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Thermal decomposition study of hydroxyl-terminated polybutadiene (HTPB) solid fuel

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Abstract

Thermal analysis has been conducted on R-45M resin, Isonate 143L crosslinking agent, and cured HTPB polymer to determine the thermal decomposition processes, energy changes, and kinetic parameters. The results show that thermal decomposition processes of the cured HTPB polymer are predominantly characterized by the R-45M resin, and confirm that the urethane bond cleavage is the first step in the decomposition. After the urethane bonds are cleaved and the diisocyanate volatilizes (above approximately 430°C), HTPB behaves as though it had never been crosslinked. Increasing the heating rate of HTPB polymer increases the extent of the first-stage decomposition and decreases its exothermicity, implying augmentation of the depolymerization process. The activation energies and pre-exponential factors of thermal decomposition for test samples were determined. Results also indicate that adding the curing agent to the polybutadiene resin has a greater influence on the energetics than on the kinetics of R-45M decomposition.

Keywords: Diisocyanate crosslinking agent; Hydroxyl-terminated polybutadiene (HTPB); Solid fuel; Thermal decomposition

1. Introduction

Hydroxyl-terminated polybutadiene (HTPB) has long been one of the most commonly used polymers in composite solid propellants. Its role in composite solid propellants is mainly two-fold: (1) to serve as a binder material to physically accommodate different propellant ingredients (such as oxidizer, metal particles, and burn-rate

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modifiers) in its matrix, and (2) to serve as a fuel constituent to release fuel-rich gaseous products when decomposed and pyrolyzed. In order to achieve fairly good mechanical properties, HTPB is usually mixed with a diisocyanate crosslinking agent, and then cast into the desired grain configuration before it is completely cured, i.e., hardened.

Recently, cured HTPB has also been considered one of the most promising solid fuels for application in hybrid propulsion systems because of its high heat of combustion when reacting with oxidizers (usually liquid oxygen (LOX) or gaseous oxygen (GOX)). The specific impulse delivered by an HTPB/GOX or HTPB/LOX system is comparable to that of solid and liquid propellants. Other advantages, such as safety in manufacturing and handling, throttling capability, less sensitivity to crack combustion, and fewer pumping mechanisms than liquid rockets fuels, render hybrid propulsion even more attractive.

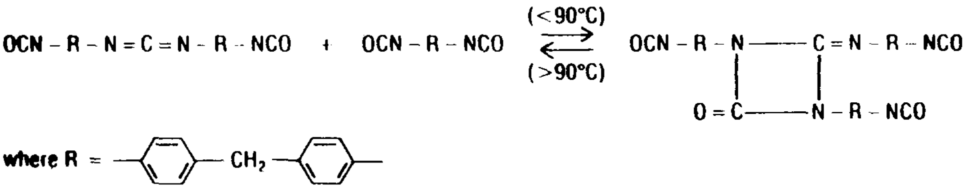
A considerable number of decomposition and pyrolysis studies on HTPB polymers have been conducted in the past [1–15]. These studies have greatly enhanced our understanding of the detailed thermal decomposition and pyrolysis characteristics of HTPB polymers. The objective of the present work was to study by thermal analysis the thermal decomposition processes, energy changes, and kinetic parameters of an HTPB resin, a modified diisocyanate curing agent, and the cured HTPB polymer. The cured HTPB polymer was used as the solid fuel for a series of experimental studies on hybrid propulsion conducted at PSU by the authors and co-workers [16].

2. Experimental

2.1. Materials

The HTPB homopolymer in the solid fuel considered was the hydroxyl-terminated Poly bd resin R-45M obtained from Elf Atochem North America, Inc. The average molecular weight of R-45M is 2800, and the hydroxyl content is 0.73 meq g^{-1}. The homopolymer comprises approximately 20% cis-1,4 structure, 60% trans-1,4 structure, and 20% vinyl-1,2 structure.

The curing agent used, a modified diisocyanate Isonate 143L with an NCO equivalence value of 144.5 g eq^{-1}, was obtained from DOW Chemical Co. The chemical structure of Isonate 143L is shown below.



