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Thermoanalytical life time testing of energetic poly(glycidyl azide) and its precursor, poly(epichlorodydrin)

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Summary

The life time analysis of energetic liquid prepolymers, polyglycidyl azide (PGA), and its precursor, polyepichlorohydrin (PECH), was carried out to estimate their useful storage time as a function of storage temperature using thermoanalytical method. Thermogravimetric Analysis (TGA) was used to determine the decomposition kinetics of prepolymers. For this purpose, Thermal Gravimetry (TG) curves of prepolymers were recorded at different heating rates and their kinetic activation energies were determined. The kinetic activation energy of PGA and PECH were found to be 120 and 167 kJ/mole, respectively. For the life time estimation, the 5% weight-loss was selected as constant failure criterion for the prepolyemers. These data were further used for the determination of the change in their useful storage time at different storage temperatures.

Introduction

Azide polymers have been synthesized during the last decade to use as an energetic binder and performance improving additive in the composite and composite modified double base propellant formulations. Poly(glycidyl azide), PGA, is a typical example of this energetic azide polymers which has the ability of self decomposition even at relatively low temperature and produces fuel rich decomposition products. PGA is a low molecular weight and hydroxyl terminated liquid prepolymer which can be synthesized via the nucleophilic substitution reaction of its precursor, Poly(epichlorohydrin), PECH, with sodium azide (NaN_3)(1-6). PGA contains energetic pendant azidomethyl groups (-CH_2-N_3) on the polyethere main chain and has a positive heat of formation (+957 kJ/kg at

293 K) (7). The high energy potential and relatively low detonation sensitivity properties allow the PGA to be considered as a monopropellant as well as polymeric binder and also to become a superior replacement for nitroglycerin in either crosslinked and uncrosslinked composite modified double base propellants. This imparts a greater degree of safety properties in handling and storage of these type of propellants. Beyond the superior thermal properties, this polymer has excellent physical-chemical properties such as low glass transition temperature (Tg= -50 °C), low viscosity and high density compare to the other widely used prepolymers in the rocket propellant technology. Because of the excellent thermal properties mentioned here, PGA has attracted the special interest of scientists dealing with solid propellants. Therefore, a lot of work has been devoted to the synthesis of branched and linear PGA prepolymers and to their application on the preparation of high energetic, high burning rate and chlorine free smokeless propellants(1-11).

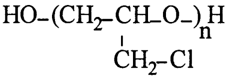
It is very important to know the temperature at which a polymeric material has to be stored without loosing its original properties so that the minimum physical properties can be retained. The commonly used methods for the life time testing of polymeric materials are mainly based on the extrapolation of the data obtained from accelerated aging experiments and the storage conditions. For this purpose, various conditions, such as temperature, humidity and UV irradiation are applied to polymeric materials and the changes in the chemical composition and physical properties are followed as a function of aging time(12-15). This procedure, while useful for particularly more stable materials, generally requires long testing time, considerable amount of test materials and special equipment. Toop, previously reported that the Thermal Gravimetric Analysis (TGA) is an alternative and accurate method for the life time testing of polymeric materials which allows us to predict the storage time of a polymeric material at a given temperature very rapidly(16). This method was later used by Krizanovsky and Mentlik to predict the thermal life of polymeric electrical insulating materials (17).

As it was reported earlier, azide groups of PGA have a tendency to decompose spontaneously at elevated temperatures(7,8). This decomposition causes the deterioration in the physicochemical properties of PGA. During the long storage time, a certain amount of unstable azide groups of PGA may decompose and form intra- and inter-molecular linked structure. This phenomenon may lead to an increase in the prepolymer viscosity and a considerable decrease in its energy capacities. The life time prediction of PGA and its precursor, PECH, in various temperature is of great importance since they reflect all mechanical and ballistic properties into their propellants. In the present study, the thermoanalytical lifetime testing of PGA and PECH prepolymers were performed by considering the approach developed by Toop using TGA technique, and the results were compared.

