The effect of nitrate esters on the thermal decomposition mechanism of GAP

Yunlan Sun, Shufen Li *
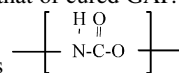
Department of Chemical Physics, University of Science & Technology of China, Hefei, Anhui 230026, China

Abstract

Thermal gravimetric analysis (TG), differential thermal analysis (DTA), and in situ Fourier Transform Infra-Red spectrometer (FTIR) experiments were used to investigate the thermal decomposition mechanism of glycidyl azide polymer (GAP) crosslinked by using the curing agent isocyanate compound N-100 and the different ratios of plasticized–cured GAP/NG/BTTN, which are of potential interest for the development of high performance energetic propellants. The results of TG show the thermal decomposition temperature of GAP shifted to lower temperatures in the presence of NG/BTTN. The decomposition peak temperatures of cured GAP/NG/BTTN (1:1:1), cured GAP/NG/BTTN (1:0.5:0.5) and cured GAP/NG/BTTN (1:0.25:0.25) decrease by approximately 20 °C, 33 °C and 39 °C compared with cured GAP, respectively. This indicates that plasticizers NG/BTTN have good acceleration effects on the decomposition of cured GAP, especially for low content of NG/BTTN. At the same time, the results of DTA show that the decomposition heat of cured GAP/NG/BTTN is larger than that of cured GAP. In situ FTIR results show NG/BTTN not only accelerate the decomposition of –N_3 groups and characteristic urethane links $\left[\begin{array}{c} \overset{H}{\underset{}{N}}\overset{O}{\underset{}{-}}\overset{\parallel}{C}-O \end{array}\right]$, but also accelerate the decomposition of C–O–C groups.

1. Introduction

Glycidyl azide polymer (GAP) is a unique energetic material with high enthalpy of formation as well as higher density. It was first reported in a patent in 1972 by Vandenburg [1] through the reaction of sodium azide in dimethylformamide with the polyepichlorohydrin, PECH-triol. GAP has a low glass transition temperature (−45 °C) and a low weight percentage of polymer weight-bearing chain. GAP decomposes very rapidly even at low temperature and produces fuel-rich decomposed products, which results in an energetically favourable binder system [2]. In addition, GAP is also used to replace inert binders in nitramine composite propellants. This replacement leads to higher burning rates and higher specific impulses. Moreover, the sensitivity property to the card gap test between the azide polymer and HTPB binder has no difference, and the binder decomposition has little effect on the sensitivity to the shock wave [3]. The safety characteristics of GAP loaded with RDX are almost the same as those for RDX compositions made with the inert HTPB binder [4]. Therefore, the studies of GAP are of particular interest, such as its synthesis [5], structure [6], physical, chemical and explosive properties [7], thermal characterization [8] and the decomposition mechanism [9]. Extensive experimental studies for GAP can be divided into two groups. The first group is devoted to the studies of the combustion of GAP [10,11], and the second to its thermal decomposition [12–14]. It can be found that the pure GAP has been studied extensively, but no studies have been conducted on the effect of nitrate esters NG/BTTN on GAP.

Nitrate esters such as NG and BTTN are colorless, odorless, viscous liquid under room conditions. They are energetic compounds that undergo self-sustained deflagration. Most of the energetic nitrate esters are explosives that possess low critical

* Corresponding author. Tel.: +86 551 3601137; fax: +86 551 3631760.
*E-mail address:* lsf@ustc.edu.cn (S. Li).

diameters, high volatility and high sensitivity, making them difficult to handle. The primary role of energetic nitrate esters in solid propellants are used as the energetic plasticizers to modify the mechanical properties. The poor mechanical properties of GAP can be improved markedly by incorporation of energetic azido functional plasticizers. GAP plasticizers are compatible with GAP polymer, as are nitrate esters such as BTTN [2].

The present work focuses on obtaining mechanism information on the thermal decomposition of the effect of nitrate esters NG/BTTN on GAP. It is hoped that this work would be useful in providing a clearer understanding of high performance energetic solid propellant studies.