The cured HTPB was prepared by complete mixing of R-45M and Isonate 143L at an NCO:OH ratio of 1.05. Thus,

$$\frac{\text{mass of 143L}}{\text{mass of R-45M}} = 1.05\frac{\text{eq}_{\text{NCO}}}{\text{eq}_{\text{OH}}} \times 0.73 \times 10^{-3}\frac{\text{eq}_{\text{OH}}}{\text{g}_{\text{R-45M}}} \times 144.5\frac{\text{g}_{\text{143L}}}{\text{eq}_{\text{NCO}}} = 0.11 \qquad (1)$$

This ratio represents 9.91% Isonate 143L and 90.09% R-45M in the prepared samples. The mixture was conditioned and cured in a vacuum chamber to drive out any gas bubbles. The urethane linkage is responsible for hardening the polymer. The curing time for R-45M/Isonate 143L is only around 10 h. The more commonly used R-45M/IPDI (isophorone diisocyanate) combination requires at least 24 h of curing time. The reduction in curing time proved to be very useful in preparing cured HTPB samples for the hybrid propulsion experimental test runs conducted at PSU.

2.2. *Apparatus*

Thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTG), and differential scanning calorimetry (DSC) measurements were made on a Mettler TG50 and DSC 27HP thermal analysis system. The heating rates ranged from 10 to 100°C min^{-1}, with a 100–200 cm^3 min^{-1} flow of nitrogen gas. The maximum temperature was around 720°C. The initial sample weights ranged from 5.83 to 20.33 mg.

3. Results and discussion

Fig. 1 shows the TGA, DTG, and DSC thermal curves of R-45M resin heated at 10°C min^{-1} up to 720°C. R-45M shows two major weight-loss stages with indistinct separation, as also noted in Refs. [2] and [3]. At this heating rate, the first stage exhibits a much smaller amount of weight loss and a much smaller maximum rate of weight loss than the second stage. The maximum rate of weight loss occurs around 382°C for the first stage, and at around 457°C for the second stage. Some of the important parameters associated with TGA and DSC analyses are given in Table 1. All of the sample was

Table 1
Some important thermal analysis parameters of different test samples

Sample	TGA				DSC	
	First stage		Second stage		First stage	
	Max. rate of weight loss/ ($\%\ s^{-1}$)	Temp. of max. rate of weight loss/°C	Max. rate of weight loss/ ($\%\ s^{-1}$)	Temp. of max. rate of weight loss/°C	Net exothermicity J g^{-1}	Temp. of exothermic peak/°C
R-45M	0.02	382	0.37	457	1220.5	376
Isonate 143 L	0.11	201	0.16	301	−7.1	145
Cured HTPB (10°C min^{-1})	0.03	351	0.32	461	795.4	366
Cured HTPB (50°C min^{-1})	0.65	387	1.19	492	699.6	392
Cured HTPB (100°C min^{-1})	2.30	377	1.84	483	502.1	404

consumed before the temperature reached 520°C. According to Ref. [3], the first stage is primarily depolymerization, cyclization, and crosslinking, accompanied by partial decomposition of the cyclized products. The major gaseous products are produced from the volatilization of low molecular weight hydrocarbons such as 1,3-butadiene (C_4H_6), cyclopentene, cyclohexadiene, and 4-vinylcyclohexene (C_8H_{12}). The second stage primarily involves decomposition of the cyclized products, with the rate of decomposition increasing with temperature; meanwhile, depolymerization and cyclization reactions gradually disappear in the second stage.

The DSC trace shows that the first stage is net exothermic, and the second stage is net endothermic. The exothermicity of the first peak was calculated on the basis of the DSC peak area, the baseline of which is also shown in Fig. 1. The calculated net heat release is 1220.5 J g^{-1}, with the exothermic peak at 376°C. The net exothermicity in the first peak indicates that the energy released from the formation of new bonds during crosslinking and cyclization of R-45M is greater than the energy absorbed for bond scission during depolymerization. It should be noted that the actual exothermicity per unit weight of