Experimental

Materials and characterization

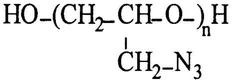
Poly(epichlorohydrin) was purchased from 3M (USA) under the trade name of HX-102. The number average molar mass $(\overline{M}n)$ and OH equivalent of PECH were found as 1800 g/mole and 1.14 mEq/g (≈2 Eq./mole) respectively. The viscosity and density of PECH were determined as 1.06×10^5 cP and 1.36 g/cm^3 respectively at 25°C. The chemical formula of PECH is as follows,



$$\mathrm{HO{-}(CH_2{-}\underset{\substack{|\\ CH_2{-}Cl}}{CH}{-}O{-})_nH}$$

(PECH)

Poly(glycidyl azide), PGA was synthesized by the nucleophilic substitution reaction of PECH with sodium azide (NaN_3) at 100 °C(1-6). The number average molar mass of PGA was determined as 2200 g/mole and hydroxyl value was determined as 0.93 mEq/g (≈ 2 Eq/mole). The viscosity and density of PGA were found as 2.4×10^3 cP and 1.29 g/cm^3 at 25 °C, respectively. The chemical formula of PGA is as follows,



$$\mathrm{HO{-}(CH_2{-}\underset{\substack{|\\ CH_2{-}N_3}}{CH}{-}O{-})_nH}$$

(PGA)

OH equivalents of PECH and PGA were determined according to the method cited by Dee et al.(18) using N-methyl imidazole as an acetylation catalyst.

Instrumentation

The $(\overline{M}n)$ values of prepolymers were determined by a Knauer type vapour phase osmometer using benzyl (MW=210.23 g/mole) as calibration standard. TGA measurements were carried out using Du Pont TGA-951 with a TA-9900 data processing system. Thermograms were recorded at different heating rates under nitrogen atmosphere. The flow rate of nitrogen inlet was 50 ml/min. The TGA system was calibrated with calcium oxalate. The weight of the samples used for TGA measurements were 2.5±0.2 mg.

Results and discussion

In order to estimate the lifetime of PGA and its precursor PECH using thermoanalytical method, their thermogravimetric characterization was performed. TGA thermograms were first recorded at a heating rate of 10 °C/min. The weight loss and derivative weight loss curves of PGA (Figure 1) indicated the two characteristic weight loss steps. The first one obtained between 210 and 269 °C is the major process which is due to the elimination of N_2 from the pendant $-N_3$ repeating units of PGA (7,8).

The second weight loss process obtained at the temperature interval between 269 and 404°C is due to the decomposition of polyether main chain of PGA. This process has the maximum weight loss rate temperature of 349 °C which is the same with the PECH main chain as shown in Figure 2. Hence, the second weight loss step of PGA nearly corresponds to the single weight loss process of PECH (Figure 2). Therefore, the predicted life time of PECH may possible be considered as a measure of the life time of polyether main chain of PGA at each storage temperature.

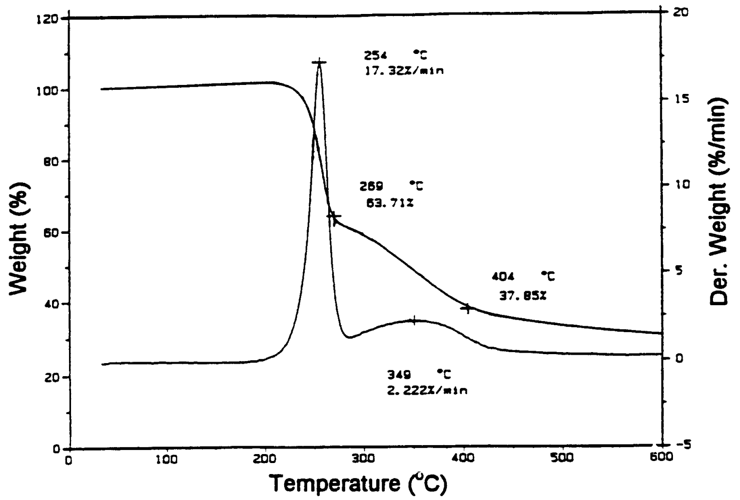


Fig. 1. TG and derivative TG curves of PGA obtained at 10 °C/min heating rate.