2. Experimental

2.1. Raw material

Glycidyl azide polymer (GAP, MW = 3000 g/mol); GAP/NG/BTTN (1:1:1, 1:0.5:0.5, 1:0.25:0.25). GAP was cured with isocyanate compound N-100 at 65 °C using a constant NCO/OH ratio of 1.3. NG/BTTN were added to the pure GAP as plasticizers and mixed, followed by curing in the case of the plasticized–cured samples. N-100 is a curing agent possessing terminal isocyanate groups. Although N-100 is not a pure material, the structure shown below is representative.
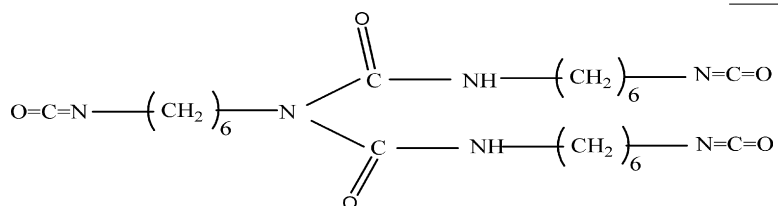
2.2. Thermal decomposition experiments

TG-DTA experiments were carried out with Shimadzu DTG-60H TG-DTA instruments at a heating rate of 10 °C/min (at atmosphere = flowing N_2 gas at a rate of 20 ml/min). The sample weights are 6–7 mg and the sample pans are alundum.

2.3. In situ FTIR experiments

In situ FTIR measurements of cured GAP and cured GAP/NG/BTTN were performed with a Nicolet Magna 750 FTIR spectrometer in the temperature range of 25–470 °C. Spectra were recorded using KBr pellets in the 4000–400 cm^{-1} region with a resolution of 2 cm^{-1}. In order to make the temperature steady, the heating rate is 2 °C/min for the temperature-controlled FTIR experiments. The heating profile is linear and the atmosphere is N_2 gas. The samples were dissolved by dichloromethane and then were prepared in KBr pellets. The samples were heated by a heater and the thermocouple contacts the samples. The FTIR analyses were performed on the solid residues of the samples during the thermal decomposition.
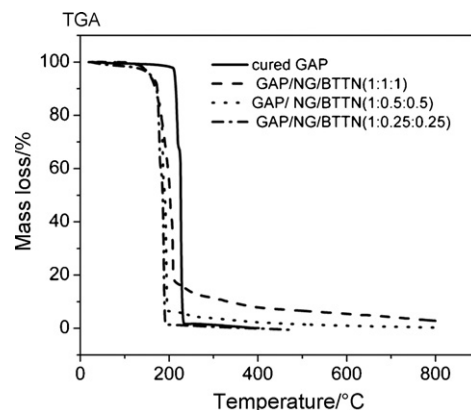

Fig. 1. The TG curves of cured GAP and cured GAP with different ratios of NG/BTTN.

3. Results and discussion

3.1. Thermal characterization of cured GAP and cured GAP/NG/BTTN

The typical TG and DTA curves for cured GAP and different ratios of cured GAP/NG/BTTN are given in Figs. 1 and 2, illustrating the decomposition characterization and the decomposition heat of cured GAP and cured GAP with addition of different content plasticizers NG/BTTN.

The representative TG curves of cured GAP, cured GAP/NG/BTTN (1:1:1), cured GAP/NG/BTTN (1:0.5:0.5) and cured GAP/NG/BTTN (1:0.25:0.25), are shown in Fig. 1. The cured GAP shows a step of mass loss. The step covers a temperature region from ∼200 °C to ∼277 °C and involves a mass loss of ∼98%. However, the cured GAP/NG/BTTN (1:1:1) shows two steps of mass loss. The first step demonstrates a mass loss of 84.6% in the temperature region of ∼92–234 °C.
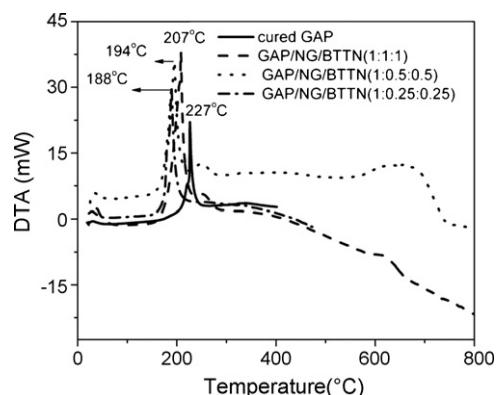

Fig. 2. The DTA curves of cured GAP and cured GAP with different ratios of NG/BTTN.