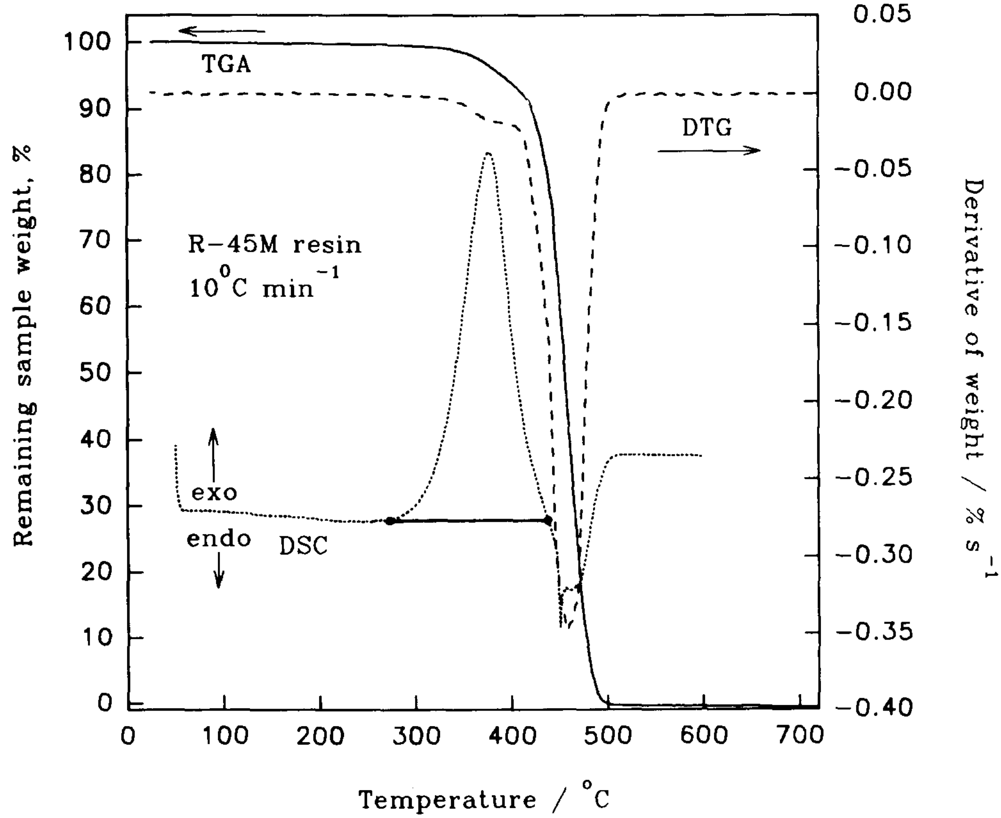


Fig. 1. TGA, DTG, and DSC traces for R-45M resin at 10°C min^{-1} heating rate. The line segment between the two dots on the DSC curve is the baseline for the exothermicity calculation.

R-45M should be greater than the value reported since the above calculation did not account for weight variation during the heating process.

The kinetic parameters of thermal decomposition of R-45M were deduced from the TGA curve using the following simple first-order reaction model

$$d\alpha/dt = A\exp(-E_a/RT)(1-\alpha) \tag{2}$$

where α is the weight fraction of the reacted sample, i.e., extent of reaction, R the universal gas constant (8.313 J mol^{-1} K^{-1}), T the temperature, t the time, E_a the activation energy in J mol^{-1}, and A the pre-exponential factor in s^{-1}. The deduced Arrhenius parameters A and E_a, along with their temperature ranges, for the first and second stages of R-45M decomposition are given in Table 2. It should be noted that the activation energy of 130.3 kJ mol^{-1} for the first-stage decomposition is very close to that reported in Ref. [3] (115.5 kJ mol^{-1}) and falls within the range reported in Ref. [13] (82.0–146.1 kJ mol^{-1}), even though the samples studied in these works are all different. The pre-exponential factor is also within the range (10^5–10^7 s^{-1}) generally quoted in the literature, e.g., Refs. [3] and [13]. The activation energy of the second stage is about twice that of the first stage. Fig. 2 shows the plot of the calculated and measured rate constants (k) versus temperature, i.e. the Arrhenius plot, where k is defined by

$$\ln k \equiv \ln A - E_a/RT = \ln(d\alpha/dt) - \ln(1-\alpha) \tag{3}$$

It is evident that the agreement is reasonably good.

