Viscoelastic Behavior of Hydroxyl Terminated Polybutadiene Containing Glycerin

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ABSTRACT: Hydroxyl terminated polybutadiene (HTPB) is widely used as a propellant binder. A plasticizer is usually added to improve the processing properties, the mechanical properties, and the burning characteristics of the propellant. Glycerin was found to be an effective additive to improve these properties. The glycerin/HTPB blend was hard enough to act as a binder for the composite propellant when the glycerin/HTPB mole ratio was less than 10. Only a small quantity of glycerin was incorporated into the network structure of the cured HTPB. Most of the added glycerin physically entered the voids in the network of the cured HTPB. Addition of a small quantity of glycerin (mole ratio less than 0.1) significantly altered the network density and the viscoelastic properties of the blends. The properties were only slightly dependent on the amount of the added glycerin in the mole ratio range of 0.1–10. The dangling ends were formed in the HTPB network by the addition of glycerin and the network structure was loosened, thereby enhancing the mobility of the chain segment. The viscoelastic properties of the blends followed the time-temperature superposition principle, and the properties were estimated accurately by the Williams-Landel-Ferry approach. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 706–713, 2011

Key words: propellant binder; glycerin; hydroxyl terminated polybutadiene; viscoelastic behavior

INTRODUCTION

A composite propellant is a type of solid propellant that consists of an oxidizer, binder, curing agent, metal fuel, burning catalyst, and other components. High-burning-rate propellants that generate a large quantity of combustion gases in a short time have been required to obtain high-performance rocket motors for enabling rockets to fly at higher speeds. Additionally, the propellant grain undergoes high stresses that are induced by a rapid acceleration, sharp turn, or rapid chamber pressure rise during launch and flying. A proper propellant must possess mechanical properties that prevent these stresses.

A plasticizer is usually a relatively low-viscosity chemically compatible liquid ingredient that is added to modify the mechanical properties of the propellant and to improve the processing properties, such as a lower viscosity for mixing and casting or a longer pot life than the uncured propellants. The burning characteristics, the mechanical properties, and the processability of composite propellants containing plasticizers have been investigated.[1–12]

In the previous paper,[13] the curing behavior, the theoretical performance, the mechanical properties, and the thermal decomposition behavior of the hydroxyl terminated polybutadiene (HTPB) containing glycerin were investigated to clarify effectiveness of glycerin as a plasticizer for HTPB. The addition of glycerin to the HTPB binder was effective in improving the processing properties and the mechanical properties of the binder.[13] Glycerin is not an energetic material, but it has three oxygen atoms in its molecular structure. For an ammonium perchlorate/HTPB-based composite propellant, the burning characteristics were improved by the addition of glycerin because the oxygen atoms in glycerin contribute to the combustion of the propellant.[14]

For the preparation of the glycerin-containing material, the HTPB is crosslinked with isophorone diisocyanate (IPDI), and the OH group of the HTPB molecule reacts with the NCO group of IPDI. In other words, the reaction of HTPB and IPDI is the urethane reaction.[15] The crosslinked HTPB has a rubbery consistency because the polybutadiene chain is very flexible. Glycerin has three OH groups in its molecular structure. Therefore, glycerin can react with IPDI and become incorporated into the network of the cured HTPB. In this manner, the network structure of HTPB can be varied by the addition of glycerin. In this study, the influence of glycerin on the viscoelastic behavior of the cured glycerin/HTPB blend was investigated. The details of these investigations are reported in this article.

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EXPERIMENTAL

Sample preparation

HTPB *R*-45*M* was used as the binder ingredient, and glycerin was used as an additive. The molecular weight of HTPB is 3270. IPDI was used as the curing agent. Glycerin was first added to the HTPB, and this mixture was then sufficiently blended for $\sim$ 5 min. Glycerin is a hygroscopic material. The moisture in glycerin was removed by molecular sieves before it was added to the HTPB. Next, the IPDI was added to this mixture, and it was mixed well for $\sim$ 10 min. IPDI was added in an amount of 8.14% of the HTPB; i.e., the ratio of the NCO group of IPDI to the OH group of the HTPB was 1.2. The glycerin/HTPB blends with IPDI were maintained in a temperature-controlled oven to cure for a week. The temperature of the oven was 333 K in this study because this temperature is suitable for the manufacture of HTPB-based propellants.[16]

Analytical methods

The FTIR spectra were recorded in the range of 4000–450 cm^{-1} using an FTIR spectrometer. The transmittance of the liquid sample and the reflectance of the cured sample were measured.