Table 1
Summarized exothermal results for DTA experiments of cured GAP and different contents GAP/NG/BTTN

Sample	ΔH_{exo} (J/g)
Cured GAP	223
Cured GAP/NG/BTTN (1:1:1)	898
Cured GAP/NG/BTTN (1:0.5:0.5)	438
Cured GAP/NG/BTN (1:0.25:0.25)	356

The second step covers a temperature region from $\sim$234 °C to $\sim$795 °C and the percentage of the mass loss is 12.3%. The cured GAP/NG/BTTN (1:0.5:0.5) also shows two steps of mass loss. The first step takes place $\sim$85 °C with a $\sim$95% rapid weight loss. The mass loss for the second step occurs from $\sim$199 °C to $\sim$575 °C and the percentage of the mass loss is 5%. It is very interesting that the cured GAP/NG/BTTN (1:0.25:0.25) like cured GAP only show a step of mass loss, and there is a mass loss of 97% in the temperature region of $\sim$65–201 °C.

By comparing the TG curves of cured GAP and different ratios of GAP/NG/BTTN, it can be seen that nitrate esters NG/BTTN make thermal decomposition temperature of GAP shift to lower temperature.

Fig. 2 shows the DTA curves of cured GAP and cured GAP/NG/BTTN (1:1:1, 1:0.5:0.5, 1:0.25:0.25). It can be seen from Fig. 2 that different contents of NG/BTTN make the decomposition peak temperatures of GAP decrease. The decomposition peak temperatures of cured GAP/NG/BTTN (1:1:1), cured GAP/NG/BTTN (1:0.5:0.5) and cured GAP/NG/BTTN (1:0.25:0.25) decrease by 20 °C, 33 °C and 39 °C compared with cured GAP, respectively. This indicates that plasticizers NG/BTTN accelerate the decomposition of GAP. Moreover, the effect of GAP/NG/BTTN (1:0.5:0.5) is the best.

Table 1 shows exothermal results for DTA experiments of cured GAP and different ratios of GAP/NG/BTTN. It can be found from Table 1 that the heat of decomposition of cured GAP/NG/BTTN is larger than that of cured GAP. Furthermore, the heat of decomposition of cured GAP/NG/BTTN increases with the increasing contents of NG/BTTN.

3.2. In situ FTIR of cured GAP

Fig. 3 shows the in situ FTIR spectra of cured GAP at 25 °C, 200 °C, 226 °C, 280 °C, 350 °C, 400 °C and 450 °C, respectively. At 25 °C, the two adsorption peaks at 2939 cm^{-1} and 2871 cm^{-1} appear due to C–H and –CH$_2$– asymmetric stretching vibrations and symmetric stretching vibrations, respectively. The frequencies are close for the two adsorption peaks of stretching vibrations. This illustrates that –CH$_2$– and C–H directly connect with the element O or N. The characteristic peak, 2100 cm^{-1} is of –N$_3$ antisymmetric stretching vibrations. The adsorption peak at 1698 cm^{-1} is attributed
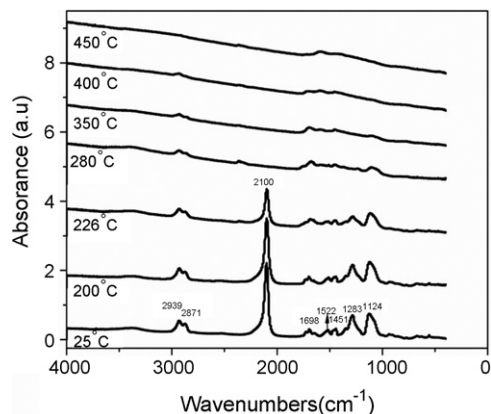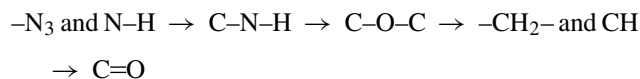

Fig. 3. The in situ FTIR curves of cured GAP at different temperatures.

to vibrations of C=O. The two peaks at 1522 cm^{-1} and 1451 cm^{-1} appear due to N–H bending of $-NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}$ and –CH$_2$– deformation, respectively. The adsorption peaks at 1283 cm^{-1} and 1124 cm^{-1} are attributed to –C–N–H stretching vibrations and C–O–C stretching vibrations.