Fig. 3 shows the TGA, DTG, and DSC traces of Isonate 143L heated at 10°C min^{-1} up to 720°C. As can be seen, Isonate 143L also exhibits two major weight-loss stages with indistinct separation. In each stage, several sub-steps can be identified by the slope changes in the DTG curve. The maximum decomposition rate and the temperature of the maximum decomposition rate are 0.11% s^{-1} and 201°C for the first stage, and 0.16% s^{-1} and 301°C for the second stage. As opposed to R-45M, Isonate 143L exhibits a slight net heat consumption for the bond scission in the first peak and a net heat release for subsequent reactions in the second peak. A significant amount of Isonate 143L residue (ranging from 10 to 30% of the initial weight) was left in the crucible after

Table 2
Kinetics parameters of different tested samples

Sample	First stage			Second stage		
	$\ln A/\mathrm{s}^{-1}$	$E_a/\mathrm{kJ\ mol}^{-1}$	Temp./°C	$\ln A/\mathrm{s}^{-1}$	$E_a/\mathrm{kJ\ mol}^{-1}$	Temp./°C
R-45M	15.6	130.3	329–376	38.8	265.9	423–480
Isonate 143 L	6.1	51.0	151–200	1.5	37.9	239–303
Cured HTPB (10°C min^{-1})	14.3	115.4	307–348	37.9	261.9	415–478
Cured HTPB (50°C min^{-1})	34.5	219.0	320–373	–	–	–
Cured HTPB (100°C min^{-1})	21.6	152.5	314–361	–	–	–

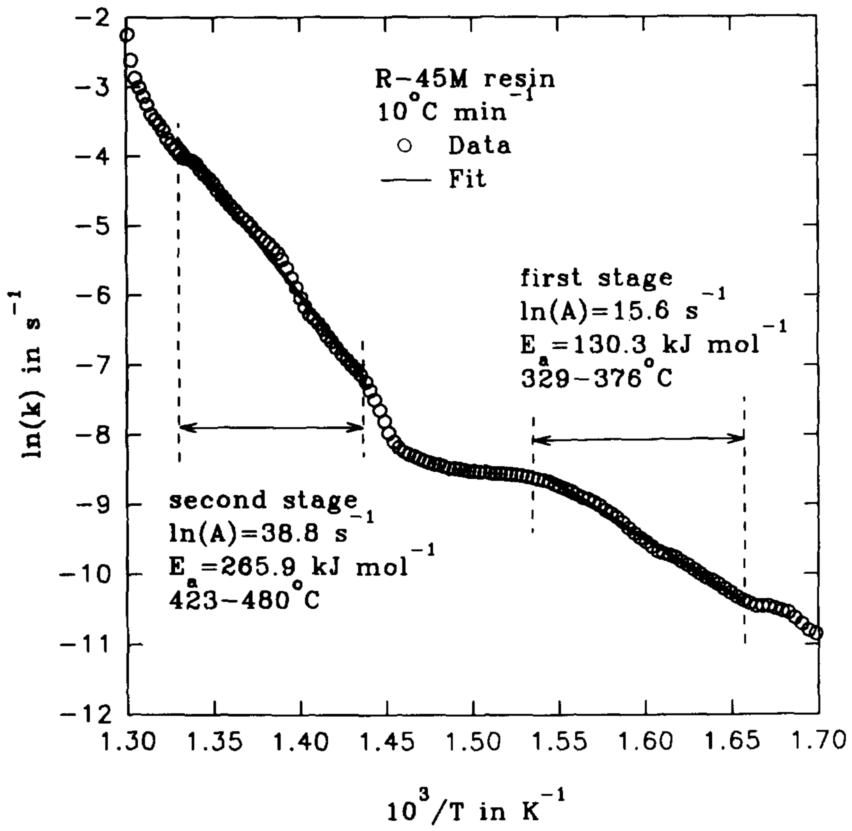


Fig. 2. Arrhenius plot for R-45M resin for the kinetics of weight loss measured by TGA.

each TGA or DSC test. The deduced Arrhenius parameters and the temperature range for the first and second stages are given in Table 2. The activation energies are very small for both stages. Fig. 4 shows the Arrhenius plot for Isonate 143L.