The network density of a crosslinked polymer was estimated by the degree of swelling by an appropriate solvent at equilibrium.[17] Toluene was used to swell the crosslinked HTPB.[18] A swelling test was carried out with a rectangular parallelepiped (20 $\times$ 20 $\times$ 2 mm) at 298 K. The weight of the swelled sample was measured directly by electric balance after removal from toluene and subsequent removal of surface solvent by means of filter paper. In a preliminary experiment, the sample was allowed to swell for 3 days, but remained at constant weight after 1 day, indicating that it had reached equilibrium. In this study, the sample was swelled for 2 days to ensure that it reached equilibrium.

The viscoelastic properties of the cured samples were measured by a commercial instrument, a dynamic mechanical analyzer (Tritec 2000, Triton Technology), in extension mode. The sample was a rectangular parallelepiped (6 $\times$ 3 $\times$ 20 mm). Both ends of the sample were mounted with clamps; one end was held and the other end was oscillated sinusoidally at a defined frequency and displacement. The gap between the clamps was 5 mm and the displacement was 0.01 mm. Temperature dependence of the blends was measured in the temperature range of 123–353 K at a frequency of 1 Hz and a heating rate of 5 K min^{-1}. Frequency dependence was measured in the temperature range of 233–333 K and the frequency range of 0.01–50 Hz. Under this strain condition, the material is in its linear viscoelastic region.

RESULTS AND DISCUSSION

Curing test

A mixture of glycerin and IPDI separated into two layers, and the glycerin was a viscous liquid even 1 week after it had been heated. This system did not have a formation of a crosslinked network although a part of the OH group of the glycerin molecule reacted with the NCO group of IPDI.

The glycerin/HTPB blend was hard enough to be of use as a binder for a composite propellant when the glycerin/HTPB mole ratio (ξ) was below 10. The cured blend was white, and the depth of the white color increased as the value of ξ increased. Above a ξ of 10, the glycerin adhered to the surface of the cured blend. Above a ξ of 20, the HTPB solidified, and glycerin remained as a liquid layer under the cured blend layer. That is to say, the blend above a ξ of 20 completely separated into two layers of the cured blend and liquid glycerin. It was found that the glycerin/HTPB blend was an emulsion in which HTPB dispersed with glycerin and the cured HTPB network contained tiny vacuoles of glycerin. Below a ξ of 10, the emulsion and the cured blend were a uniform white color and the cured blend did not separate into two layers of cured HTPB and liquid glycerin; this result indicates that HTPB and glycerin were mutually compatible and that glycerin dispersed uniformly in HTPB.

As described above, glycerin did not form a crosslinked network by IPDI. When the glycerin/HTPB blend was cured with IPDI, the main curing reaction was the urethane reaction between the OH group of HTPB and the NCO group of IPDI as reported in Ref. 15. Therefore, this blend system became a solid due to the formation of a network of mainly crosslinked HTPB.

HTPB in the blend above a ξ of 20 solidified as mentioned above. This indicated that the OH group of HTPB reacted with the NCO group of IPDI even when a large amount of glycerin was added. Most of the added glycerin separated into the liquid phase, and a part of the glycerin physically entered the voids in the network of the cured HTPB. The HTPB solidified and glycerin adhered to the surface of the cured HTPB above a ξ of 10, and the mixture with a ξ above 20 completely separated into two layers of the cured blend and liquid glycerin. These results suggested that for the blend with a ξ above 10, the glycerin could not physically enter the matrix of the cured HTPB.

The viscoelastic behaviors of the blends were investigated with ξ values below 10 in the following experiments. Table I lists the formulations of the blends prepared with ξ values below 10 used in this study.

TABLE I
Formulations of the Blends Used in this Study

Glycerin/HTPB mole ratio, ξ (–)	Mass fraction (%)		
	Glycerin	HTPB	IPDI
0	0	92.47	7.53
0.1	0.26	92.23	7.51
0.5	1.28	91.29	7.43
1.0	2.53	90.13	7.34
2.5	6.11	86.82	7.07
5.0	11.51	81.83	6.66
10.0	20.65	73.38	5.97

FTIR spectra

The FTIR spectra obtained for the liquid HTPB, IPDI, and glycerin are presented in Figure 1. For the HTPB, the band around 2920 cm^{-1} belongs to alkanes. The bands around 2260 cm^{-1} for IPDI and 3400 cm^{-1} for glycerin belong to the NCO group and the OH group, respectively.

