A Study on Liner-Reaction Speed based on the Aging of a Curing System

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Abstract

In this study, the hardening reaction speed of a rocket motor liner based on the aging of a curing system comprised of a hardener and hardening catalyst was observed. It was indicated that as the aging time of the curing system increased, the liner viscosity build-up was accelerated. The raw material having the biggest impact on the hardening reaction of the curing system's liner was triphenylbismuth (TPB). Stirring isophorone diisocyanate and TPB forms activated complex, and the activated complex facilitates urethane reaction. If TPB is ligand bound with isocyanate, it forms TPB-isocyanate complex. This is a type of TPB's oxide, and the formation of activated complex through changes in its color. In addition, lining hardening time can be adjusted by the aging period of the curing system through this study, and adhesive strength with the liner and propellant can be improved.

1. Introduction

A common solid rocket motor uses a liner and a heat-resistance material inside a motor to protect the propellant grain and combustion pipe. The liner is made of an elastic rubber material and located between the heat-resistance material and propellant inside the combustion pipe. The liner improves adhesive strength between them, protects the propellant grain from external vibrations, and also forms interfacial bonding with the propellant. This prevents the double-sided combustion of the propellant, and it can maintain the desired pressure of the designed motor. For the heat-resistance materials, rubbers such as NBR and EPDM are mainly used. These are located inside a combustion pipe, and the materials are widely used to protect the combustion pipe from fire during the propellant combustion and to maintain its gas tightness [1,2,3,4].

To spread the liner inside the combustion pipe, the case-rolling or spray methods are applied [5,6]. If defects such as holes or cracks exist inside the liner after it is spread, the adhesive strength with the propellant is decreased. This can lead to the presence of defects such as nonadhesiveness and cracks. Such defects can cause explosion due to the increased area of combustion [6,7]. Occurrence of such defects is closely related to the curing system of the liner. If the hardening reaction is too quick, the viscosity of the liner increases rapidly. This can lead to a high chance of nonconformity occurrence due to the difficulty of removing bubbles inside the liner when it is spread [8,9].

Previously, various studies were conducted owing to the significance of the propellant or liner curing system. These include a study on the speed of a propellant hardening reaction based on molecular weight and functional number of hydroxyl terminated polybutadiene (HTPB) binder [10], a study on adjusting the content and ratio of curing catalysts [9,11], and a study on setting an optimum hardening condition by adjusting (Step hardening) curing temperature [12], etc.

In general, triphenylbismuth (TPB) is used as a liner curing catalyst, whereas, maleic anhydride (MA) and MgO are mainly used as cocatalysts [13]. TPB is a curing catalyst, and MA is a cocatalyst that is

characterized by slowing down the initial reaction speed and accelerating the speed at the point when the curing catalyst is activated [14]. MgO is a solid-base catalyst, mainly used with TPB and MA [15].

However, since this catalyst is in solid state, it is applied by melting in a hardener to increase its dispersion efficiency instead of using it in the raw form. In this study, a hardener of isophorone diisocyanate (IPDI), a curing catalyst of TPB, and a curing cocatalyst of MA were mixed to increase the dispersion efficiency of the catalyst. In addition, the liner hardening reaction speed based on the aging of the curing system was observed. Moreover, the lining hardening time can be adjusted using the aging period of the curing system through this study, and the adhesive strength between the liner and propellant can be improved.

2 Test

2.1 Manufacturing of liner

When manufacturing the liner, the HTPB of Samyang Chemical Industries Co., Ltd was used as the binder, and hydroxyl index was 0.75 meg/g. For hardener, IPDI of Bayer Material Science LCC was used, and isocyanate index was 8.90 meg/g. HX-868 (1,1,1-(1,3,5-benzene Tricar-bonyl)tri-2-ethyl-aziridine) of Geowon Technology Co., Ltd was applied as the bonding agent, TPB of Dongin Chemical Co., Ltd and MA of Sungwon Chemi Cyan were used as curing catalysts. The equivalent ratio was 1.25, and the hardening was proceeded at temperature of 70°C for 18 h. The detail compositions of the liner are indicated in Table 1.

