

Effects of addition of surfactants on viscosity of uncured ammonium perchlorate / hydroxyl - terminated polybutadiene propellant

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For the preparation of ammonium perchlorate (AP) / hydroxyl - terminated polybutadiene (HTPB) composite propellant, the lower viscosity of uncured propellant during mixing and casting is desirable. In this study, the effects of the addition of 11 kinds of surfactants on the viscosity of an uncured propellant are investigated. The results are as follows; 1) Sodium lauryl sulfate is the most effective to decrease the viscosity of the AP/HTPB mixture. The apparent viscosity of the AP/HTPB mixture with sodium lauryl sulfate can be made 30% lower than that of the AP/HTPB mixture alone. 2) The optimum added amount of sodium lauryl sulfate is 0.005wt% to HTPB, in order to obtain the sufficient effect of decreasing the viscosity of AP/HTPB mixture. 3) The apparent viscosity of AP/HTPB mixture can be decreased by the improvement of the wettability between AP and HTPB prepolymer. 4) The addition of sodium lauryl sulfate is effective to decrease the apparent viscosity of uncured propellant and to delay the potlife.

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 the preparation of AP/HTPB composite propellant, it is desirable for an uncured AP/HTPB propellant, which is a mixture of AP, HTPB and a curing agent, to have a lower viscosity.

In general, a surfactant is effective to decrease the viscosity of a solid/liquid mixture. It was reported that some surfactants were effective to decrease the viscosity of an ammonium nitrate

(AN) / HTPB mixture¹¹). However, the effects of the addition of surfactants on the viscosity of the AP/HTPB mixture without a curing agent or the uncured propellant have little been reported to date. In this study, the effects of the addition of 11 kinds of surfactants on the viscosity of the AP/HTPB mixture without a curing agent or the uncured propellant are investigated, and it is found that most of the surfactants used are effective to decrease the viscosity of such a mixture. In addition, because of the decrease in the viscosity of the uncured propellant based on the addition of a curing agent, potlife could be extended. Details on these investigations are reported in this paper.

2 Experimental

2.1 Samples

AP prepared by the freeze-drying method²⁾ is used. AP particles used in this study have the mean volume- surface diameter of $4 \times 10^{-6} \text{m}$, be-

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Table 1 Surfactant used in this study

Surfactant	Symbol
Sodium lauryl sulfate	A
Sodium dodecylbenzene sulfate	B
Sodium myristate	C
Linolic acid sodium salt	D
Laurylamine	E
Laurylamine acetate	F
Furflural	G
Tween 20	H
Tween 80	I
Emulgen 905	J
Trax	K

ing fine and unimodal unlike ones contained in the common propellant. The authors think that the effects of the addition of surfactants on the viscosity of AP/HTPB mixture could appear more clearly with use of AP/HTPB mixture of higher viscosity. 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 are used in this study. HTPB R-45M (ARCO Co.) prepolymer is 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 is 8wt% relative to HTPB³⁾, being an ordinary volume.

Surfactants used in this study are shown in Table 1. Surfactants A~D are anionic ones. Surfactants E and F are cationic ones. Surfactants G~K are nonionic ones. They were 0.001, 0.005 or 0.010wt% relative to HTPB.

2.2 Measurement of viscosity

The viscosity of an AP/HTPB mixture or an uncured propellant is measured by a flow tester (Shimadzu CFT-500C). A schematic diagram of the flow tester is shown in Fig. 1. For the AP/HTPB mixture, end correction in the capillary flow was carried out. For the uncured propellant, the end correction could not be carried out. The reason is as follows: Four viscosity data (combination between two dies and two loads) are required for the end correction in the capillary flow⁴⁾. Four viscosity data of the uncured