Figure 1 also shows the FTIR spectra obtained for the cured HTPB and the cured glycerin/HTPB blends. The band around 2260 cm^{-1} belonging to the NCO group of IPDI is observed with low intensity in these FTIR spectra. This result indicates that the NCO group reacted with the OH group, thus forming the urethane bond. The hydroxyl band peak around 3400 cm^{-1} increases with increasing ξ; indicating that the quantity of the OH groups in the cured blend increases with increasing ξ. The OH group corresponded to glycerin that did not react with the NCO group of IPDI because the OH group of HTPB reacted with the NCO group of IPDI, as described in "Curing Test" section.

Determination of network density by swelling behavior

As described in "Analytical Methods" section, a crosslinked sample was swelled with toluene and the sample was swelled for 2 days to ensure that it reached equilibrium. The mass of the sample was measured before and after immersion in toluene, and the volumes were calculated. The density of toluene is 0.86 g cm^{-3}, and those of cured HTPB and the blends were in the range of 0.89–0.94 g cm^{-3}. The volume fraction of the crosslinked polymer in the swollen sample (v_s) was determined by dividing the volume before swelling by that of swollen HTPB. From the swelling experiment, v_s was calculated and is listed in
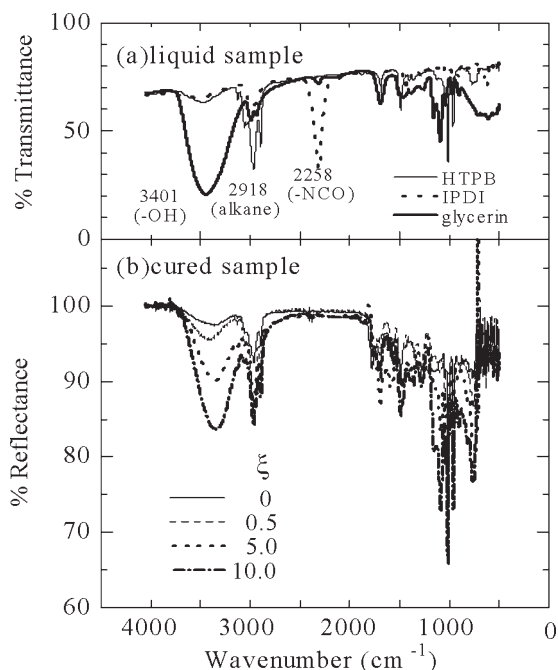

Figure 1 FTIR spectra of the liquid sample and cured blend.

Table II. The network density (N) of the polymer can be estimated by the value of v_s as follows [17]:

$$\ln(1 - v_s) + v_s + \chi v_s^2 = -NV_1\left(v_s^{1/3} - \frac{v_s}{2}\right) \qquad (1)$$

where χ is the polymer–solvent interaction parameter and V_1 is the molar volume of the solvent. The χ of the polybutadiene-toluene system is 0.35, and V_1 of toluene is 106 cm^3 mol^{-1}.[17] It can be assumed that χ of glycerin/HTPB blends would be almost the same as that of HTPB because only a small quantity of glycerin was incorporated into the network structure of the cured HTPB, as described in "Curing Test" section. The χ of the polybutadiene-toluene system, 0.35, was used as the polymer-solvent interaction parameter of the samples in this study. The N was calculated with eq. (1), and the results are also listed in Table II. The N decreases remarkably upon the addition of a small amount of glycerin, and the value is almost constant above a ξ of 0.5.