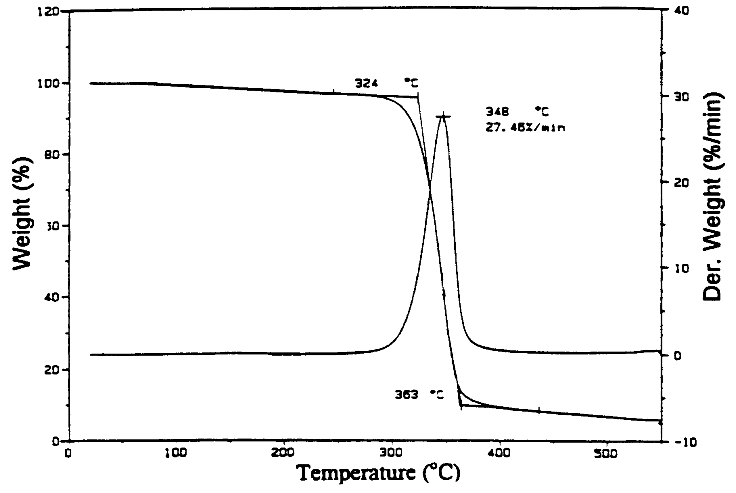


Fig. 2. TG and derivative TG curves of PECH obtained at 10 °C/min heating rate

As it was reported earlier the thermal crosslinking of PGA chains accompanying the -N_3 groups elimination from the main chain of the prepolymer starts at nearly 235 °C (8). The reading off this temperature from the weight loss curve in Figure 1 gives 5% weight loss. Therefore, for the life time estimation of PGA, the 5% weight-loss was selected as constant failure criterion. The constant failure criterion for the PECH, the 5% weight loss was also selected (19).

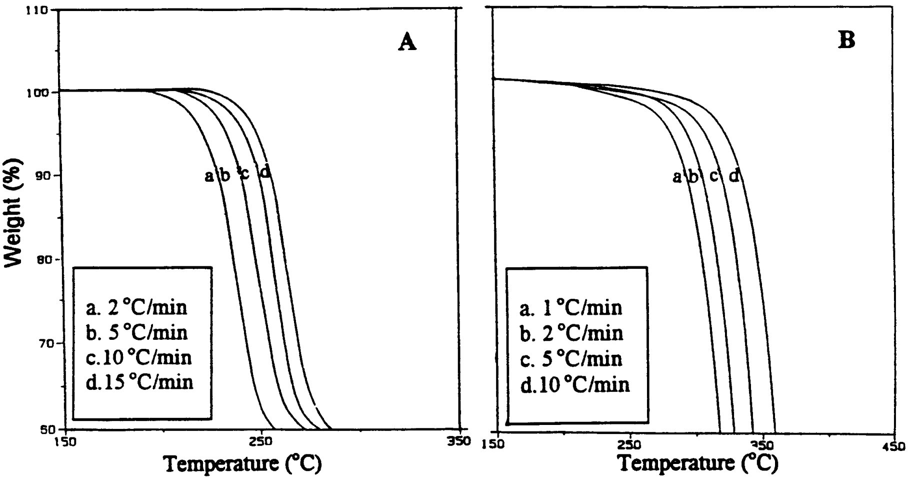


Fig.3.TG curves of prepolymers obtained at various heating rates.**(A)** PGA.**(B)** PECH

To obtain the changes of the estimated lifetime of prepolymers with storage temperature their TG curves were recorded at various heating rates under nitrogen atmosphere. The first 40% weight loss of PGA and PECH are plotted in Figure 3A and Figure 3B, respectively. As it was previously reported, in the course of the first step weight loss, pendant -CH_2-N_3 groups of PGA decompose to form gaseous N_2 and H_2 and an acrylonitrile structure(7,8). Therefore the first step weight loss process of PGA complies with the simple reaction mechanism as shown below,

A (S) ---------------> B (S) + C (g) + D(g)

In this reaction mechanism, A and B are regarded as undecomposed and decomposed polymer, respectively, and C and D is regarded as the volatile decomposition products.

The kinetic activation energies of the first step decomposition process of PGA and the main chain decomposition of PECH were determined by employing the method of Flynn and Wall to the weight loss curves obtained at different heating rates (20),

$$E_a = -R/0.457[d\log\beta/d(1/T)]$$

where, E_a is the kinetic activation energy (J/mol), β is the heating rate (°C/min), R is the gas constant (8.314 J/mol K), and T is the absolute temperature.

The plot of the logarithm of the heating rate versus reciprocal of the temperature at each decomposition levels obtained from the Figure 3A and Figure 3B gives us the straight lines for PGA and PECH as shown in Figure 4A and Figure 4B, respectively. From the slope of the lines obtained for the 10% weight loss level, the calculated kinetic activation energies of PGA and PECH prepolymers were determined as 120 and 167 kJ/mole, respectively. The kinetic activation energy of the first step weight loss process of PGA is lower than the kinetic activation energy of PECH. This is due to the lower stability of the pendant -N_3 groups of PGA.

