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Characterization of diglycidylamine epoxy resins based on bis-hydrazones

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Abstract

A series of hydrazones based viscous epoxy resins having N–N bonds in their backbones have been developed as energetic binders for composite solid propellants. A few typical resins have been characterized by their molecular weight distribution, ^{13}C NMR spectra and glass transition temperature. The gel permeation chromatography studies carried out show the composition profile in the glycidyl amine synthesis. Spectral studies confirm the epoxidation of the hydrazones. The cured dicarboxyl bishydrazone based resins have glass transition temperatures in the range −13 to 55°C © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

One of the major uses of polymers in rocketry is in the area of solid propellants, as fuels and binders. In fact, the spectacular growth of solid propellant technology owes much to the advancements made in the area of polymers. A solid propellant essentially comprises of an oxidizer, such as ammonium perchlorate powder held together in a polymeric matrix which also acts as a fuel in the combustion process. Though the binder is present in small quantity compared to the oxidizer, its role in the overall combustion process is quite significant. The overall performance of a propellant composition can be enhanced by using energetic polymers, which usually incorporate groups like nitro and azide in their backbones. However, many of these polymers have problems of incompatibility, high cost and poor mechanical properties. Of late, Jain and coworkers have reported polymers with N–N bonds in the backone as promising binders for composite solid propellants. These resins when used with oxidizers such as ammonium perchlorate and ammonium nitrate are found to be compatible, and at the same time enhance the burning rate significantly. The synthesis and characterization of these resins, combustion properties like burning rate and performance evaluation of propellants with different oxidizers, have been reported earlier [1–6]. The present paper reports further studies pertaining to some of the other aspects such as molecular weight distribution, ^{13}C NMR, glass transition temperature studies of some of the typical resins, which were not reported earlier.

2. Experimental

The epoxy resins synthesized were based on bis-carbonohydrazones, bis-thiocarbonohydrazones and

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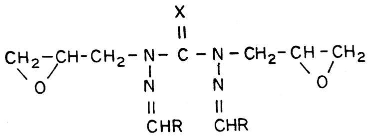
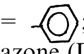
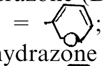
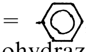
N,*N*′-aliphatic dicarboxyl bis- hydrazones. Structures of these resins are as follows.

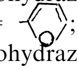


where

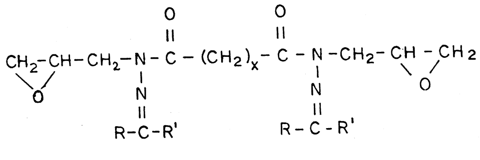
X = O, R = ;Diepoxide of bisbenzaldehydecarbonohydrazone (DEBCH)

X = O, R = ; Diepoxide of bisfurfuraldehydecarbonohydrazone (DEFCH)

X = S, R = ; Diepoxide of bisbenzaldehydethiocarbonohydrazone (DEBTCH)

X = S, R = ; Diepoxide of bisfurfuraldehydethiocarbonohydrazone (DEFTCH)

and

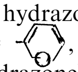


where

x = 1, R = CH_3, R′ = CH_2CH_3, Diepoxide of malonyl bis(butanone hydrazone) (DEMBuH)

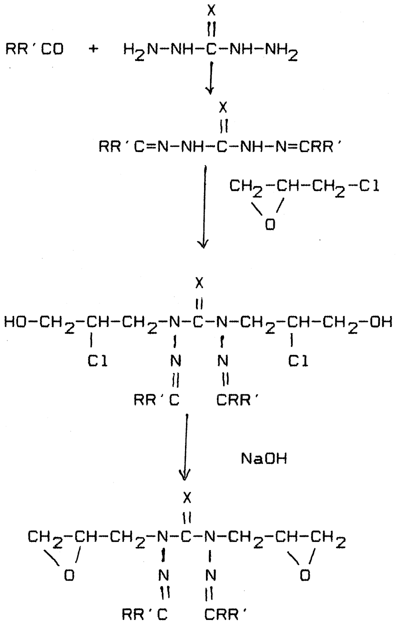
x = 4, R = CH_3, R′ = CH_2CH_3, Diepoxide of adipoylbis(butanone hydrazone) (DEABuH)

x = 8, R = CH_3, R′ = CH_2CH_3, Diepoxide of sebacoylbis(butanone hydrazone) (DESBuH)

x = 1, R = H, R′ = , Diepoxide of malonylbis(furfuraldehyde hydrazone) (DEMFH)

x = 8, R = H, R′ = , Diepoxide of sebacoylbis(furfuraldehyde hydrazone) (DESFH)

A typical synthesis reaction involves the following steps:



where X = S or O; R and R′ = substituents.