The decrease in N suggests that the degree of crosslinking, that is, network density reduces. In this study, the sample was mixed with HTPB, glycerin, and IPDI and the mass ratios were not constant. The network structure of the blend could not be

TABLE II
Values of v_s and N Determined by the Swelling Test

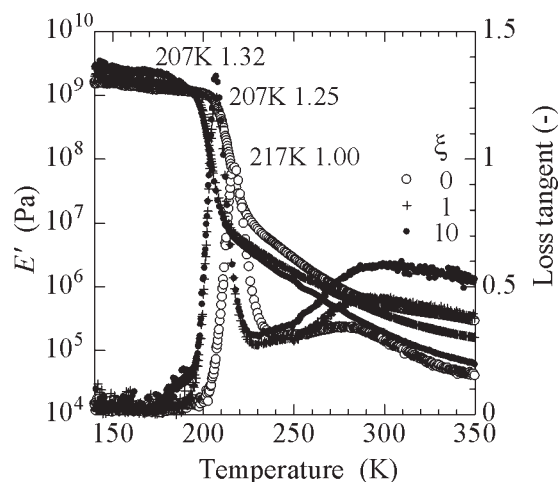| ξ (–)	0	0.1	0.5	1.0	2.5	5.0	10.0
v_s (–)	0.181	0.115	0.102	0.104	0.090	0.104	0.101
N ($\times 10^{-5}$ mol cm^{-3})	14.2	5.5	4.4	4.6	3.4	4.6	4.3

Figure 2 Temperature dependences of E' and loss tangent.

completely evaluated with the value of N alone; however, the decrease in N suggested that the network became looser. The N values of the blends were definitely smaller than that of HTPB, as shown in Table II. This result indicated that the network structure of HTPB became looser by the addition of glycerin. Incidentally, the cured HTPB ($\xi = 0$) was swollen very little by glycerin, and the value of v_s was above 0.99.

As described in "Curing Test" section, the glycerin-IPDI system was a viscous liquid, and therefore, a part of the OH group of the glycerin molecule reacted with the NCO group of IPDI. This suggests that a part of the glycerin in the blend could have reacted with IPDI and become incorporated into the network structure of the cured HTPB. In addition, the possibility exists that glycerin interfered with the HTPB-IPDI reaction. Therefore, the dangling ends were formed in the HTPB network by the addition of glycerin and the network structure was loosened.

Dynamic mechanical properties

Temperature dependence

Figure 2 shows the temperature dependences of the modulus (E') and the loss tangent for the cured blends with ξ values of 0, 1, and 10. The E' of the cured HTPB ($\xi = 0$) is almost constant below 200 K, but above that temperature, it decreases as the temperature increases. This thermogram has a remarkable decrease in the range of 205–225 K. For the cured blends, E' is almost constant below 185 K, but

above that, it decreases with increasing temperature. It decreases significantly in the range of 195–215 K. The E' of the blends is lower than that of the HTPB above ~ 195 K.

The loss tangent of the cured HTPB has a peak at 217 K. In contrast, the thermograms of the loss tangent for the blends have a peak around 207 K, and those for the blends have a broad peak around 290 K. The melting point of glycerin is 291 K. As mentioned in "Curing Test" section, a small quantity of glycerin can enter the voids in the network of the cured HTPB. The broad peak around 290 K may be due to the melting of the glycerin.

The temperature of the maximum loss tangent on the thermogram is the glass transition point (T_g). Table III shows T_g and the maximum loss tangent. The T_g of the cured HTPB is 217 K, while those of the cured blends are almost constant at 207 K and are lower than that of HTPB. The maximum loss tangent of the HTPB is 1.00, and those of the blends are almost constant in the range of 1.25–1.32. The maximum loss tangents of the cured blends are larger than that of the cured HTPB.

The values of T_g and the maximum loss tangent change with the addition of glycerin to the HTPB; indicating that the network structure of the sample matrix is altered by the addition of glycerin. However, they were scarcely dependent on the amount of glycerin. Glycerin can physically enter the network of the cured HTPB as described above. The amount of glycerin occluded in the network of the cured HTPB increased with increasing ξ. If the variations in the maximum loss tangent and T_g were caused by the glycerin that physically entered the matrix of the blend, these values should vary as ξ changes. As shown in Table III, the values of T_g and the maximum loss tangent were almost independent of ξ between $0.1 \leq \xi \leq 10.0$. Therefore, in this concentration range the changes in T_g and the maximum loss tangent are not due to the glycerin that physically entered the matrix of the blend.

