Experimental study on processability of ammonium perchlorate/hydroxyl-terminated polybutadiene composite propellant (I)

—Influences of operating temperature on viscosity of uncured propellant—

by Makoto KOHGA* and Yutaka HAGIHARA*

In the preparation of ammonium perchlorate (AP)/hydroxyl-terminated polybutadiene (HTPB) composite propellant, the lower viscosity of uncured propellant dough is desirable to mix and cast the uncured propellant dough easily. The viscosity of HTPB prepolymer to which a curing agent was added increases as the time passes, but the viscosity could be expected to decrease with an increasing temperature in the first stage when an increase in viscosity resulting from curing reaction is small. This indicates that there must be an optimum operating temperature in the preparation of AP/HTPB propellant. In order to obtain the lowest viscosity during mixing and casting of uncured propellant, it's necessary to use the optimum operating temperature. In the present study the relationships between the viscosity of HTPB with a curing agent or uncured propellant and the curing time were investigated at temperatures from 313K to 353K, and an attempt was made to find out the optimum operating temperature for mixing and casting of uncured propellant experimentally. The influence of temperature on the relationship between the apparent viscosity of uncured propellant and the curing time is similar to that between the apparent viscosity of HTPB with a curing agent and the curing time. It is found that the optimum operating temperature for mixing and casting of uncured propellant is identical with the temperature at which the apparent viscosity of HTPB with a curing agent is the lowest.

1. Introduction

Ammonium perchlorate (AP)/hydroxyl-terminated polybutadiene (HTPB) composite propellant was adopted in this study, because AP/HTPB composite propellant is the most widely used one at present. In order to design the formulation of AP/HTPB composite propellant, it's necessary to spread the range of a specific impulse of AP/HTPB composite propellant widely, especially towards a high specific impulse region. Specific impulse of AP/HTPB composite propellant increases with an increasing AP content and when the AP content is about 90wt%, the maximum specific impulse can be realized theoretically[1]. Because an upper limit of AP content in propellant exists technically for the size distribution of AP used[2], the upper limit of specific impulse must be so. In order to increase the upper limit of specific impulse, it's necessary to increase the upper limit of AP content. The purpose of this study was to find out the optimum operating temperature under the optimum operating conditions.

In the preparation of AP/HTPB composite propellant, AP is mixed with HTPB prepolymer and a curing agent is added to the AP/HTPB mixture. The AP/HTPB mixture with a curing agent, i.e., the uncured propellant is mixed again and cast into the rocket motor. A lower viscosity of uncured propellant dough is desirable to mix and cast the uncured propellant dough easily. The viscosity of uncured propellant is influenced by AP content, size distribution of AP, curing time, temperature, etc. In the case of the propellant with the same particle distribution and content of AP, it is likely that the viscosity of uncured propellant is greatly dependent on that of liquid prepolymer HTPB and the viscosity of uncured propellant decreases with a decreasing viscosity of HTPB prepolymer. The viscosity

Received on November 4, 1997
*Department of Chemistry, National Defense Academy
1−10−20, Hashirimizu, Yokosuka-shi, Kanagawa, 239-8686, JAPAN
TEL 0468-41-3810 ext. 3585
FAX 0468-44-5901