The molecular weight determination of the glycidyl amine resins based on carbono- and thiocarbonohydrazones was carried out on a HP liquid chromatograph, (Model No. 1081B) using two styragel columns of pore size 5 and 1 mμ connected in series, at 20°C using a refractive index detector. Standardization was done with polystyrene samples having molecular weights 580, 800 and 1060. A calibration curve was obtained by plotting log molecular weight versus elution time. The ^{13}C NMR of the parent compounds and the resins were recorded on a 100.61 MHz Bruker AMX 400 spectrometer. Thermomechanical analysis (TMA) of cured epoxy castings was carried out using a TMA-40 Thermomechanical analyser unit connected to a Schimadzu DT-40 thermal analysis system. The dimensional changes measured as a function of temperature (−160 to 125°C) were recorded. All the measurements were carried out in a flowing nitrogen (40 ml/min) atmosphere, at a heating rate of 10°C/min.

3. Results and discussion

The GPC chromatograms for the resins DEFTCH, DEFCH, DEBTCH, and DEBCH shown in Fig. 1, indicate the impurity profile of the resin synthesized using the synthetic route reported earlier [2]. The molecular weights computed based on the elution time, and relative intensity of each peak are given in Table 1. The peaks in the chromatogram correspond to the epoxy resin monomers, oligomers, solvent, and some chlorohydrin, as impurity. It can be seen that the per-

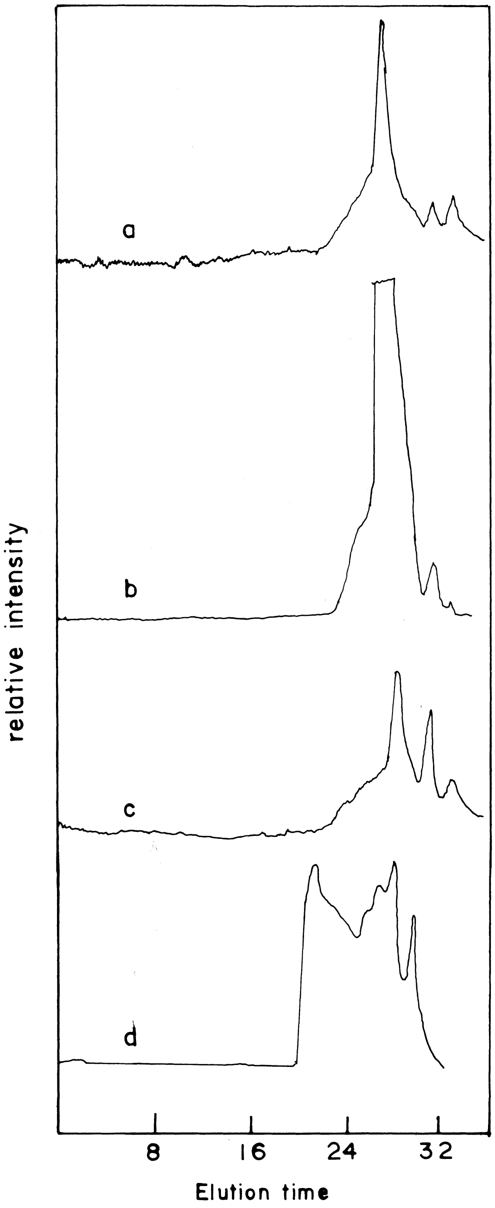


Fig. 1. GPC chromatograms of (a) DEFTCH, (b) DEBTCH, (c) DEFCH, and (d) DEBCH.

Table 1
GPC data for various resins

Resin	Molecular weights		Relative intensity
	Expected	Observed	
DEFTCH	374	384	73
		122	6
		75	9
DEFCH	358	327	62
		145	21
		89	10
DEBTCH	394	372	98
		130	1.2
		93	0.2
DEBCH	378	2411	51
		372	38

centage of monomers in these samples is relatively high. The complete removal of the solvent is difficult from highly viscous resins. However, it can be seen that the monomer content of DEBTCH is very high (98%). On the other hand, the carbonohydrazone resin show relatively lesser amount of the monomer. Apart from the peaks corresponding to the monomer units, two more peaks are seen in the chromatograms which could be attributed to epichlorhydrin (mol. wt 92.5) and 1,3-dichloro-2-propanol (mol wt. 129), a product of HCl and epichlorhydrin reaction [7]. It is obvious that the percentages of these impurities in benzaldehyde based resins are much lower, may be because they are less viscous in nature and thereby facilitate removal of the volatile impurity. Glycidyl amines synthesis usually are reported to lead to a mixture of products because of the possible side reactions in the multistep synthesis [8]. The product profiles in the present cases show the relative efficiency of the reported synthetic route.