The dynamic mechanical properties of a polymer are strongly influenced by its internal structure. The motion of the chain segments in the polymer structure has a profound effect on T_g and the loss tangent. The loss tangent is a sensitive indicator of crosslinking. As the degree of crosslinking decreases, the motion of the chain segments increases, thereby increasing the loss tangent.[19,20]

TABLE III
T_g and Maximum Loss Tangent Determined by the Temperature Dependence of the Cured Blend

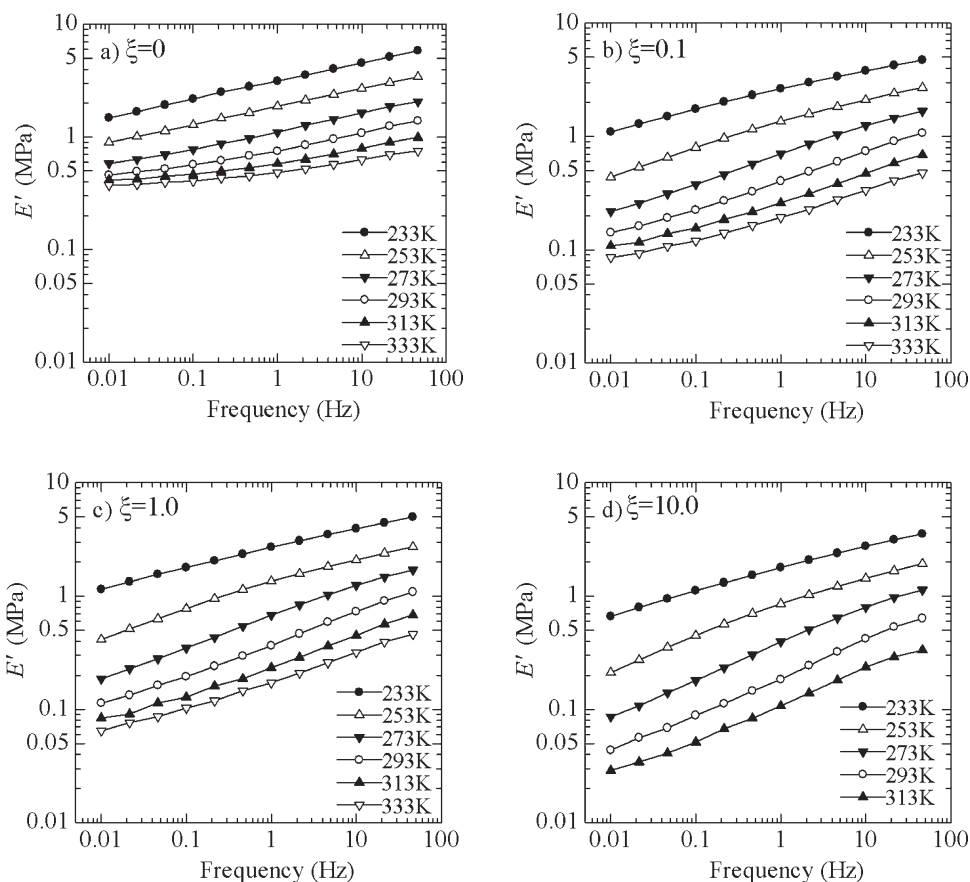| ξ (−)	0	0.1	0.5	1.0	2.5	5.0	10.0
T_g (K)	217	207	208	207	207	207	207
Maximum loss tangent (−)	1.00	1.26	1.26	1.25	1.26	1.29	1.32

Figure 3 E' as a function of frequency.

As described in "Determination of Network Density by Swelling Behavior" section, the dangling ends were formed in the HTPB network by the addition of glycerin and the network structure was loosened. Therefore, the mobility of the chain segment of the blends was enhanced by the addition of glycerin. As a result, T_g shifted to a lower temperature and the maximum loss tangent increased.

Frequency dependence

Figure 3 shows the frequency dependence of E' of the blend at ξ values of 0, 0.1, 1, and 10. For the blend with a ξ of 10, the data of E' above 323 K could not be obtained because the modulus was beyond the measureable range of the apparatus due to the softness of the material. For all the samples, E' increases with increasing frequency and decreases with increasing temperature. The variation in E' with frequency becomes greater as ξ increases.

Figure 4 shows the frequency dependence of loss tangent of the blend at ξ values of 0, 0.1, 1, and 10. For HTPB ($\xi = 0$), the frequency dependence at 233 K is not observed below 1 Hz, and above that the value of loss tangent increases with increasing frequency. The frequency dependence at 253 K is

scarcely detected in the range of 0.01–50 Hz. The frequency dependence at 273 K is observed below 0.5 Hz: the loss tangent increases with increasing frequency. Above 0.5 Hz, the value of loss tangent is almost constant. Above 293 K, the loss tangent at low frequency range decreases with increasing temperature, and this frequency range spreads to higher values as the temperature increases. At 313 and 333 K, the loss tangent increases with increasing frequency. Above 253 K, the value of loss tangent at 50 Hz is almost constant at ~ 0.3.