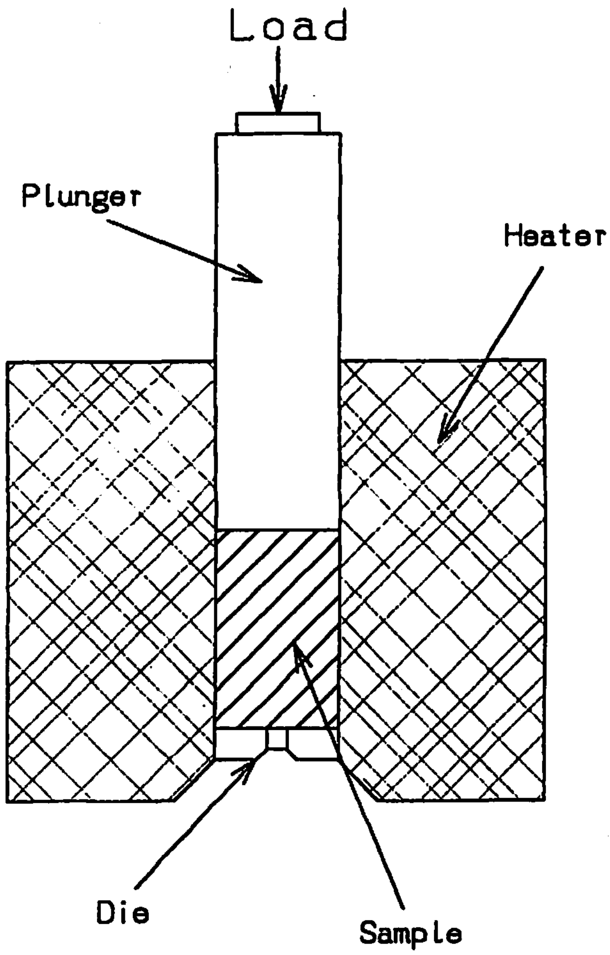

Fig. 1 Schematic diagram of the flow tester

of HTPB prepolymer decreases with an increasing temperature. On the other hand, after a curing agent is added to HTPB, the viscosity of HTPB containing a curing agent increases as the time passes. In addition, with an increasing temperature the rate of the curing reaction of HTPB increases and, therefore, its viscosity increases. This indicates that the optimum operating temperature exists to obtain the lowest viscosity during mixing and casting of uncured propellant. It is important for the preparation of AP/HTPB composite propellant to find out the optimum operating temperature for mixing and casting of uncured propellant. In the present study, the relationships between the viscosity of HTPB prepolymer or uncured propellant dough and the curing time were investigated at various temperatures, and an attempt was made to find out the optimum operating temperature for mixing and casting of uncured propellant experimentally.

2. Experimental

2.1 Samples

AP prepared by the freeze-drying method[3] was used. The mean volume-surface diameter of AP is 4×10^{-6}m. AP particles used in this study are fine and unimodal unlike ones contained in the common propellant. When the AP content is constant in the composition, the viscosity of AP/HTPB mixture increases with a decreasing size of AP used. Therefore fine AP particles were used in this study. HTPB R-45M (ARCO Co.) prepolymer was used as a material of binder. HTPB was cured with isophorone diisocyanate (IPDI) of a crosslinking agent. The amount of added IPDI in this study was 8 wt% relative to HTPB[2] and it is an ordinary volume.

2.2 Measurement of viscosity of HTPB prepolymer or uncured propellant dough

The apparent viscosities of HTPB or uncured propellant were measured by a flow tester (Shimadzu CFT-500C). A schematic diagram of the flow tester is shown in Fig.1. End correction in the capillary flow could not be carried out in this study. The reason was as follows: Four viscosity data (combination between two dies and two loads) are required for the end correction in the capillary flow[4]. Four viscosity data had to be taken simultaneously, because the curing reaction of HTPB with IPDI or uncured propellant proceeds continuously. Since it's difficult to take four viscosity data simultaneously, the end correction in the capillary flow could not be carried out in this study. The apparent viscosities of HTPB and uncured propellant were measured at temperatures from 313K to 353K. HTPB or uncured propellant was always maintained at the measuring temperature in a constant temperature box. The measurement of apparent viscosity of HTPB was conducted using a die with $\phi 0.5\times 1$ mm under a load of 0.98MPa. On the other hand, that of uncured propellant was conducted using a die with $\phi 1\times 1$ mm under a load of 1.96MPa.

3. Results and discussion

3.1 Relationship between apparent viscosity of HTPB prepolymer and curing time

First the influences of temperature on viscosity of HTPB without IPDI were investigated. The apparent viscosities of HTPB prepolymer alone were measured at temperatures from 313K to 353K and the relationship between the apparent viscosity of HTPB prepolymer alone and the temperature is plotted in Fig.2. The apparent viscosity of HTPB without IPDI decreases with an increasing temperature. On the other hand, after IPDI is added to HTPB, the viscosity of HTPB with IPDI increases as the time passes and the rate of an increase in viscosity increases with an increasing temperature. These suggest that in the first stage