It can be seen from Fig. 3 that the IR spectra at 200 °C is in accordance with that at 25 °C, which suggests decomposition of cured GAP would not occur when heated to 200 °C. This is consistent with the result of TG. As for the IR spectra of cured GAP at 226 °C, all of the intensities of adsorption peaks weaken compared with those at 25 °C, indicating the occurrence of decomposition reaction of cured GAP. With further heating to 280 °C, the two peaks at 2100 cm^{-1} and 1522 cm^{-1} disappear and the intensities of the adsorption peaks at 2939 cm^{-1}, 2871 cm^{-1}, 1451 cm^{-1}, 1283 cm^{-1} and 1124 cm^{-1} remarkably decrease, suggesting the main decomposition reactions of cured GAP taking place in the temperature region. This can be also testified by the experimental result of the TG, which involves a mass loss of $\sim$98% in the temperature region. At the same time, it is worth noting that the –N$_3$ groups have disappeared completely, but the C–O–C groups have existed at 280 °C. From this result we are able to infer that the rate of –N$_3$ bond cleavage is faster than that of monomer frame cleavage of GAP. When heated to 350 °C, the peak at 1283 cm^{-1} disappears and the intensity of others peaks continue to decrease. At 400 °C, the peak at 1124 cm^{-1} disappears. Heating to 450 °C, the adsorption peaks almost completely disappear.

As discussed in the above mentioned, it can be concluded that the order of adsorption peaks disappears as following:

$$-N_3 \text{ and } N\text{–}H \rightarrow C\text{–}N\text{–}H \rightarrow C\text{–}O\text{–}C \rightarrow -CH_2- \text{ and } CH$$
$$\rightarrow C=O$$

Cured GAP is formed by polyaddition reaction of isocyanate group (–NCO) with alcoholic hydroxyl groups (–OH).
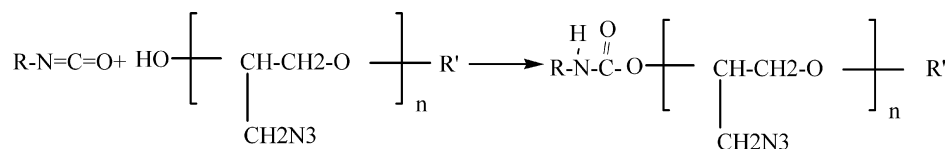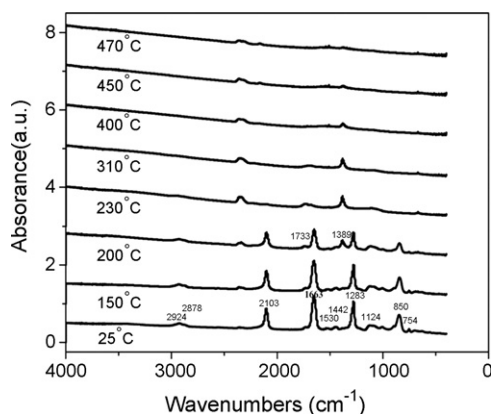
Fig. 4. The in situ FTIR curves of cured GAP/NG/BTTN (1:1:1) at different temperatures.

According to the order of adsorption peaks disappearance, one can see that the –N$_3$ groups of cured GAP initially decompose, then cured GAP begins to decompose to the monomer. The decomposition of the monomer frame obviously lags behind than that of the –N$_3$ groups. This can be certified from the results that the C–O–C groups disappear above 350 °C. As the temperature increases, the frame of cured GAP begins to decompose. When the temperature continues to increase, the compound completely decomposes.

According to the above results, it is obvious that the decomposition of the cured GAP is believed to start with the initial decomposition of –N$_3$ groups, and then the characteristic urethane links $\left[\begin{array}{c} \text{H} \ \text{O} \\ | \ || \\ \text{N-C-O} \end{array}\right]$ decompose. Finally, the monomer frames decompose. This finding is consistent with the results of thermal decomposition mechanism of the gaseous products from thermal decomposition of GAP cured with isocyanate compounds [15], where R.I. Wagner et al. found that in addition to the gaseous products from GAP, most of the N-100 crosslinking agent is liberated as hexamethylene diisocyanate (HMDI). Furthermore, the initial products detected in the gaseous phase were the isocyanate compound HMDI formed by breaking of the urethane bond and evaporation of the intact isocyanate molecule N-100.