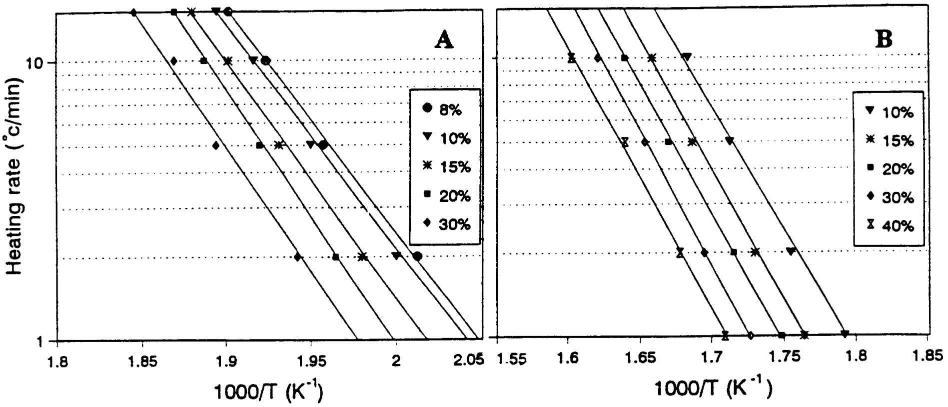


Fig. 4. Plot of the logarithm of heating rates versus reciprocal corresponding absolute temperature at various weight loss level of the the curves of Figure 3A and figure 3B. For PGA **(A)**. For PECH **(B)**.

Assuming the first order kinetics and simple reaction mechanism, Toop (16) previously reported the following relationship between the lifetime of a polymeric material and its kinetic activation energy,

$$\log t_f = (E_a / 2.303RT_f) + \log [\, E_a p(x_f) / \beta R] \qquad (1)$$

$$x_f = E_a / RT_c \qquad (2)$$

where, t_f is the time to failure (hours), E_a is the kinetic activation energy of prepolymer (J/mol), R is the gas constant (8.314 J/mol K), T_f is the failure temperature (K), β is the heating rate (°C/hour) and T_c is the temperature corresponding to the constant failure criterion (5% weight loss) at the slowest TG curves of prepolymers in Figure 3A and Figure 3B. T_c was obtained as 218 and 282 °C for PGA and PECH, respectively, by reading off 5% weight loss from the TG curves of prepolymers recorded at 2 °C/min heating rate shown in Figure 3A and Figure 3B. x_f was calculated from eq 2 and thus, $p(x_f)$ was obtained from the numerical integration in reference (16). For PGA and PECH, $p(x_f)$ was found as 1.858×10^{-16} and 1.387×10^{-19}, respectively. By considering these values in the eq 1, the life time of PGA and PECH prepolymers were determined as a function of the storage temperature. As shown in Figure 5, the calculated life time value of PGA is extremely lower at each temperature compared to the value of PECH. This is due to the pendant CH_3-N_3 repeating units of PGA.

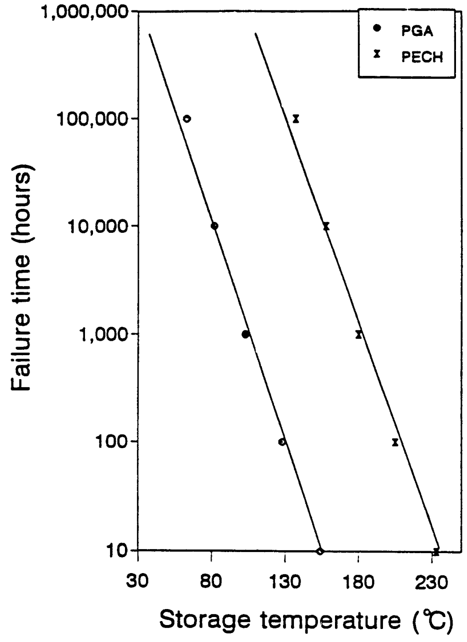


Fig. 5. The change of the failure time of PGA and PECH with storage temperature.

In conclusion, the life time analysis of PGA and PECH was performed using the method proposed by Toop. From these results we can say that in view of the azide groups decomposition and main chain degradation, rather than hydroxyl functional groups decomposition, the lifetime of PGA prepolymer is nearly 120 years when stored at room temperature. This result shows that the long time storage of PGA at room temperature does not cause to a considerable changes in its high energy properties and viscosity.

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