The TGA, DTG, and DSC curves of crosslinked R-45M/Isonate 143L polymer heated at 10°C min^{-1} up to 720°C are shown in Fig. 5. As can be seen, the thermal decomposition of the cured HTPB predominantly exhibits the characteristics of R-45M (compare Fig. 1). This is expected since R-45M constitutes more than 90% of the sample weight. The difference is that the first-stage decomposition of the cured HTPB is slightly more pronounced and occurs somewhat earlier than for R-45M resin. This finding agrees with the postulation that the cleavage of the urethane linkage of the cured HTPB is the first step during thermal decomposition [2,9]. No distinct sub-step separation is shown in the first weight-loss stage; this simply implies that urethane bond cleavage and depolymerization, crosslinking, and cyclization of R-45M all occur close to one another without much temperature difference. This weight-loss pattern is very similar to that of the HTPB/DDI (dimeryl diisocyanate) sample shown in Ref. [2]. The

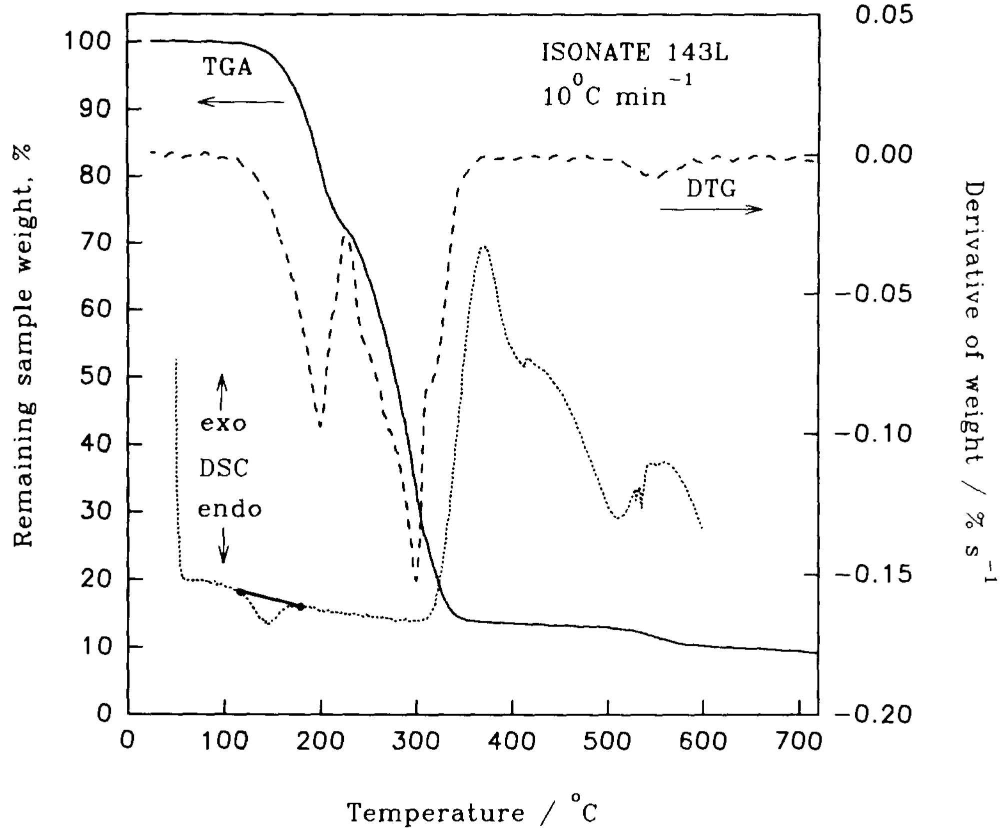


Fig. 3. TGA, DTG, and DSC traces for Isonate 143L at 10°C min^{-1} heating rate. The line segment between the two dots on the DSC curve is the baseline for the exothermicity calculation.

maximum rate of weight loss occurs at around 351°C for the first stage, and at around 461°C for the second stage. Other important parameters associated with TGA and DSC analyses are again given in Table 1.