3.3. In situ FTIR of cured GAP/NG/BTTN

The room temperature at 25 °C and high-temperature FTIR spectra of cured GAP/NG/BTTN (1:1:1) are shown in Fig. 4. At 25 °C, the absorption peaks at 2924 cm^{-1} and 2878 cm^{-1} correspond to C–H and –CH$_2$– antisymmetric stretching vibrations and symmetric stretching vibrations, respectively. The absorption peak observed at 2103 cm^{-1}, which is the characteristic peak of GAP, is of the –N$_3$ antisymmetric stretching vibrations. Absorption peaks observed at 1530 cm^{-1} and 1442 cm^{-1} may be attributed to N–H bending of -NH-C-O- ($\overset{\text{O}}{||}$) and –CH$_2$– deformation, respectively, while that at 1663 cm^{-1} and 1283 cm^{-1} are assignable to the –NO$_2$ antisymmetric and symmetric stretching vibrations, respectively, in the plasticizer. The absorption

peak at 1124 cm^{-1} is attributed to C–O–C stretching vibrations. The absorption peak at 850 cm^{-1} appears due to O–N stretching vibrations. At 754 cm^{-1}, the absorption peak is attributed to O–NO$_2$ bending vibrations.

The IR spectra of cured GAP/NG/BTTN (1:1:1), subjected to different temperatures from 25 °C to 470 °C show preferential loss in the intensity of peaks. For cured GAP/NG/BTTN (1:1:1), the absorbance peaks at 25 °C almost match those at 150 °C, no new absorbance peak appearing, only the intensities of these peaks weaken. This shows that some components such as NG and BTTN begin to decompose. Increasing the temperature to 200 °C, the absorbance peak of N–H bending of -NH-C-O- ($\overset{\text{O}}{||}$) disappears, while new absorption peak appears at 1389 cm^{-1}. This is characteristic of the NO$_3$$^-$ stretching vibrations. In the meantime, the absorbance peak of C=O stretching vibrations at 1733 cm^{-1} increases in the intensity. The increase in the intensity of the peak at 1733 cm^{-1} implies that nitrate esters begin to decompose and the initial decompositions start with rupture of weak O–NO$_2$ bond, elimination of molecular NO$_2$ and producing aldehyde group. The product of NO$_3$$^-$ is due to the KBr absorbing the NO$_2$ [16]. Further heated to 235 °C, this resulted in remarkable changes in the spectra. There are only the absorbance peaks of C–H and –CH$_2$– antisymmetric stretching vibrations and symmetric stretching vibrations, NO$_3$$^-$ stretching vibrations, C–O–C stretching vibrations and the C=O groups stretching vibrations. Others absorbance peaks completely disappear. This implies that in the temperature range of 150–230 °C, fast decomposition reactions of cured GAP/NG/BTTN occur. This is consistent with the TG results. It can be observed that the main thermal decomposition of the cured GAP/NG/BTTN (1:1:1) occurred in the temperature range of 150–230 °C. Moreover, the O–NO$_2$, –NO$_2$ and –N$_3$ groups completely decompose in this temperature range. At the same time the intensities of absorbance peaks at 1389 cm^{-1} and 1733 cm^{-1} reach maximum. This indicates that the O–NO$_2$ groups of nitrate ester have completely ruptured. However, the intensity of absorbance peak of C–O–C is still very strong. This illuminates that cured GAP/NG/BTTN (1:1:1) still contains the undecomposed polyether. When the temperature gets to 310 °C, the intensities of absorbance peaks at 1389 cm^{-1} and 1733 cm^{-1} decrease and the absorption peak of C–O–C basically disappears. Heated to 400 °C, the absorption peaks of C–O–C and C=O completely disappear, and the intensity of absorption peak of NO$_3$$^-$ continues to decrease. Heating to 470 °C, the intensity of absorption peak of NO$_3$$^-$ is very little. According to the FTIR results, it can be noted that the first weight loss step of cured GAP/NG/BTTN (1:1:1) in TGA experiment mainly involves the rupture of O–NO$_2$ and –N$_3$. The second weight loss step mainly involves the decomposition of the products of the first step and residual polyether.