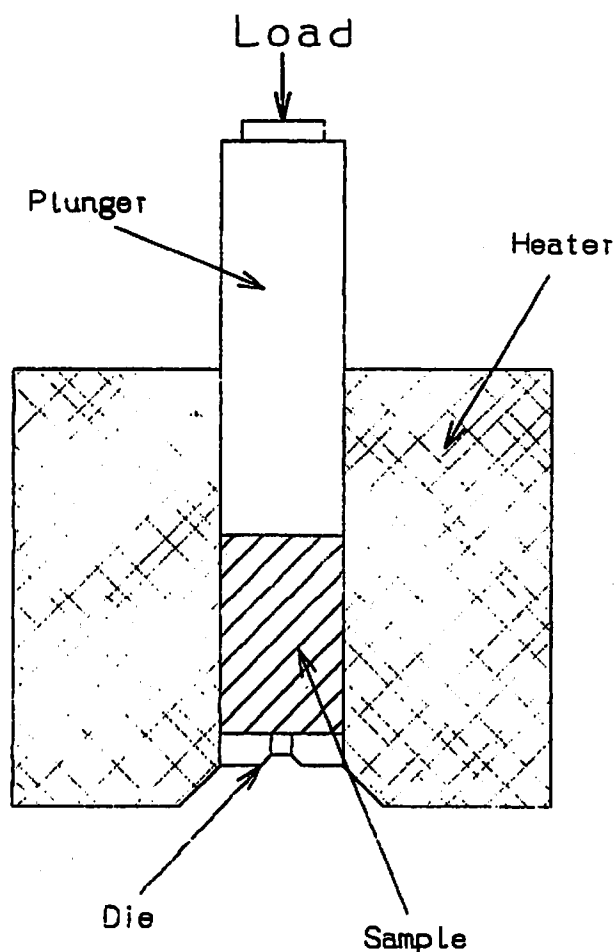


Fig. 1 Schematic diagram of the flow tester

propellant have to be obtained simultaneously, because the curing reaction of the uncured propellant proceeds continuously. Since it is difficult to obtain four viscosity data simultaneously, the end correction in the capillary flow can not be carried out with the uncured propellant. The viscosity of the AP/HTPB mixture or the uncured propellant was measured at temperature range between 313K and 353K. The accuracy of the temperature control was ± 1 K. The uncured propellant was always maintained at the measuring temperature in a constant temperature box. The measurement of viscosity of AP/HTPB mixture was conducted using a die with $\phi 1 \times 1$ mm or $\phi 1 \times 2$ mm under a load of 1.96MPa or 3.92MPa. 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.

2.3 Measurement of wettability

The wettability is measured by the penetration rate method⁵⁾. Contact angle, θ (deg) is rep-

resented by the following equation.

$$r \cdot \cos \theta = \frac{2\eta_L}{(S \cdot \epsilon_{\min} \cdot \rho_L)^2 \cdot \gamma_L} \cdot \frac{t}{W_L^2} \times 10^{-12} \quad (1)$$

where r (m) is a capillary diameter, S (m²) is a cross-sectional area of vessel, ϵ_{\min} (-) is a void fraction of powders at close packing measured by the tapping, ρ_L (kg/m³) is a density of disperse phase, γ_L (N/m) is a surface tension of disperse phase, t (s) is time and W_L (kg) is an osmotic mass of disperse phase. It is reported that it is difficult to measure r exactly⁵⁾. Other properties except r could be measured, easily. The wettability between AP and HTPB prepolymer was evaluated in the following way. In the case of the same AP sample under the constant tapping condition, it could be considered that the packing structure was almost constant, that is, r could be regarded as constant. The contact angle between AP and HTPB prepolymer is designated as θ_0 (deg) and the contact angle between AP and HTPB prepolymer in a case of containing a surfactant is designated as θ_1 (deg). By the calculating of the ratio of $r \cdot \cos \theta_1$ to $r \cdot \cos \theta_0$, r could be reduced and the wettability could be evaluated from the value of $\cos \theta_1 / \cos \theta_0$. That is to say, when $\cos \theta_1 / \cos \theta_0$ is more than unity, the wettability could be improved. Consequently, even if r can't be measured, the effects of an addition of surfactants on the wettability between AP and HTPB prepolymer can be evaluated from $\cos \theta_1 / \cos \theta_0$. The tapping was carried out with the tapping instrument (Hosokawa mikuron Co.). The value of t / W_L^2 was measured with the penetration rate instrument (Hosokawa mikuron Co., Peneto-analyzer).

