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COMPATIBILITY OF POLYMERS WITH HIGHLY ENERGETIC MATERIALS BY DTA: PART II

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ABSTRACT

An areal method previously developed by the author and utilized to assess compatibility of mixtures of various polymers and highly energetic materials (HEM) was extended to various other polymers and HEM. Thus, pentaeryrithritol tetranitrate (PETN) and nitroguanidine (NGN) were used along with additional polymers such as Celcon, Delrin 500, polyvinylpyrrolidone, poly(mono-chlor-*p*-xylylene), polysulfone and carboxymethylcellulose. As in part I, changes in reproducible overall values of activation energy (E) and reaction order (n) were used as reliable indices for judging compatibility of HEM in various admixtures of polymers.

INTRODUCTION

In part I[1], an areal method previously developed by the author for the estimation of kinetic parameters during polymer pyrolyses, i.e., activation energy (E) and reaction order (n), was utilized for the assessment of compatibility of various polymers with highly energetic materials (HEM) by means of DTA. Thus, changes in values of E and n for admixtures of HEM and polymers, as opposed to HEM alone, were used as indices for judging compatibility.

Although this method afforded reproducible overall values of E and n during decompositions, values of E appeared to be consistently higher than such values reported for similar decompositions. As previously indicated[1], such differences may in part be due to the utilization by others of other types of techniques, e.g., isothermal studies using gasometric techniques. Further, such differences may be attributed to autocatalysis, relatively high degree of exothermicity, and the type of expressions employed for estimating E and n. Thus, in analyzing isothermal rate curves for HEM decompositions, the estimation of kinetic parameters may be complicated by the onset of autocatalysis. These effects are associated with the accumulation of decomposition products in the sample. Thus, depending upon which part of the isothermal rate curve is analyzed, different values of kinetic parameters may be arrived at, e.g., in the decomposition of ethylenedinitramine (EDNA) analysis of the initial decomposition afforded an enthalpy of activation (ΔH^*) of 31 kcal mole^{-1} whereas analysis of higher decomposition data (where autocatalysis becomes predominant) afforded a value of ΔH^* for EDNA of 72 kcal mole^{-1} [2,3]. Furthermore, HEM decompositions are generally strongly exothermic so that as reaction temperature increases, self-heating effects become important and an acceleration of decomposition reaction occurs. Besides these effects, differences in reported values of E (and/or n) may arise from the type of equations employed to calculate these values. This factor was previously mentioned[1]. However, it may also be noted here that in the Reich method[1,4–6] unless $1 \gg 2RT/E$, the calculated value of E should be multiplied by $1-(2RT/E)$. The inclusion of this factor can reduce the calculated value of E by about 2–3% (the experimental error is usually greater than this correction). From the preceding, it can be readily seen that overall values of E calculated from data obtained by dynamic techniques (DTA) should be higher than corresponding values obtained from static methods (e.g., isothermal, wherein temperature control is better and initial portions of the rate data may be employed). In this connection, it may also be remarked that other dynamic methods (DSC) may afford different values of E since such techniques may afford data which are dependent on sample encapsulation techniques used[1]. [Also, the author observed that when RDX was subjected to DSC using an open pan and a nitrogen flow, only a melting endotherm could be observed. The molten RDX apparently volatilized during and/or shortly after the melting stage so that no decomposition exotherm could be observed (the wt. % of RDX remaining before the temperature which corresponded to the decomposition peak maximum was only ca. 7). However, in the presence of still air, a melting endotherm and a decomposition exotherm were observed for the RDX sample in an open pan.] At any rate, the values of E and n are very reproducible by the Reich method and can be used, as previously reported[1], to assess compatibility of mixtures of HEM and various polymers.

The aim of this paper is to extend the DTA technique to various other HEM in order to judge their compatibility with various polymers.

EXPERIMENTAL

Starting materials

In addition to the polymer powders used previously[1], the following additional materials were employed: Celcon (acetal copolymer from Celanese); Delrin 500 (polyformaldehyde from duPont); polyvinylpyrrolidone, General Aniline and Film Corporation (PVP); parylene C [poly(mono-chlor-*p*-xylylene, courtesy of T. C. Castorina]; polysulfone 1700, Union Carbide (PSF); carboxymethylcellulose, LaPine Scient. Co. (CMC). For convenience, the polymer abbreviations used previously[1] (and in this paper) are elucidated here: polyethylene (PE), polystyrene (PSt), polyisobutylmethacrylate (PIBM), polymethylmethacrylate (PMMA), polyethylmethacrylate (PEMA), polyacrylamide (PAA).

The highly energetic materials used were: cyclotrimethylene trinitramine (RDX), T_m (onset) ca. 202 °C, recrystallized from acetone and γ-butyrolactone (courtesy of J. R. Autera); pentaerythritol tetranitrate (PETN) and nitroguanidine (NGN) (both of these materials were obtained through the courtesy of the Explosives Laboratory and conformed to minimum quality requirements[7]).