On comparison of Figs. 3 and 4, it is evident that the additions of nitrate esters within the cured GAP accelerate the disappearance of N–H bending of -NH-C-O- ($\overset{\text{O}}{||}$) and –CH$_2$– deformation, and make them disappear at 200 °C and 235 °C, respectively.
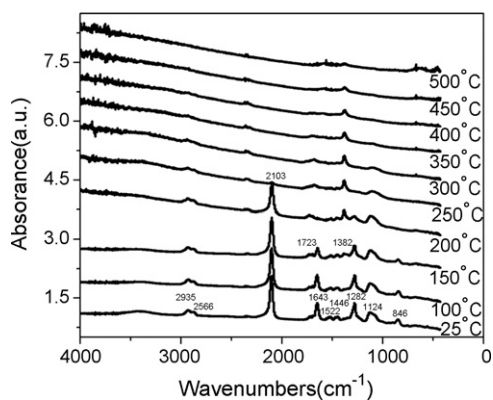
Fig. 5. The in situ FTIR curves of cured GAP/NG/BTTN (1:0.25:0.25) at different temperatures.

While without addition of nitrate esters in the cured GAP, the absorption peaks of N–H bending of $-NH\overset{\overset{O}{\|}}{-C}-O-$ and $-CH_2-$ deformation disappear at 280 °C and 400 °C, respectively. As far as the $-N_3$ groups of cured GAP/NG/BTTN (1:1:1) disappear at 235 °C, but the $-N_3$ groups of cured GAP disappear at 280 °C. C–O–C groups of the monomer frame of GAP basically disappear at 310 °C and 350 °C, respectively, for the cured GAP/NG/BTTN (1:1:1) and cured GAP. Therefore, the effect of the addition of nitrate esters within cured GAP not only accelerate the decomposition of $-N_3$ groups and characteristic urethane links $-\left[-N\overset{\overset{H}{|}\overset{O}{\|}}{-C}-O-\right]-$, but also accelerate the decomposition of C–O–C groups.

Fig. 5 shows the IR spectra of cured GAP/NG/BTTN (1:0.25:0.25). At 150 °C, the intensities of absorbance peaks began to weaken, especially for the $-NO_2$ antisymmetric vibrations at 1643 cm^{-1}. At the same time, new absorption peaks appear at 1382 cm^{-1}. When the temperature increases to 200 °C, the most significant changes were found in the ranges of the characteristic frequencies of nitro group ($-NO_2$), indicating that NG/BTTN basically decompose completely at this temperature.

On comparison of Figs. 4 and 5, it can be found that absorption peaks of $-NO_2$ groups basically disappear for GAP/NG/BTTN (1:0.25:0.25) at 200 °C, while the intensity of absorption peak of $-NO_2$ groups for GAP/NG/BTTN (1:1:1) is still very strong at this temperature. This confirms that NG/BTTN in GAP/NG/BTTN (1:0.25:0.25) decompose in advance compared with that in GAP/NG/BTTN (1:1:1). Furthermore, the decompositions of NG/BTTN occur exothermal reaction, and heat generation accelerates the decomposition of GAP, so that the decomposition peak temperature of GAP/NG/BTTN (1:0.25:0.25) shifts to lower temperature compared with that of GAP/NG/BTTN (1:1:1) as shown Fig. 2.

4. Conclusions

Thermal properties of cured GAP and cured GAP/NG/BTTN were determined by TG-DTA analyses. The addition of different contents NG/BTTN within cured GAP makes the thermal decomposition temperature of cured GAP shift to lower temperatures and the decomposition peak temperatures of the cured GAP/NG/BTTN (1:1:1), cured GAP/NG/BTTN (1:0.5:0.5) and cured GAP/NG/BTTN (1:0.25:0.25) decrease by 20 °C, 33 °C and 39 °C compared with cured GAP, respectively, so plasticizers NG/BTTN have good acceleration effects on the decomposition of cured GAP, especially for the cured GAP/NG/BTTN (1:0.25:0.25). The decomposition heat of GAP is increased by the addition of NG/BTTN, and the decomposition heat increases with the contents NG/BTTN increasing.

In situ FTIR analysis shows that nitrate esters NG/BTTN accelerate the decomposition of $-N_3$ groups and characteristic urethane links $-\left[-N\overset{\overset{H}{|}\overset{O}{\|}}{-C}-O-\right]-$ and C–O–C groups. Hence, the additions of the NG/BTTN make the decomposition temperatures of cured GAP decrease. Nitrate esters NG/BTTN in GAP/NG/BTTN (1:0.25:0.25) decompose in advance compared with that in GAP/NG/BTTN (1:1:1), so that the decomposition peak temperature of GAP/NG/BTTN (1:0.25:0.25) shifts to lower temperature compared with that of GAP/NG/BTTN (1:1:1).

Acknowledgement

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