For the blend with a ξ of 0.1, the loss tangent at 233 K decreases below 0.1 Hz as the frequency increases, and it is almost constant in the range of 0.1–10 Hz and increases above 10 Hz. At 253 K, the loss tangent decreases with increasing frequency below 10 Hz, and above that it is almost constant. The relationship between loss tangent and frequency at 273 K has a peak at 0.2 Hz, and the relationship at 293 K has a peak at 1 Hz. The loss tangent at 313 and 333 K increases with increasing frequency. These relationships of the other blends are similar to those of the material with a ξ of 0.1. However, the distribution width of loss tangent increases with increasing ξ.

The frequency dependences of E' and the loss tangent of the blend containing glycerin were definitely
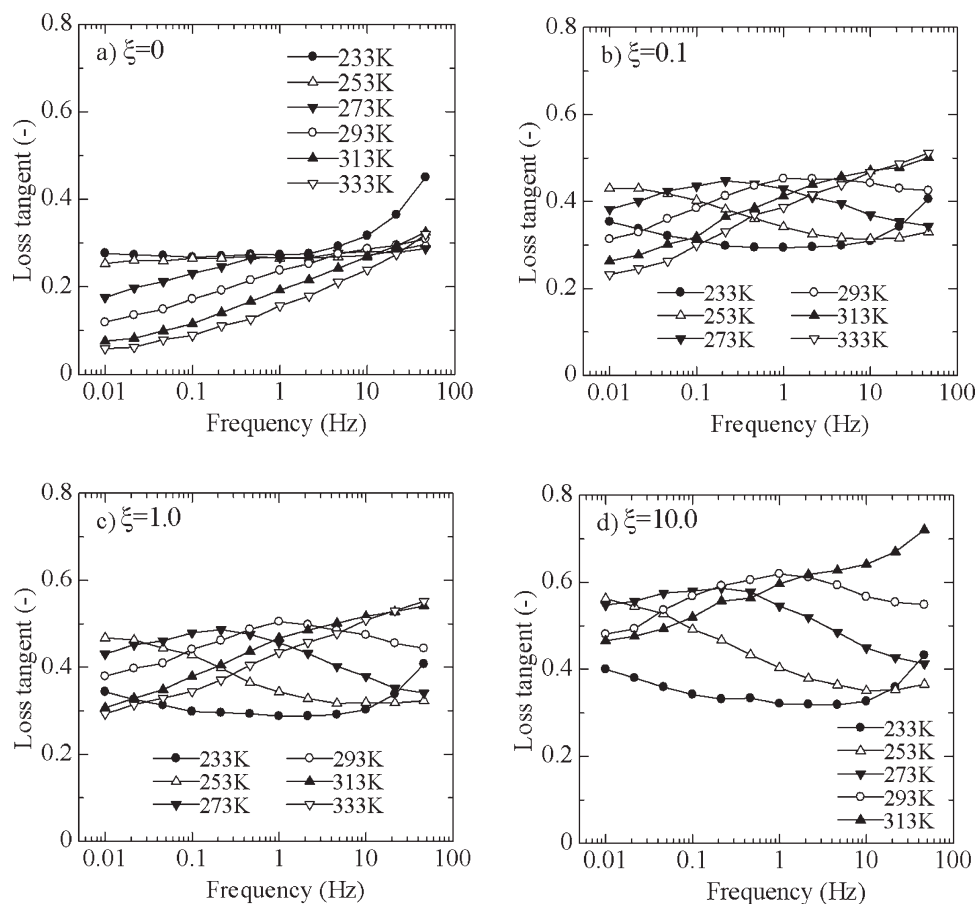
Figure 4 Loss tangent as a function of frequency.

different from those of HTPB, although they were only slightly dependent on ξ, i.e., the amount of glycerin. As mentioned above, only a small quantity of glycerin became incorporated into the network structure of the cured HTPB, and the amount of incorporated glycerin did not increase even when ξ increased. In contrast, the amount of the glycerin that physically entered the voids in the network of the cured HTPB increased with increasing ξ. And the glycerin that was physically occluded in the network of the cured HTPB could act as a lubricant to increase the lubricity of the network.