3. Results and Discussion

3.1 Effect of addition of surfactant on viscosity of AP/HTPB mixture

3.1.1 Selection of most effective surfactant to decrease viscosity of AP/HTPB mixture

Because AP used in this study was fine particles(mean volume - surface diameter: 4×10^{-6} m), a propellant containing more than 80wt%AP could not be prepared. In this study the AP/HTPB mixture containing 80wt%AP was pre-

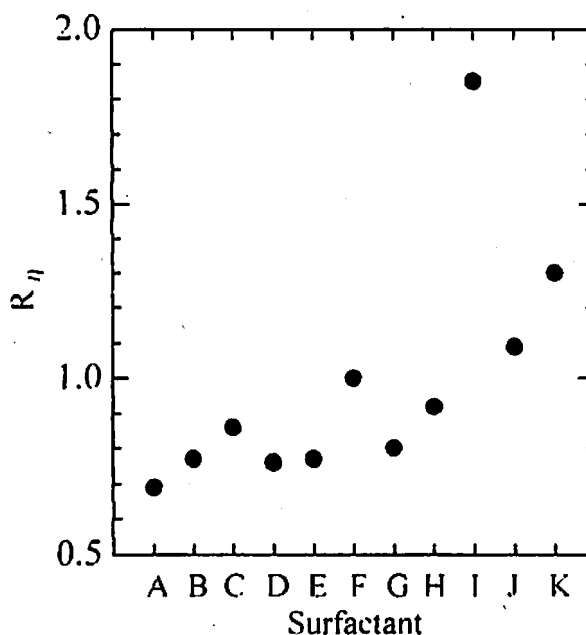


Fig. 2 Effect of surfactants on viscosity of uncured propellant (R_η : ratio of an apparent viscosity of AP/HTPB mixture with surfactant to an apparent viscosity of AP/HTPB mixture without surfactant)

pared, and the surfactants shown in Table 1 were added to the AP/HTPB mixture. The surfactant of 0.005wt% to HTPB was added to the AP/HTPB mixture without IPDI. The apparent viscosities of their AP/HTPB mixtures were measured at 333K. The ratio(R_η) of an apparent viscosity of AP/HTPB mixture with surfactant to an apparent viscosity of AP/HTPB mixture without surfactant was calculated. The results of R_η are shown in Fig. 2. Surfactants A~E, G and H were effective to decrease the viscosity of AP/HTPB mixture. Surfactant F had little influence on the viscosity of AP/HTPB mixture. The apparent viscosities of the AP/HTPB mixtures with surfactants I~K were larger than that of the AP/HTPB mixture alone. It is found that the surfactant effects on the apparent viscosity of AP/HTPB mixture are varied according to the added surfactant. By the addition of surfactants A, B, D and E, R_η was less than 0.80, and especially when surfactant A was added, R_η was minimized($R_\eta = 0.70$). It was found that surfactant A turned out the most effective to decrease the viscosity of the AP/HTPB mixture in this study. Surfactant A was used in the following investigation.

With respect to ammonium nitrate(AN)/HTPB

Table 2 Apparent viscosity and $\cos \theta_1 / \cos \theta_0$ of AP/HTPB mixture with surfactant A

SLS* (wt%)	Apparent viscosity ($\times 10^2 \text{Pa} \cdot \text{s}$)	$\cos \theta_1 / \cos \theta_0$
0.000	3.2	1
0.001	2.7	1.04
0.005	2.4	1.16
0.010	2.4	1.16

*Proportion of SLS to HTPB

mixture, the minimum of R_n is about 0.4¹⁾. This means that the effect of the addition of surfactant A on the decreasing viscosity of AP/HTPB mixture is smaller than that on AN/HTPB mixture.