Apparatus and procedure

The apparatus and procedure were similar to those previously reported[1]. When relatively large differences in E and n were found, thermograms were obtained for the polymeric material alone in order to ascertain whether or not endotherms or exotherms existed in the temperature range of interest. When such peaks were found, appropriate corrections were made to the thermogram involving a mixture of HEM and the particular polymer (cf. Tables 1 and 2).

RESULTS AND DISCUSSION

Mixtures containing RDX

Additional compatibility runs were carried out using RDX[1]. Since another batch of RDX was used along with different instrument settings than were used previously[1], parameters for the RDX sample were now, $T_m = 237 \pm 1$ °C, $E = 82 \pm 2$ kcal mole^{-1}, and $n = 0.71 \pm 0.01$ (averages of three runs). These values were similar to those used previously. Upon mixing RDX with parylene (46 wt. % RDX), the following values were obtained, $T_m = 236$ °C, $E = 80$ kcal mole^{-1}, and $n = 0.70$, indicating that a compatible mixture was obtained. RDX was also mixed with Delrin and Celcon (cf. Fig. 1). In the case of Delrin alone (a polyformaldehyde) the DTA thermogram indicated two endotherms. The first relatively sharp endotherm (melting and decomposition of chains containing free –OH end groups)[6] commenced at ca. 160 °C and was over at ca. 181 °C. This was immediately followed by a second broad decomposition endotherm (decomposition of chains containing acetylated end groups)[6] which commenced at ca. 181 °C and was over at ca. 288 °C. Up to ca. 210 °C, there was a weight loss of ca. 30% whereas, at 240 °C there was a weight loss of ca. 90%. As previously indicated[1] for RDX alone the decomposition range of interest lies between ca. 210–245 °C. Thus, there would appear to be an overlapping of peaks for the two materials. However, when RDX (ca. 56 wt. %) was mixed with Delrin and the mixture subjected to DTA, an initial endotherm was obtained between ca. 165–178 °C, as anticipated, followed by a second endotherm which was much sharper than that for Delrin alone. At the end of this endotherm, ca. 200 °C, the weight loss of Delrin was ca. 100%. Thus, no Delrin should be present prior to the RDX decomposition. Apparently, the RDX catalyzed the decomposition of Delrin (probably due to the presence of acidic groups in the RDX—acids or bases catalyze polyformaldehyde decomposition)[8]. The Delrin unzipped to afford formaldehyde which has been reported to accelerate RDX decomposition[9]. However, the resulting decomposition exotherm afforded the values, $T_m = 237$ °C, $E = 75$ kcal mole^{-1}, and $n = 0.68$, indicating that RDX and Delrin compatibility was satisfactory. [Vacuum stability tests[1] at 100 °C also indicated compatibility between RDX and Delrin.] A possible explanation for why the liberated formaldehyde did not affect the RDX decomposition is that at ca. 200 °C the Delrin had completely and rapidly decomposed, just prior to

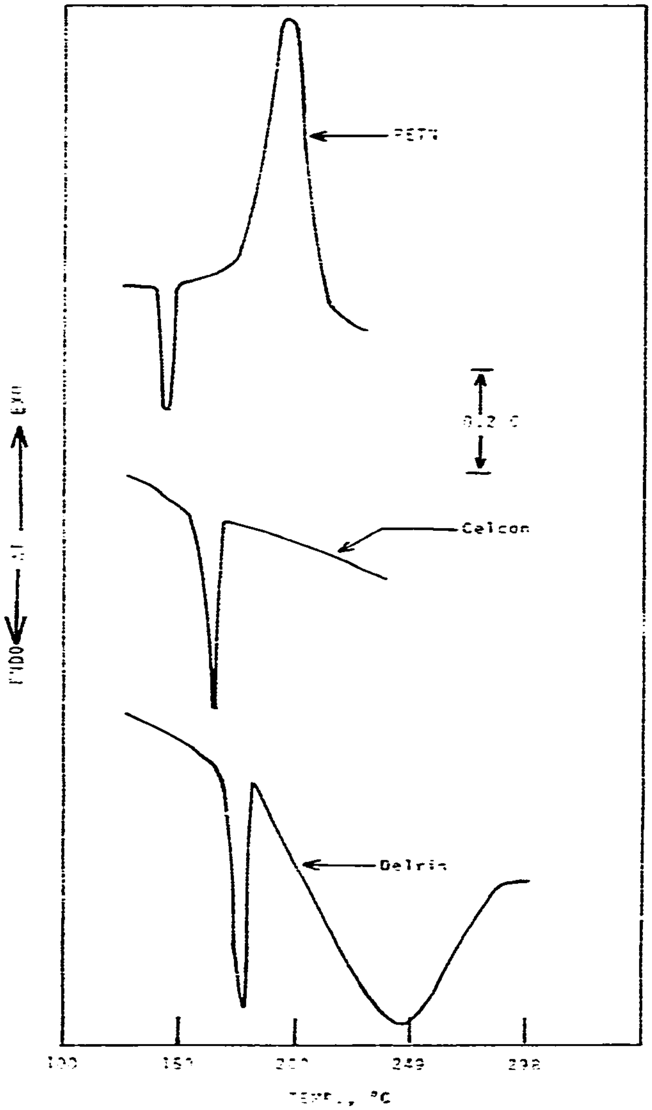

Fig. 1. DTA thermograms for PETN (1.9 mg), Celcon (2.2 mg), and Delrin (2.7 mg); heating rate in nitrogen = 6 °C/min.