Table 1 Composition of Liner

Function		Composition	Content, wt%
Prepolymer		Hydroxyl terminated polybutadiene	94.00
Bonding agent		HX-868	
Solid		Carbon black	
Curing system	Curative	IPDI	6.00
	<i>Cure catalysis</i>	TPB	
		MA	

2.2 Manufacturing of curing system

The curing system adds TPB and MA to IPDI solution and performs stirring as shown in Fig 1. The stirring was performed at room temperature, and aging was proceeded from a minimum of 0 h to a maximum of 216 h (9 d).

2.3 Liner viscosity measurement

The viscosity of the liner in the slurry state was measured using Discovery HR-2 hybrid rheometer of TA Instruments Inc. The shear rate was fixed at 0.3/s, and it was measured using a 40-mm Plate at 70°C.

2.4 Adhesive strength test

Table 2 Test condition

Test condition		
Method	Speed	Machine
Peel	2.0 in/min	Instron
Shear	0.5 in/min	
Cubic tension	0.5 in/min	

Adhesive strength test between heat-resistance materials/liner/propellant was conducted based on KSM 3725 (peel), KSM 3734 (shear), and KSM 3722 (cubic tension). The lab temperature was maintained at 20°C and humidity was maintained at 38% (RH).

3 Result And Discussion

3.1 Reactivity based on Aging Time of Curing System

Figure 2 compares reactivity based on the aging time of the curing system. The test result indicated that as the aging time of the curing system increased, the liner viscosity build-up was accelerated. To confirm an accurate liner-reaction speed, gel time was compared as shown in Fig. 3. The gel time was 2.30 h if the liner was manufactured after 3.0 h of the aging of the curing system, and 1.16 h if it was manufactured after 216 h (9 d) of aging time. It can be seen that gel time was reduced by approximately 50%. Through the test result, the aging time of the curing system was confirmed as the factor that adjusts the liner’s hardening speed.

3.2 Factors that effect reaction speed in curing system

To confirm raw materials that effect reaction speed in the curing system, the test was conducted using three cases as shown in Table 3. Each case created a curing system and 168 h (7 d) of aging was performed. After the aging, the liner was manufactured to confirm viscosity build-up. When manufacturing the liner, TPB excluded from case 2 and MA excluded from case 3 were directly injected as solid state. As shown in Fig. 4, cases 1 and 3 had the reaction speed accelerated at the same level. However, case 2 showed that the reaction speed slightly increased compared with the case of manufacturing the liner without going through the aging of the curing system. This did not have a major impact on the reaction speed in the curing system. On the other hand, cases 1 and 3 both contain TPB, and it is determined that TPB dissociated in the IPDI solution is the raw material that has major impact

on a liner’s hardening reactivity. Mixing IPDI and TPB can form activated complex as shown in Fig. 5. The activated complex reduces activation energy, and facilitates the urethane reaction of Fig. 6 [16,17].

Table 3 Effect of Aging time on Viscosity Build-up.

Curing system	Composition	Aging time
Case 1	IPDI	168 h (7 d)
	TPB	
	MA	
Case 2	IPDI	
	MA	
Case 3	IPDI	
	TPB	

3.3 Activation of curing catalyst

The raw material that has a major impact on reaction speed in the curing system is the curing catalyst of TPB. Color changes of TPB can be confirmed during the aging of the curing system after it is manufactured. It is determined that such changes in color are related to the activation of TPB. Figure 7 indicates color changes of the curing system based on aging, and it is confirmed that the color has changed to dark yellow as the aging proceeds. Through this, it can be seen that the TPB catalyst is activated. The color of bismuth changes from faint-yellow to dark-yellow if it is oxidated [18]. As shown in Fig. 5, if TPB is ligand bound with isocyanate, it forms TPB-isocyanate complex. This is an oxide of TPB, and through the color changes, the formation of activated complex can be confirmed indirectly.