3. 1. 2 Added amount of surfactant A

In order to investigate the effects of an added amount of surfactant A on the decreasing viscosity of the AP/HTPB mixture, surfactant A of 0.001, 0.005 or 0.010wt% to HTPB was added to the AP/HTPB mixture and each apparent viscosity of their AP/HTPB mixtures prepared with each added amount of surfactant A was measured. IPDI wasn't added to the AP/HTPB mixture in the same manner as section 3. 1. 1. The results are shown in Table 2. The apparent viscosity of the AP/HTPB mixture with 0.005wt% surfactant was almost the same as that of the AP/HTPB mixture with 0.010wt% one. The apparent viscosity of the AP/HTPB mixture with 0.001wt% surfactant was larger than that of the AP/HTPB mixture with 0.005 or 0.010wt% one. In order to obtain a sufficient effect of decreasing the viscosity by the addition of surfactant A, it was found that surfactant A of 0.005wt% to HTPB should be added to AP/HTPB mixture.

In order to investigate the effects of an addition of surfactant A on the wettability between AP and HTPB prepolymer, the following investigation was carried out. Surfactant A of 0.001, 0.005 or 0.010wt% to HTPB was added to HTPB prepolymer. $r \cdot \cos \theta_1$ and $r \cdot \cos \theta_0$ were measured, and $\cos \theta_1 / \cos \theta_0$ was calculated. The results on $\cos \theta_1 / \cos \theta_0$ are shown in Table 2. The $\cos \theta_1 / \cos \theta_0$ was larger than unity for all added amounts of surfactant A. This indicates that the

wettability between AP and HTPB can be improved by the addition of surfactant A. The $\cos \theta_1 / \cos \theta_0$ in the case of 0.005wt% surfactant was almost the same as that in the case of 0.010wt% one. The $\cos \theta_1 / \cos \theta_0$ in the case of 0.001wt% surfactant was smaller than that in the case of 0.005 or 0.010wt% one. It was found that this result of the wettability was similar to the tendency of a decrease in the apparent viscosity of AP/HTPB mixture with surfactant A, which showed that the wettability between AP and HTPB prepolymer through the addition of surfactant A was improved. This suggests that it is necessary to improve the wettability between AP and HTPB further in order to obtain the much lower apparent viscosity of AP/HTPB mixture. However, it is difficult to improve the wettability between AP and HTPB prepolymer further by the addition of surfactant A. Other techniques except the addition of surfactant should be devised for the improvement of the wettability. Surfactant A of 0.005wt% to HTPB was added in the following investigation.

3. 2 Effect of addition of surfactant on viscosity of uncured propellant

The viscosity of HTPB prepolymer decreases with an increasing temperature. On the other hand, after a curing agent is added to HTPB prepolymer, the viscosity of HTPB containing the 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 of the uncured propellant, which is an AP/HTPB mixture with IPDI, increases. The viscosity of the uncured propellant relates to the operating temperature⁶⁾. As mentioned in section 3. 1, the apparent viscosity of AP/HTPB mixture could be decreased by the addition of surfactant A. Therefore the viscosity of uncured propellant can be decreased by the addition of surfactant A. In order to investigate the influences of the operating temperature on viscosity of the uncured propellant with surfactant A, the apparent viscosities of the uncured propellant with surfactant A were measured at various temperatures between 313K and 353K. The relationships between the apparent