Application of Williams-Landel-Ferry approach

Making a master curve on the basis of the time–temperature superposition principle is a useful method to estimate the frequency dependence in a wide range.[21] If a master curve could be obtained, the frequency dependence in a wide frequency range that cannot be measured could be predicted with the data in a restricted frequency range.

Figure 5 shows the master curve of E'. The reference temperature of the master curve is 273 K. The plots fit on the master curves. It was found that the

viscoelastic properties of the blends followed the time–temperature superposition principle. This result suggested that the properties would be estimated accurately by the Williams-Landel-Ferry approach. According to this theory, the shift factor (α_t) is expressed as[21]

$$\log a_t = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)} \quad (2)$$

where T is temperature, T_0 is a reference temperature, and C_1 and C_2 are constants. The T_0 is usually taken as the sum of T_g plus a value less than 100 K. As shown in Table III, T_g of the samples was ∼ 210 K. The value of T_0 was 273 K, and this temperature was in the middle of the temperature range (233–333 K) measured in this study.

Figure 6 shows the plot of $\log \alpha_t$ as a function of T at ξ values of 0, 0.1, 1, and 10. The plots almost fit the eq. (2). The relationships of all the blends are almost the same, but they do not agree with that of HTPB (ξ = 0). From Figure 6, C_1 and C_2 were calculated, and the values are tabulated in Table IV. The C_1 and C_2 of the blends are almost constant, respectively, and are smaller than those of HTPB.
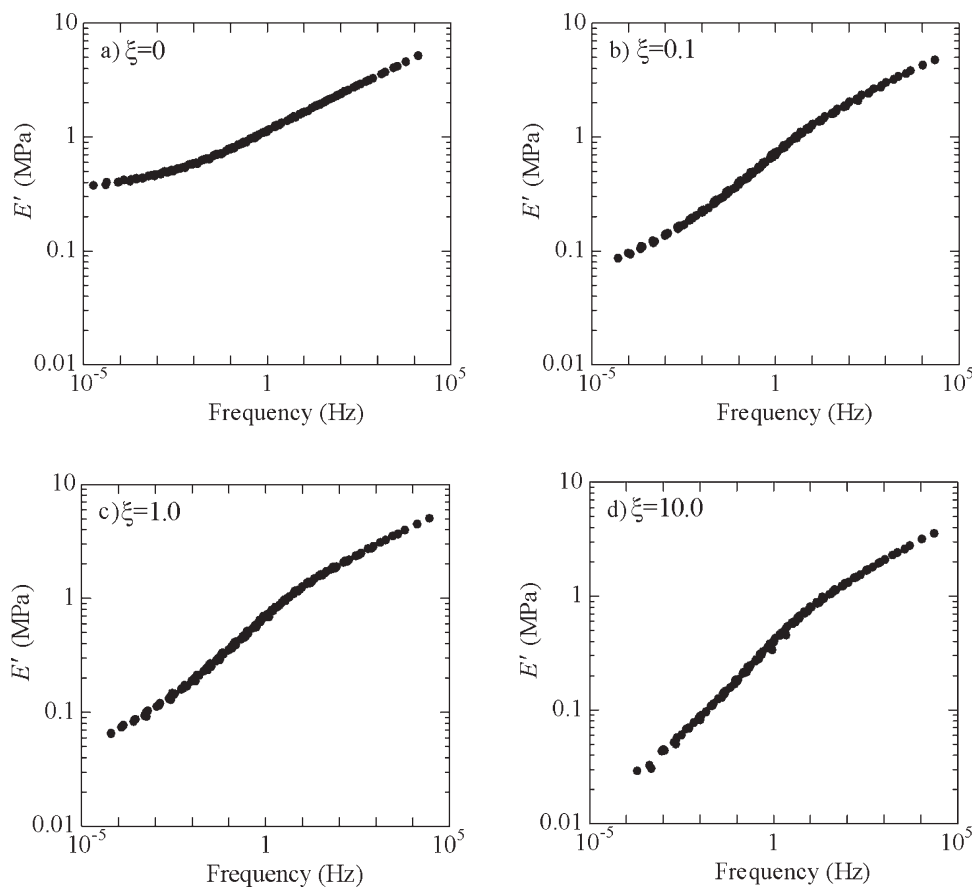
Figure 5 Master curve of E'.