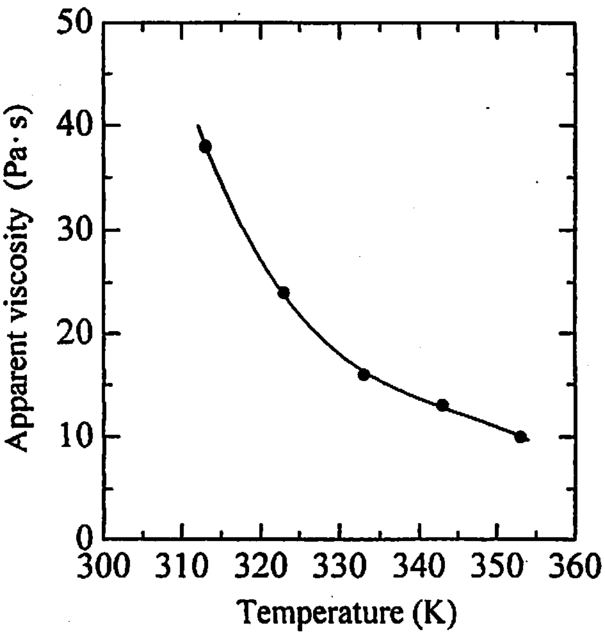

Fig. 2 Relationship between apparent viscosity of HTPB prepolymer without IPDI and temperature

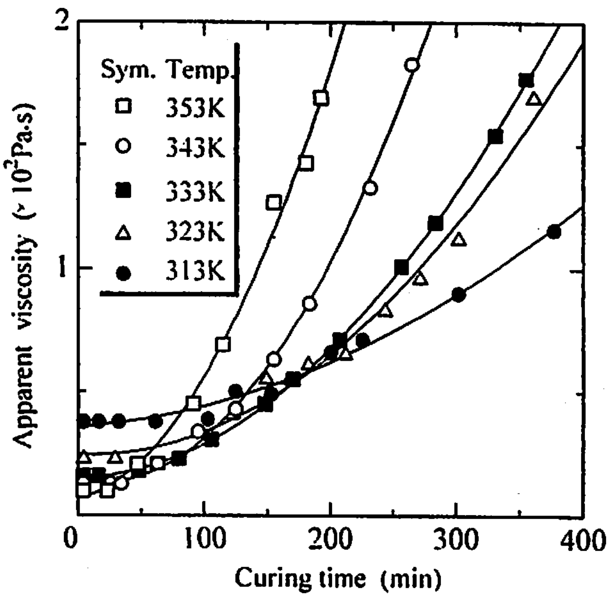

Fig. 3 Relationship between apparent viscosity of HTPB prepolymer with IPDI and curing time at some temperatures from 313K to 353K

of curing reaction, an absolate value of decreasing rate of viscosity of HTPB with IPDI resulting from an increment of the temperature was larger than that of an increasing rate of viscosity resulting from curing reaction. In order to verify this suggestion, the influences of temperature on viscosity of HTPB with IPDI were investigated. The apparent viscosities of HTPB with IPDI were measured at various temperatures from 313K to 353K and the relationships between the apparent viscosity of HTPB prepolymer with IPDI and the curing time are plotted in Fig.3. At each temperature, the apparent viscosities of HTPB with IPDI are almost the same as those of HTPB without IPDI shown in Fig.2 for the first 30minutes. This suggests that the rate of curing reaction of HTPB is slow for the first 30minutes. When the temperature is 353K, the apparent viscosity of HTPB with IPDI is smallest for the first 30minutes but increases rapidly thereafter. When the temperature is 343K, the apparent viscosities of HTPB with IPDI are almost the same as those at 333K for the first 80minutes but increase rapidly thereafter. When the temperature rises from 313K to 333K, for 180minutes the apparent viscosities of HTPB with IPDI decrease with an increasing temperature and thereafter increase with an increasing temperature. These facts indicate that from 313K to 333K absolute value of a decrease in apparent viscosity of HTPB with IPDI resulting from an increment of the temperature is larger than that of an increase in apparent viscosity resulting from curing reaction for 180minutes, and at higher temperatures than 343K the rate of the curing reaction increases largely.

3.2 Relationship between apparent viscosity of uncured propellant dough and curing time

A propellant containing more than 80wt%AP could not be prepared, because AP used in this study was fine particles. First the apparent viscosities of the AP/HTPB mixture with IPDI, i.e., the uncured propellant dough containing 80wt%AP were measured at various temperatues from 313K to 353K. The relationships between the apparent viscosity of the uncured propellant dough containing 80wt%AP and the curing time are plotted in Fig.4. At each temperature, the increase in the apparent viscosities of uncured propellants was small for the first 30minutes. This indicates that the rate of the curing reaction of HTPB is slow for the first 30minutes. At the temperature of 353K, the apparent viscosity of uncured propellant is the smallest for the first 40minutes but thereafter increases rapidly. At the temperature of 343K, the apparent viscosities are almost the same as those at 333K for the first 50minutes but thereafter increase rapidly. At 343K or 353K, it's necessary to mix and cast the uncured propellant in short time, because the rate of the increase in the apparent viscosity grows rapidly. In the temperature range from 313K to 333K, for 180minutes the apparent viscosities decrease with an increasing temperature and thereafter increase with an increasing temperature. In order to investigate the variation of the relationships between the apparent viscosity and the curing time with AP content, the uncured propel-