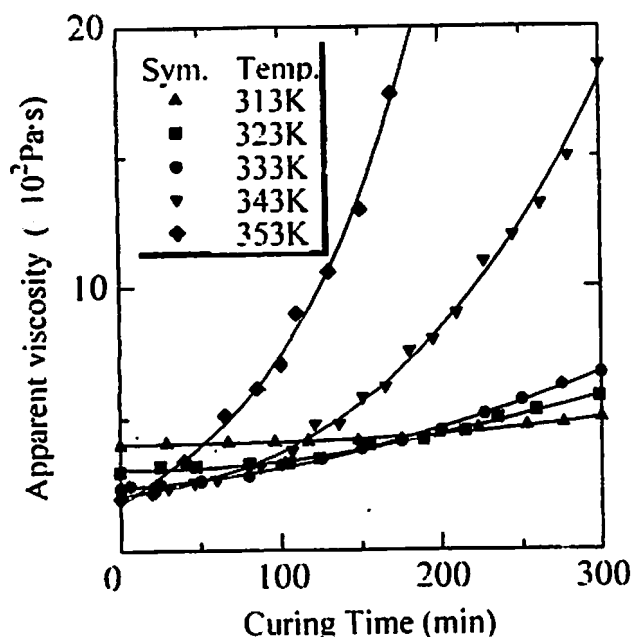


Fig. 3 Relationship between apparent viscosity of uncured propellant with surfactant A and curing time at some temperatures between 313K and 353K

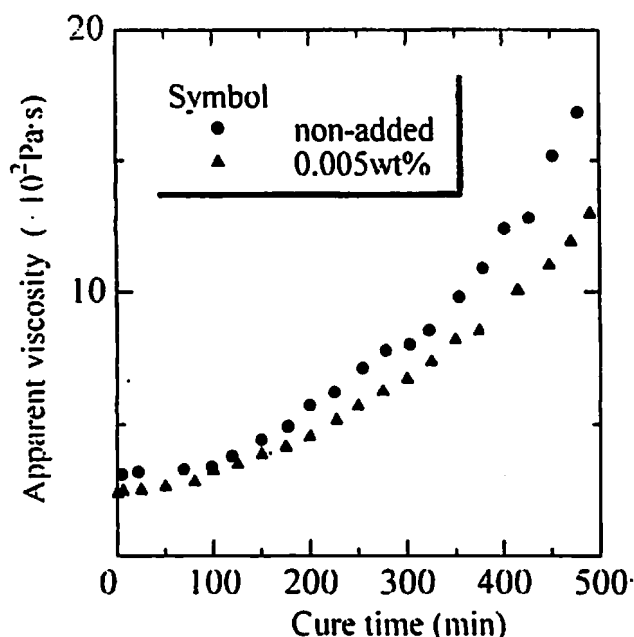


Fig. 4 Relationship between apparent viscosity of uncured propellant with or without surfactant A and curing time at 333K

viscosity of the uncured propellant with surfactant A and the curing time are plotted in Fig. 3. At a temperature of 353K, the apparent viscosity of uncured propellant with surfactant A remained the smallest for the first 20 minutes but increased rapidly thereafter. At a temperature of 343K, the apparent viscosities were smaller than those at 333K for the first 50 minutes but increased rapidly thereafter. In the temperature range from 313K to 333K, for the first 180 minutes they decreased with an increasing temperature and thereafter increased with increasing temperature. A lower viscosity of uncured propellant is desirable for the propellant processability. The operating temperature could be determined dependent on the time spent from the addition of a curing agent toward the end of casting⁶⁾. For example, when the time spent from the addition of the curing agent toward the end of casting was about 180 minutes, it turned out that 333K was the optimum operating temperature for the mixing and casting of uncured propellant. This result is the same as that of uncured propellant without surfactant⁶⁾. In following investigation, the operating temperature was 333K.