The apparent activation energy of relaxation (E_a) is expressed as[21]

$$E_a = 2.303R\frac{d\log a_t}{dT^{-1}} \qquad (3)$$

The E_a can be calculated from the slope of the $\log\alpha_t$ versus T^{-1} plots. Figure 7 shows the plot of
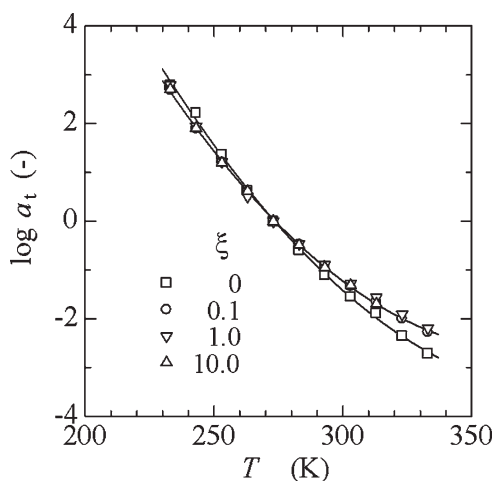

Figure 6 $\log\alpha_t$ as a function of T.

$\log\alpha_t$ as a function of T^{-1} at ξ values of 0, 0.1, 1, and 10. The relationship is represented by a straight line. Therefore, the plots almost fit the eq. (3). The E_a was calculated from Figure 7, and the values are tabulated in Table V. The E_a of HTPB is 86.9 kJ mol^{-1}, and that of the blend is almost constant at $\sim$ 75 kJ mol^{-1}. The E_a of the blend is smaller than that of HTPB. This result suggested that the relaxation of HTPB was made easier by the addition of glycerin. A low molecular weight chemical with limited compatibility can readily interfere with segment motions in HTPB. This indicates that a system in which the heterogeneity is increasing would exhibit changes in activation energy.

The viscoelastic properties of the blend containing glycerin were clearly different from those of HTPB, and they showed only a slight dependence on ξ. As mentioned above, only a small quantity of glycerin was incorporated into the network structure of the

TABLE IV
Values of C_1 and C_2

ξ (−)	0	0.1	0.5	1.0	2.5	5.0	10.0
C_1 (−)	12.78	7.23	7.75	7.98	7.77	8.79	7.45
C_2 (−)	210.09	137.12	150.75	162.04	137.26	161.91	138.18

Figure 7 $\log \alpha_t$ as a function of T^{-1}.

TABLE V
Values of E_a

ξ (—)	0	0.1	0.5	1.0	2.5	5.0	10.0
E_a (kJ mol^{-1})	86.9	75.3	73.4	72.4	77.9	76.6	76.0

bility of the chain segment of the blends. In this manner, the glycerin incorporated into the network structure of the cured HTPB affected the viscoelastic properties. The glycerin physically occluded in the matrix of the cured HTPB barely influenced the viscoelastic properties. It was found that the viscoelastic properties of the blends followed the time–temperature superposition principle, and the properties were estimated accurately by the Williams-Landel-Ferry approach.

cured HTPB, and most of the glycerin physically entered the voids in the network of the cured HTPB. The glycerin incorporated into the network affected the viscoelastic properties, while the glycerin physically occluded in the matrix of the cured HTPB did not.

CONCLUSIONS

The influence of glycerin on the viscoelastic behavior of the cured glycerin/HTPB blend was investigated. The glycerin/HTPB blend was hard enough to act as a binder for a composite propellant when the glycerin/HTPB mole ratio was less than 10. Only a small amount of the added glycerin was incorporated into the network structure of the cured HTPB, and the amount of incorporated glycerin did not increase even when the amount of the added glycerin increased. Most of the added glycerin physically entered the voids in the network of the cured HTPB. The network density was reduced by the addition of glycerin. The change in network density did not depend on the amount of the added glycerin. The dynamic mechanical properties of HTPB were not consistent with those of the glycerin/HTPB blends. The viscoelastic properties of the blends were only slightly dependent on the amount of the added glycerin. The dangling ends were formed in the HTPB network by the addition of glycerin and the network structure was loosened, thereby enhancing the mo-

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