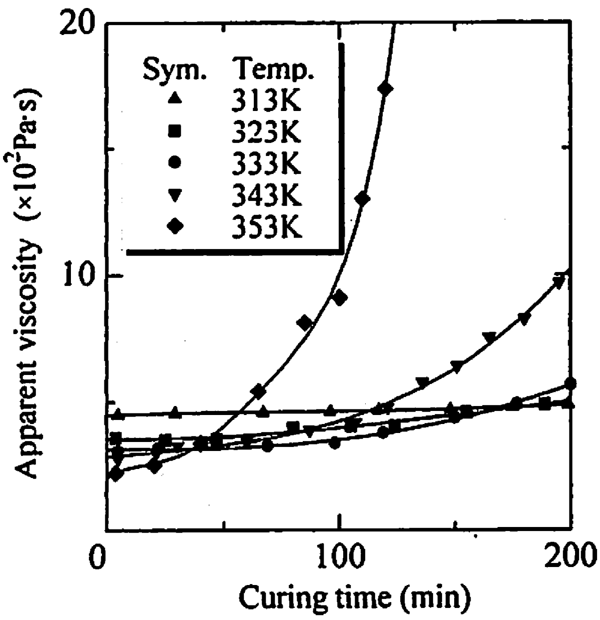

Fig. 4 Relationship between apparent viscosity of uncured propellant dough containig 80wt%AP and curing time at some temperatures from 313K to 353K

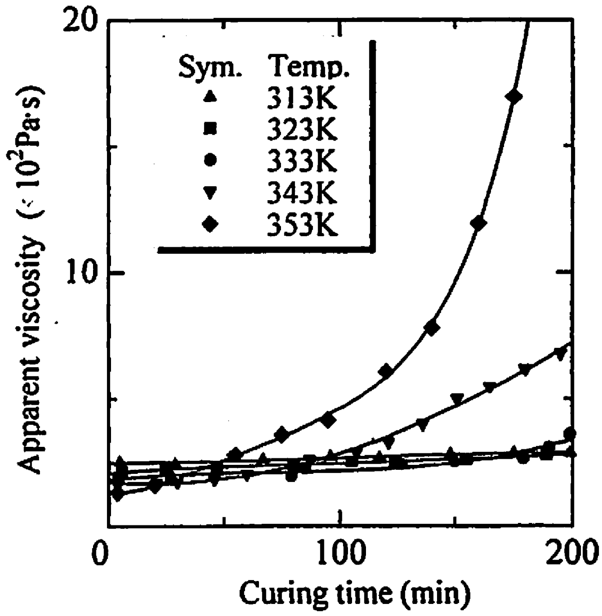

Fig. 5 Relationship between apparent viscosity of uncured propellant dough containig 78wt%AP and curing time at some temperatures from 313K to 353K

lant dough containing 78wt%AP was prepared and its apparent viscosities were measured at various temperatures from 313K to 353K. The relationships between the apparent viscosity of the uncured propellant dough containing 78wt%AP and the curing time are plotted in Fig.5. The difference in apparent viscosity resulting from a variation of the temperature of the uncured propellant containing 78wt%AP is smaller than that of the uncured propellant containing 80wt%AP. Therefore, the rate of the increase in apparent viscosity of the uncured propellant containing 78wt%AP is smaller than that of the uncured propellant containing 80wt%AP. It could be speculated that these facts are attributable to an increase in the proportion of liquid prepolymer HTPB. At the same time, the apparent viscosity of the uncured propellant containing 78wt%AP is different from that of the uncured propellant containing 80wt%AP. However, the relationships between the apparent viscosity of the uncured propellant containing 78wt%AP and the curing time are similar to those of the uncured propellant containing 80wt%AP. From these results, it is found that the influence of temperature on the relationship between the apparent viscosity of the uncured propellant and the curing time is similar to that of HTPB with IPDI. This indicates that the viscosity of uncured propellant is greatly dependent on that of HTPB. When rearranging the results, it is seen that the optimum operating temperature for mixing and casting of uncured propellant can be determined based on the relationship between the apparent viscosity of HTPB with IPDI and the curing time shown in Fig.3. As mentioned above, the lower viscosity of uncured propellant is desirable to mix and cast the uncured propellant easily. For example when the time spent from the addition of IPDI to the end of casting was less than 180minutes, it turned out that 333K was the optimum operating temperature for mixing and casting of uncured propellant.