The apparent viscosity of the uncured propellant with surfactant A and that of the uncured propellant without surfactant A are showed against elapsing time in Fig. 4, being measured at 333K. The apparent viscosity of the uncured propellant with surfactant A is less than that of the uncured propellant without surfactant A. And the increasing rate of the apparent viscosity of the uncured propellant with surfactant A is slightly less than that of the uncured propellant without surfactant A. From the experimental results described above, it was found that the addition of surfactant A was effective not only to decrease the apparent viscosity of the AP/HTPB mixture, but also to decrease the apparent viscosity of uncured propellant. It could be considered that the reasons for the decrease in the apparent viscosity of the uncured propellant are the following two: 1) The improvement of the wettability between AP and HTPB, and 2) the interference of the curing reaction of HTPB. The influence of the addition of surfactant A on the viscosity of HTPB containing IPDI was investigated at 333K. The relationship between the apparent viscosity of HTPB containing IPDI with surfactant A and the curing time was almost the same as that of HTPB containing

IPDI without surfactant A. And if the uncured propellant with surfactant A was being cured at 333K for a week, the uncured propellant could be cured completely. These results indicate that the addition of surfactant A has little influence on the curing reaction of HTPB. From the results of these investigations, the decrease in the apparent viscosity of the uncured propellant was attributed to the improvement of the wettability between AP and HTPB in the same manner as for the AP/HTPB mixture without IPDI.

According to the experiment in this laboratory, the upper limit of apparent viscosity of the uncured propellant required to be cast is $4\sim5\times 10^2\text{Pa}\cdot\text{s}$. The range of viscosities was apparent ones and the particular values in this viscosity obtained by using this flow tester were not any universal ones. About the uncured propellant without surfactant A, the apparent viscosity obtained when 180minutes elapsed after the addition of IPDI is approximately $5\times 10^2\text{Pa}\cdot\text{s}$ and it is the upper limit of apparent viscosity required for casting in this study. Therefore, the potlife of the uncured propellant without surfactant A is approximately 180minutes. On the other hand, the apparent viscosity obtained when 230minutes elapsed after the addition of IPDI, of the uncured propellant with surfactant A is approximately $5\times 10^2\text{Pa}\cdot\text{s}$ and, therefore, the potlife of the uncured propellant with surfactant A is approximately 230minutes. These results indicate that the potlife can be extended by 50minutes through the addition of surfactant A. From the experimental results described above, it is seen that the addition of surfactant A is effective to decrease the apparent viscosity of uncured propellant and to prolong its potlife.

4. Conclusions

For the preparation of ammonium perchlorate (AP) / hydroxyl - terminated polybutadiene (HTPB) composite propellant, the lower viscosity of uncured propellant during mixing and cast-

ing is desirable. In this study, the effects of the addition of 11 kinds of surfactants on the viscosity of the uncured propellant are investigated. The results were as follows; 1) Sodium lauryl sulfate is the most effective to decrease the viscosity of the AP/HTPB mixture in this study. The apparent viscosity of the AP/HTPB mixture with sodium lauryl sulfate can be made 30% lower than that of the AP/HTPB mixture alone. 2) The optimum added amount of sodium lauryl sulfate is 0.005wt% surfactant to HTPB. 3) The apparent viscosity of the AP/HTPB mixture can be decreased by the improvement of the wettability between AP and HTPB prepolymer. 4) The addition of sodium lauryl sulfate is effective to decrease the apparent viscosity of uncured propellant and to delay the potlife.

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未硬化状の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粘度に及ぼす界面活性剤添加の効果

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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、捏和と注型の間の未硬化状の推進薬の粘度は低い方が望ましい。本実験では、未硬化状の推進薬の粘度に及ぼす11種類の界面活性剤添加の効果を調べた。その結果、次のような知見が得られた。1) 本実験において、ラウリル硫酸ナトリウムがAP/HTPB混合物の粘度を最も低下できた。ラウリル硫酸ナトリウムを添加したAP/HTPB混合物の見かけの粘度は、添加しない場合のそれより30%小さかった。2) 粘度減少に対する十分なラウリル硫酸ナトリウムの添加効果を得るためには、HTPBに対して0.005 wt%添加しなければならない。3) AP/HTPB混合物の見かけの粘度は、APとHTPB間の濡れを良くすることによって減少する。4) ラウリル硫酸ナトリウムを添加することによって、未硬化状の推進薬の見かけの粘度を減少させ、ポットライフを増加できた。

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