^{13}C NMR studies carried out on the carbono- and thiocarbono-hydrazones and their respective resins are reported in Table 2. It is observed that the spectrum of the parent compound BTCH shows all the resonances corresponding to various ^{13}C nuclei; phenyl carbons at δ, 126–144, C=N at δ, 149 and C=S at δ, 174 ppm. The peaks corresponding to the epoxy carbons at δ, 45–46 and δ, 51–53 ppm observed for DEBTCH, confirm the epoxidation of the hydrazones in the adopted synthetic route. Other ^{13}C resonances in the resin remain almost unaffected. The spectrum of DEFTCH shows peaks corresponding to furfural carbons at δ, 112–118, 145 ppm apart from those corresponding to epoxy carbons. The resonance peak at δ, 69 ppm seen in the spectra of resins can be attributed to C–(OH) arising from the oligomer or chlorohydrin impurities present in the resin. The poor solubility of hydrazones and some resins in DMSO is responsible for the low intensity of the peaks, particularly of the C=O and C=S groups. These results supplement the IR and ^{1}H NMR studies carried out earlier on these systems [4,5].

The glass transition temperature (T_g) is an important parameter in determining the suitability of a polymer for a specific application. The T_g of dicarboxyl hydrazone epoxies cured with DDM at 80°C for two days is given in Table 3.

It can be seen from the TMA curves (Fig. 2) that T_g

Table 2
^{13}C NMR chemical shifts of hydrazones and resins

Compound	Chemical shift (δ, ppm)						
	Furfural	Phenyl	C=N	C=O	C=S	epoxy	C–OH
FCH	112–118, 145		153	161		–	–
FTCH	112–118, 145		153		174	–	–
BCH		126–144	149	161		–	–
BTCH		126–144	149		174	–	–
DEFTCH	112–118, 145		153		179	45–46, 51–53	69
DEFCH	112–118, 145		153	n.d[a]		45–46, 51–53	69
DEBTCH		126–144	153		n.d	45–46, 51–53	69
DEBCH		126–144	153	n.d		45–46, 51–53	69

[a] n.d: not detected.

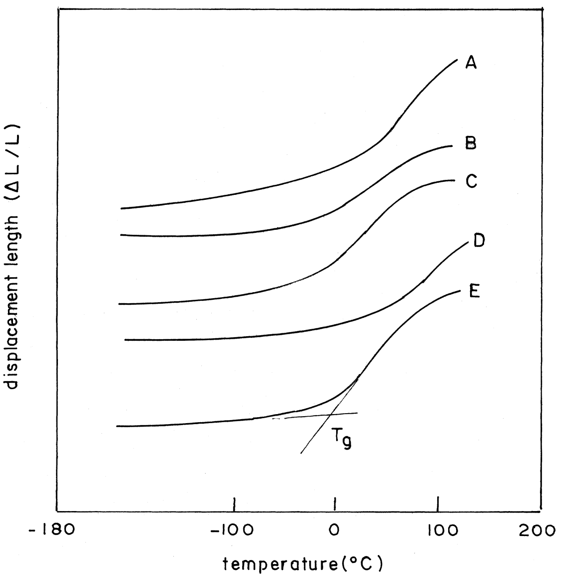


Fig. 2. TMA curves of cured polymers: (A) DEMBuH, (B) DEABuH, (C) DESBuH, (D) DEMFH, (E) DESFH.

Table 3
T_g of various resins

Resin	T_g (°C)
DEMBuH	40
DEABuH	20
DESBuH	−13
DEMFH	55
DESFH	−5

lies between −13 and 55°C. It decreases with increasing number of methylene spacer (CH_2) groups in the molecule. The cured sebacoyl resins having eight CH_2 groups, are inherently flexible with low glass transition temperatures. On the other hand, the resins which are based on malonyl and adipoyl hydrazones have higher glass transition temperatures. This could be due to the low cross link density and chain flexibility resulted by the presence of more number of methylene spacer groups. Also, furfuraldehyde hydrazones resins are found to have higher T_g than those of butanone hydrazones, perhaps due to the presence of aromatic groups.

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