The viscosity of the uncured propellant is influenced not only by operating temperature but also by AP content and size distribution of AP. In future, when the influences of AP content and size of AP on viscosity of uncured propellant are to be investigated, the optimum operating temperature should be allowed for. The optimum operating temperature could be determined from the relationship between the apparent viscosity of HTPB with IPDI and the cure time shown in Fig.3.

4. Conclusions

In the preparation of ammonium perchlorate (AP)/hydroxyl-terminated polybutadiene (HTPB) composite propellant, the lower viscosity of uncured propellant is desirable to mix and cast the uncured propellant easily. The viscosity of HTPB prepolymer with a curing agent increases as the time passes. However, the viscosity of HTPB with a curing agent decreases with an increasing temperature in the first stage when an increase in viscosity of HTPB resulting from curing reaction is small. This indicates that the optimum operating temperature exists. In order to obtain the lowest viscosity during mixing and casting of uncured propellant, it's necessary to find out the optimum operating temperature. In the present study the relationships between the viscosity of HTPB prepolymer to which a curing agent is added or an uncured propellant dough and the curing time were investigated at temperatures from 313K to 353K, and an attempt was made to find out the optimum operating temperature for mixing and casting of uncured propellant experimentally. The influence of temperature on the relationship between the apparent viscosity of uncured propellant and the curing time is similar to that of HTPB with a curing agent. This indicates that the viscosity of uncured propellant is greatly dependent on that of HTPB prepolymer containing a curing agent. It is found that the optimum operating temperature for mixing and casting of uncured propellant is identical with the temperature at which the apparent viscosity of HTPB with a curing agent becomes the lowest during mixing and casting of uncured propellant. Therefore, the optimum operating temperature could be determined from the relationship between the apparent viscosity of HTPB with a curing agent and the curing time.

Acknowlededgment

The authors are sincerely grateful to Professor M. Mizomoto of Univ. Keio for many valuable discussions in the course of this work.

References

1) N. Kubota; Combustion Phenomena of Solid Propellants(2), J. Ind. Expl. Soc., 41, 3, 125-130(1980)
2) M. Kohga and Y. Hagihara; AP-HTPB Composite Propellant Using Ultra Fine Ammonium Perchlorate Prepared by Freeze-drying Method(3), ibid., 54, 2, 64-69(1993)
3) idem; Preparation of Fine Ammonium Perchlorate by Freeze-Drying, Kagaku Kogaku Ronbunshu, 23, 2, 163-169(1997)
4) E. B. Baglay; End Corrections in the Capillary Flow of Polyethylene, J. Appl. Phys., 28, 5, 624-627(1957)

過塩素酸アンモニウム/末端水酸基ポリブタジエン系推進薬の製造性に関する実験的研究
ー未硬化推進薬の粘度に及ぼす操作温度の影響ー

甲賀　誠*，萩原　豊*

過塩素酸アンモニウム(AP)/末端水酸基ポリブタジエン(HTPB)系推進薬の製造において，未硬化推進薬の捏和と注型を容易にするために，未硬化推進薬の粘度は低いことが要求される。架橋剤を添加したHTPBの粘度は，時間の経過とともに増加する。しかし，架橋反応があまり進行していない初期段階において，その粘度は温度が高いほど小さいと考えられる。したがって，未硬化推進薬の捏和と注型における最適操作温度が存在する。本実験では，313～353Kにおいて，HTPBプレポリマ及び未硬化推進薬ドウの粘度と時間の関係を調べ，未硬化推進薬の捏和と注型の最適操作温度を見いだすことを試みた。未硬化推進薬の粘度と時間の関係は，架橋剤を添加したHTPBのそれらの関係とほぼ同じ傾向を示した。捏和と注型の最適な操作温度は，架橋剤を添加したHTPBの粘度が最も低い温度である。

(*防衛大学校 化学教室　〒239-8686 横須賀市走水1－10－20)