3.4 Relationship between liner hardening speed and mechanical properties

It was confirmed that the liner’s hardening reaction time is changed depending on the aging time of the curing system. Hardening reaction speed and the liner’s mechanical properties are compared in Table 4. Aging times of the curing system were divided into two cases for cases 4 and 5. The test result indicated that hardening reaction speed is not related to the mechanical properties of the liner. Since the catalyst’s role is not to be directly involved in the reaction but only affects reaction speed, it does not affect the properties of the product [19].

Table 4 Effect of Aging time on Mechanical properties of liner.

Curing system	Aging time, h	Sm , MPa	Em , %	E , MPa	Hs
Case 4	24	6.77	320.90	5.06	63
Case 5	3	6.54	327.60	5.41	61

3.5 Comparison of adhesive strength between liner and propellant based on the liner's hardening speed

The adhesive strength between the liner and propellant based on the liner's hardening speed was compared in Table 5. Aging times of the curing system were divided into two cases of cases 6 and 7. The adhesive strength test was conducted as shown in Table 2. The test result indicated that the curing system in the cubic tension mode had the adhesive strength increased by approximately 66% in case 7 compared with case 6. The shorter the aging time of the curing system, the slower the reaction speed of the liner. Thus, in the case of curing the liner at a temperature of 70°C for 18 h as shown in Fig. 8, the liner that applied the curing system of case 7 was not completely hardened. The liner has the most excellent adhesive strength when it is less hardened compared with when it is completely hardened. In addition, it is generally known that the lower the hardness of the liner, the higher the adhesive strength [20,21]. To achieve a strong adhesive strength after the adhesion is completed, it is more advantageous when the adhesive strength at interface between the adhesive and substrate molecules is greater than the cohesiveness between the adhesive's own molecules [3]. The shorter the aging time of the curing system, the slower the hardening speed of the liner. This leads to functional groups remaining on the liner's surface reacting with functional groups of the propellant. Thus, it is determined that adhesive strength between the liner and propellant was improved.

Table 5 Effect of Aging time on the adhesion.

Curing system	Aging time, h	Peel, daN/cm	Shear, MPa	Cubic tesion, MPa
Case 6	24	1.18	0.44	0.53
Case 7	3	1.06	0.65	0.89

4 Conclusion

In this study, the liner's hardening reaction speed based on the aging of the curing system was observed.

It was confirmed that as the aging time of the curing system increased, the liner viscosity build-up accelerated.

The raw material having the biggest impact on the liner's hardening reaction in the curing system was TPB. Once IPDI and TPB are stirred, it forms an activated complex, which reduces activation energy to

facilitate a urethane reaction.

Color changes of the curing system based on the aging time of the system were indicated, and it was confirmed that the color was changed to dark yellow as the aging proceeded. If TPB is a ligand bound with isocyanate, it forms TPB-isocyanate complex. This is a type of a TPB oxidate. The formation of activated complex was indirectly confirmed through the changes in color.

Although the liner's hardening reaction speed accelerates by the aging time of the curing system, the hardening reaction speed is not related to the mechanical properties of the liner. However, adhesive strength between the liner and propellant was improved when the aging time of the curing system was reduced.