Similar to R-45M, the entire cured HTPB sample was consumed before the temperature reached 520°C, despite the presence of 10% Isonate 143L in the original sample. It should also be noted that R-45M and crosslinked HTPB polymer exhibit almost identical thermal decomposition behavior when the temperature is above about 430°C, as indicated by the similarity of the TGA and DTG curves in Figs. 1 and 5. The slight difference in maximum decomposition rate is simply due to the effect of the difference in initial sample weight (18.175 mg for cured HTPB vs. 20.33 mg for R-45M) [3,13]. At a temperature of 430°C, the remaining weight of R-45M is about 91.0% (from Fig. 1), and that of cured HTPB 81.7% (from Fig. 5). The percentage difference is very close to the mass fraction of Isonate 143L in the initial cured HTPB sample. The above observations indicate that once the urethane linkages are cleaved and the Isonate 143L volatilizes, the remaining HTPB polymer behaves essentially as though it had never

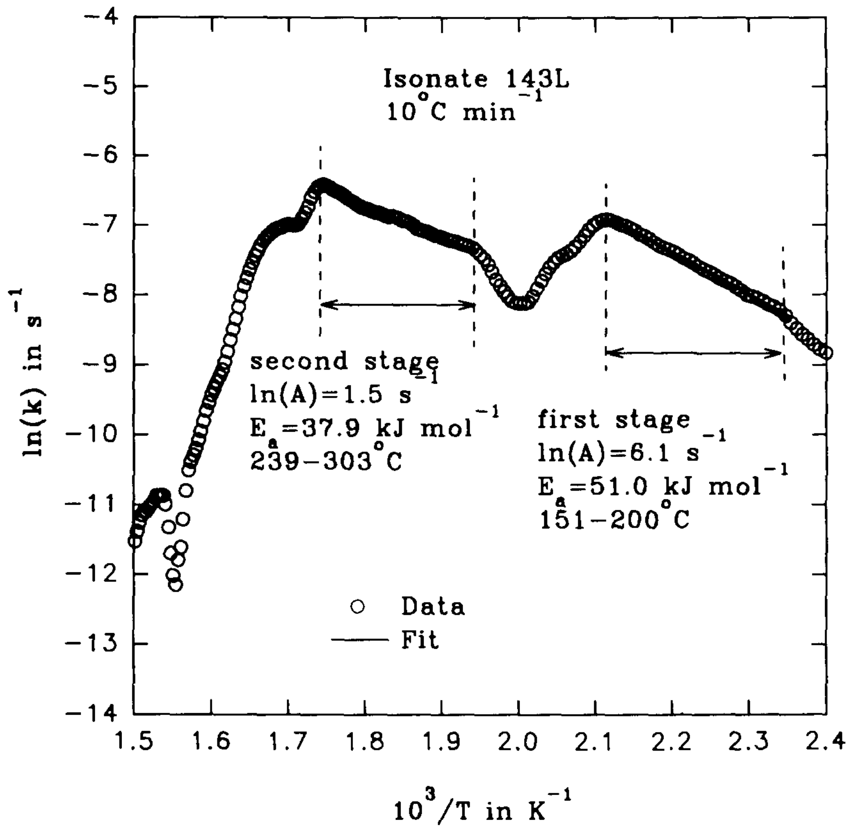


Fig. 4. Arrhenius plot for Isonate 143L for the kinetics of weight loss measured by TGA.

been urethane-crosslinked. This postulation agrees with the IR spectrum analysis of HTPB residues reported in Ref. [2]. It is interesting to note that the co-existence of R-45M and Isonate 143L in the cured HTPB polymer improved the process of decomposition of Isonate, since no Isonate 143L residue was left from the cured HTPB sample as opposed to that of the pure Isonate sample.

The DSC trace shows that the first stage is net exothermic, and the second stage is net endothermic. Note that the influence of the slight endothermic reactions of Isonate 143L which peaked at around 145°C was totally absent in the trace of the cured HTPB sample. The calculated exothermicity of the first-stage decomposition is 795.4 J g^{-1}, which is about 35% smaller than that of R-45M. The deduced activation energy is 115.4 kJ mol^{-1} and the natural log of the pre-exponential factor is 14.3 s^{-1} for the first stage (from 307 to 348°C), and 261.9 kJ mol^{-1} and 37.9 s^{-1} for the second stage (from 415 to 478°C). Thus, compared to the results for R-45M, it is clear that mixing the urethane crosslinking agent in R-45M has a greater influence on the energetics than on the kinetics for the decomposition of HTPB polymer. Fig. 6 shows the Arrhenius plot of the cured HTPB sample.

