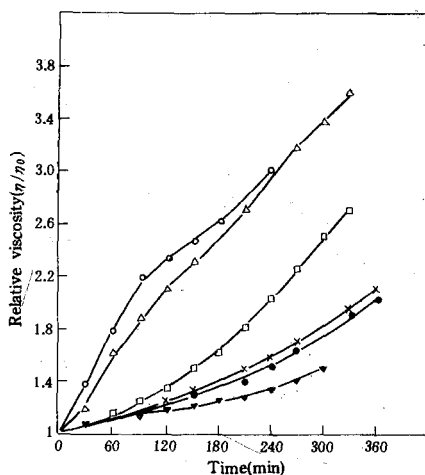


Fig. 1 Relative viscosity (η/η_0) versus time (min) for HTPB/TDI adducts in cyclohexanone with triethylamine catalyst at 60°C
○—E; ●—F; △—G; ▼—H; □—I; ×—J

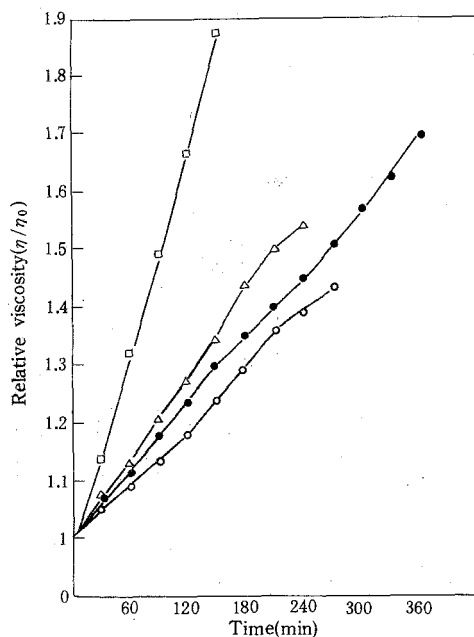


Fig. 2 Relative viscosity (η/η_0) versus time (min) for HTPB/TDI adducts in cyclohexanone with chloroacetic acid catalyst at 60°C
○-A; ●-B, △-C; □-D

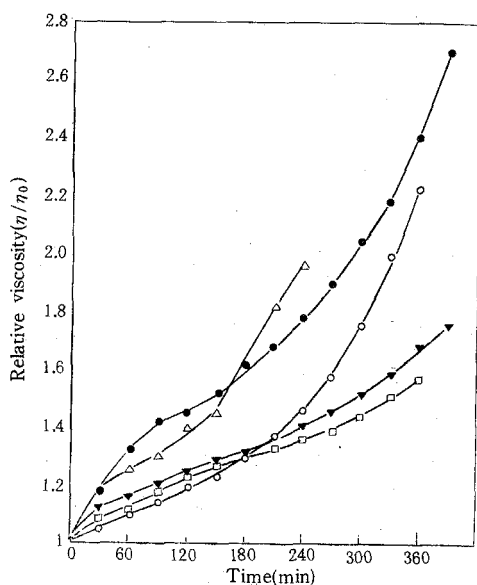


Fig. 3 Relative viscosity (η/η_0) versus time (min) for HTPB/TDI adducts in cyclohexanone with chloroacetic acid catalyst at 60°C
○-E; ●-F, △-G; ▼-H; □-I

curing agent (TDI) are liquids, added to the extent of 20% and the rest being solids like ammonium perchlorate and aluminium powder. Hence the dissociation of TDI adducts should be studied in the presence of some solids. The viscosity studies were done with harmless solids like ammonium sulphate. A mixture of HTPB (8g) and ammonium sulphate (4g) was mixed with a solution of cyclohexanone (2ml) containing phenol TDI adduct (1g). TEA (0.1ml) was then added and the viscosity measured at 50°C. The viscosity versus time plot for 50% solid loaded plots for phenol TDI adduct is shown in Fig. 4. The viscosity of the slurry was found to be 290 mPa.s for the phenol TDI adduct (A) mixture at 50°C, which increases slowly to 390 mPa.s in 3 hours. In thiophenol TDI adduct the viscosity was found to increase from 585 mPa.s to 655 mPa.s in 3 hours.

CONCLUSION

Cure characteristics of a wide variety of blocked toluene diisocyanates with HTPB in the presence of basic or acidic catalysts will help us to choose the right type of blocked TDI for our TDI/HTPB binder system.

Keywords :

Hydroxyl terminated polybutadiene; Blocked toluene diisocyanate; Cure characteristics

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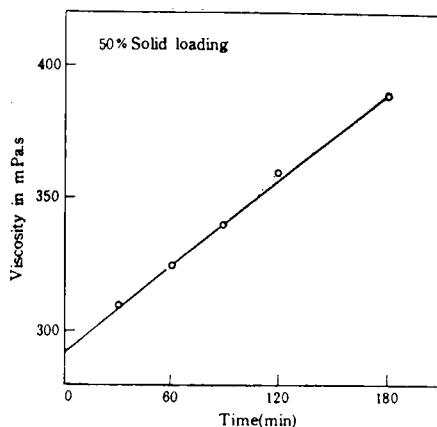


Fig. 4 Viscosity versus time plot for HTPB (8g) + $(\text{NH}_4)_2\text{SO}_4$ (4g) + Phenol TDI adduct (1g) in cyclohexanone (2ml) + TEA (0.1ml) at 50°C, 50% Solid loading

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