References

1. Hong, M. P., Seo, T. S. & Yim, Y. J. A study on the adhesion of HTPB liner and PCP propellant. *Korean Society of Propulsion Engineers***5**, 60–70 (2001).
2. Twichell, S. E. & Keller, R. B. Solid rocket motor internal insulation. *NASA SP***8093**, 1-6 (1976).
3. Ahmed, A. F. & Hoa, S. V.. Thermal insulation by heat resistant polymers for solid rocket motor insulation. *Compos. Mater.***46**, 1549–1559 (2012). <https://doi.org/10.1177/0021998311418850>.
4. Davenas, A. *Solid rocket propulsion Technology*, 1st ed (Oxford, Pergamon Press, 1992).
5. Lee, G.J, Park, J,H and Kim, S,J. *KR Patent 101858366* (Seoul, Republic of Korea: Hanwha Corporation, 2018).
6. Sutton, G. P. & Biblarz, O. *Rocket Propulsion Elements*. 8th ed (New York, NY: John Wiley & Sons Inc., 2010).
7. Ha, J. S., Kim, J. H. & Crack, P.-I. Propagation behavior in a particle-reinforced composite, *J. Mod. Phys. Conf. Ser.***6**, 178–183 (2012).
8. Yim, Y. J., Park, E. J., Kwon, T. H. & Choi, S. H. Effect of AP particle size on the physical properties of HTPB/AP propellant. *Korean Society of Propulsion Engineers***20**, 14–19 (2016).
9. Park, S. J. *et al.* Solid propellants for propulsion system including a yellow iron oxide. *Korean Society of Propulsion Engineers***22**, 65–71 (2018).
10. Kim, J. E., Ryu, T. H., Hong, M. P. & Lee, H. J. Investigation on rheological and mechanical properties of propellant with chemical structures of HTPB binder. *Korean Society of Propulsion Engineers* **21**, 84–90 (2017). <https://doi.org/10.6108/KSPE.2017.21.1.084>.
11. Eom, S. Y., Lee, H. I. & Lee, K. Y. Study on reaction behavior of rigid polyurethane foam with various types and contents of gelling catalysts. (*Korea*)**39**, 210–218 (2015). <https://doi.org/10.7317/pk.2015.39.2.210>.
12. Choi, Y. K. Research on the Formulation and Process of Base Bleed Unit for reducing of Curing Time. *Korean Society of Propulsion Engineers***12**, 24–32 (2008).

13. 13. Ducote, M. E. Maleic anhydride adjunct to triphenylbismuthine to improve mechanical properties of hydroxy terminated binders, US Pat. H934, **(1990)**.
14. 14. Rodic, V. & Petric, M. The effect of additives on solid rocket propellant characteristics. *Tech. Rev.***54**, 9–14 **(2004)**.
15. 15. Oberth, A. E. *Principles of Solid Propellant Development* (USA: Chemical Propulsion Information Agency, **1987**).
16. 16. Sonnenschein, M. F. *Polyurethanes: Science, Technology, Markets, and Trends*. 1st ed (New York: John Wiley & Sons Inc., 2015).
17. 17. Luo, S. G. *et al.* Catalytic mechanisms of triphenyl bismuth, dibutyltin dilaurate, and their combination in polyurethane-forming reaction. *Appl. Polym. Sci.***65**, 1217–1225 **(1997)**.
[https://doi.org/10.1002/\(SICI\)1097-4628\(19970808\)65:6<1217::AID-APP17>3.0.CO;2-Q](https://doi.org/10.1002/(SICI)1097-4628(19970808)65:6<1217::AID-APP17>3.0.CO;2-Q).
18. 18. Dalvand, L. F., Hosseini, F., Dehaghi, S. M. & Torbati, E. S. Catalytic mechanisms of triphenyl bismuth, inhibitory effect of bismuth oxide nanoparticles produced by *Bacillus licheniformis* on methicillin-resistant *Staphylococcus aureus* Strains (MRSA). *J. Biotechnol.***16**, 279–286 **(2018)**.
19. 19. Masel, R. I. *Chemical Kinetics and Catalysis*. 1st ed, Wiley-Interscience (New York, NY, 2001).
20. 20. Park, S. J. *et al.* A study on improvement of adhesion HTPB propellant/liner/insulation. *Korean Society of Propulsion Engineers* **23**, 92–97 (2019). <https://doi.org/10.6108/KSPE.2019.23.4.092>.
21. 21. Park, S. J. *et al.* Study on the improvement of adhesion strength between composite solid propellant, liner, and heat-resistant material. *Explos. Pyrotech.***45**, 1227–1233 (2020).
<https://doi.org/10.1002/prop.202000031>.

Figures

Figure 1

Curing system (IPDI+TPB+MA)

Figure 2

Effect of Stirring time on Viscosity Build-up

Figure 3

Gel time of liner according to stirring time

Figure 4

Reaction rate depending on the type of Curing System

Figure 5

Bond polarization mechanisms of catalyst action

Figure 6

TPB catalyst mechanism on urethane reaction

Figure 7

Changing the color of the curing system

Figure 8

Effect of liner curing time on the hardness