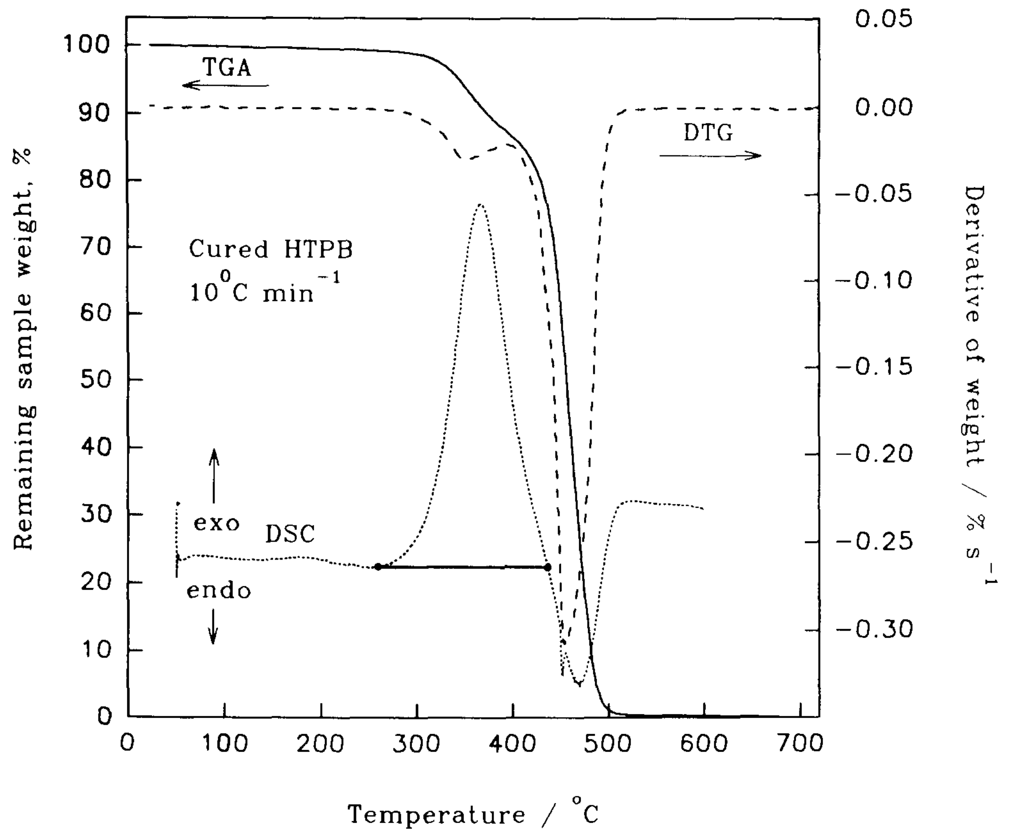


Fig. 5. TGA, DTG, and DSC traces for cured HTPB at 10°C min^{-1} heating rate. The line segment between the two dots on the DSC curve is the baseline for the exothermicity calculation.

Cured HTPB polymer was also heated at higher heating rates of 50 and 100°C min^{-1}; some of the important parameters determined from thermal analysis are included in Tables 1 and 2. The results indicate that the increase in heating rate increases the maximum rate of weight loss in both stages and renders the rate of the first-stage decomposition closer to and even greater than that of the second stage. Depolymerization (endothermic process) increases with higher heating rates, while crosslinking and cyclization (exothermic processes) decrease; this leads to the decrease in exothermicity in the first peak (see Table 2). The temperature of the DSC exothermic peak increases with the heating rate. Even though the pattern of two major weight-loss stages still exists at higher heating rates, there are other more pronounced sub-steps in each stage, which makes it more difficult to model weight loss by the simple first-order reaction mechanism represented by Eq (2); this is especially true for the second-stage decomposition.

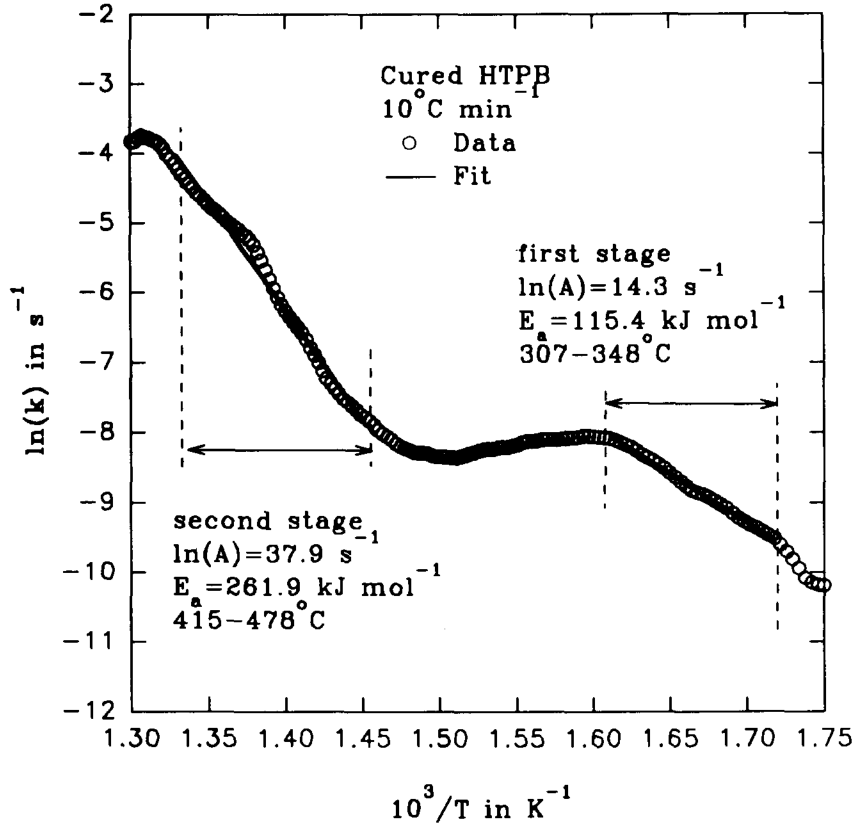


Fig. 6. Arrhenius plot for cured HTPB for the kinetics of weight loss measured by TGA.

4. Conclusion

Thermal analysis has been conducted on R-45M resin, Isonate 143L crosslinking agent, and cured HTPB polymer to determine thermal decomposition processes, energy changes, and kinetic parameters. Results indicate that the effect of the 10% Isonate 143L in the HTPB polymer is minimal, and that the thermal decomposition processes of the HTPB polymer are predominantly characterized by that of R-45M resin: (1) there are two major weight loss stages with indistinct separation, and (2) the first stage is exothermic and the second endothermic. Nevertheless, the onset of thermal decomposition of HTPB polymer occurs at a lower temperature than R-45M, in agreement with the postulation that the urethane bond cleavage is the first step of polymer decomposition. After the urethane bonds are cleaved and the diisocyanate volatilizes (above approximately 430°C), the HTPB behaves as though it had never been crosslinked, as manifested by the similarity of the Arrhenius parameters and the TGA and DTG curves for the R-45M and cured HTPB samples.

Increasing the heating rate of HTPB polymer increases the extent of the first-stage decomposition and the maximum rate of decomposition of both stages. This may imply augmentation of the depolymerization process, which leads to the release of a larger amount of low molecular weight products. The decrease in exothermicity of HTPB polymer at higher heating rates also supports the above statement. The activation energy and natural log of the pre-exponential factor for the first-stage decomposition of HTPB polymer are 115.4 kJ mol^{-1} and 14.3 s^{-1}, respectively, at a heating rate of 10°C min^{-1}. The results also indicate that adding the curing agent to the polybutadiene resin has a greater impact on the energetics than on the kinetics of the R-45M decomposition.

Information on the thermal decomposition of HTPB polymer is very useful for hybrid propulsion systems since this polymer is considered one of the most promising solid fuels. The kinetic parameters of thermal decomposition may be used in modeling the overall solid-fuel pyrolysis and combustion processes of hybrid rocket motors, especially in the ignition process where the heating rate to the solid fuel is low compared to that in the combustion process.

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