the RDX melting point, so that very little, if any, formaldehyde was absorbed by the RDX in the solid phase. In the case of Celcon alone (acetal copolymer containing formaldehyde moieties)[10], DTA revealed only a single melting and decomposition endotherm (cf. Fig. 1) which commenced at ca. 150 °C and was over at ca. 167 °C. Thereafter, no peaks were observed up to ca. 290 °C in contrast to Delrin (the copolymer units attributed to this high thermal stability). At 290 °C, a weight loss of only ca. 25% was observed. However, in the presence of RDX, the Celcon loss in weight amounted to ca. 100% at ca. 200 °C, indicating that, as in the case of Delrin, the RDX was catalyzing the Celcon decomposition (probably also due to the presence in RDX of acids or bases which catalyze Celcon decomposition). However, in contrast to Delrin, a second relatively broad endotherm now appeared which peaked at ca. 202 °C (the second endotherm for Delrin, in the presence of RDX, peaked at ca. 190 °C). Thus, in the case of Celcon, formaldehyde was probably being liberated during the melting of RDX. This could result in absorption of formaldehyde by the molten RDX followed by subsequent chemical interaction. The ensuing decomposition exotherm indicated that this interaction probably occurred since the following parameters were obtained (averages for two runs), $T_m = 228 \pm 1$ °C, $E = 106 \pm 8$ kcal mole^{-1}, and $n = 0.61$. Thus, mixtures of Celcon and RDX appear to be incompatible based upon the DTA technique employed. [Vacuum stability tests at 100 °C, however, indicated compatibility for mixtures of Celcon and RDX.]

Mixtures containing PETN

In Table 1 are summarized values of parameters for mixtures of PETN with various polymers. Average values for PETN alone were based on five runs. From this table, the following polymers are compatible with PETN: PE, PSt, Epon 828 (BF_3-cured), PIBM, CMC, and parylene. The following show incompatibility: Epon 828 (anh. cured), PSF, PAA, and Gantrez [the parameters for these materials appear to be satisfactory in regard to T_m and one parameter but are unsatisfactory in regard to the

TABLE 1

SUMMARY OF COMPATIBILITY DATA FOR PENTAERYTHRITOL TETRANITRATE (PETN)

Run no.	*HEM*	*Polymer*	*Wt. % HEM*	*Decomposition peak temp. (°C)*	*n*	*E (kcal mole^{-1})*
P-1	PETN	—	100	196±0.5	1.0±0.1	59±3
P-2	PETN	PE	60	196	1.0	60
P-3	PETN	PSt	53	196	1.1	59
P-4	PETN	Epon 828 (BF_3-cured)	50	196	1.1	58
P-5	PETN	Celcon	60	197	—[a]	—[a]
P-6	PETN	Delrin	60	198	—[a]	—[a]
P-7	PETN	Epon 828 (anh. cured)	47	195	1.5	57
P-8	PETN	PSF	33	196	1.5	60
P-9	PETN	PIBM	48	198	1.2	54
P-10	PETN	Gantrez	50	196	1.4[b]	66[b]
P-11	PETN	PMMA	33	199	1.0[b]	46[b]
P-12	PETN	CMC	50	195	1.0[b]	61[b]
P-13	PETN	PAA	50	195	0.95[b]	65[b]
P-14	PETN	Parylene	53	195	1.1	58
P-15	PETN	PVP	60	192	1.7	51

[a] These polymers decomposed in the PETN decomposition temperature range (cf. Results and Discussion for treatment of data). [b] Resulting thermograms corrected for changes in polymer thermograms over the temperature range of interest.

remaining parameter indicating the importance of utilizing three parameters as opposed to one or two for judging compatibility]. As previously reported for RDX[1], PETN is incompatible with polymers containing anhydride groups (Gantrez and Epon 828, anh. cured). PSF also demonstrates incompatibility which was also reported by others[11] who used T_m as a criterion for compatibility. Other materials which show a greater degree of incompatibility are PMMA and PVP [relatively large changes were observed for two or more parameters]. As indicated previously[1], the PMMA sample was used without purification despite the strong odor it possessed (it was also imcompatible with RDX). PVP may show incompatibility because it is a cyclic amide and small amounts of acid or base in PETN may thus promote cleavage

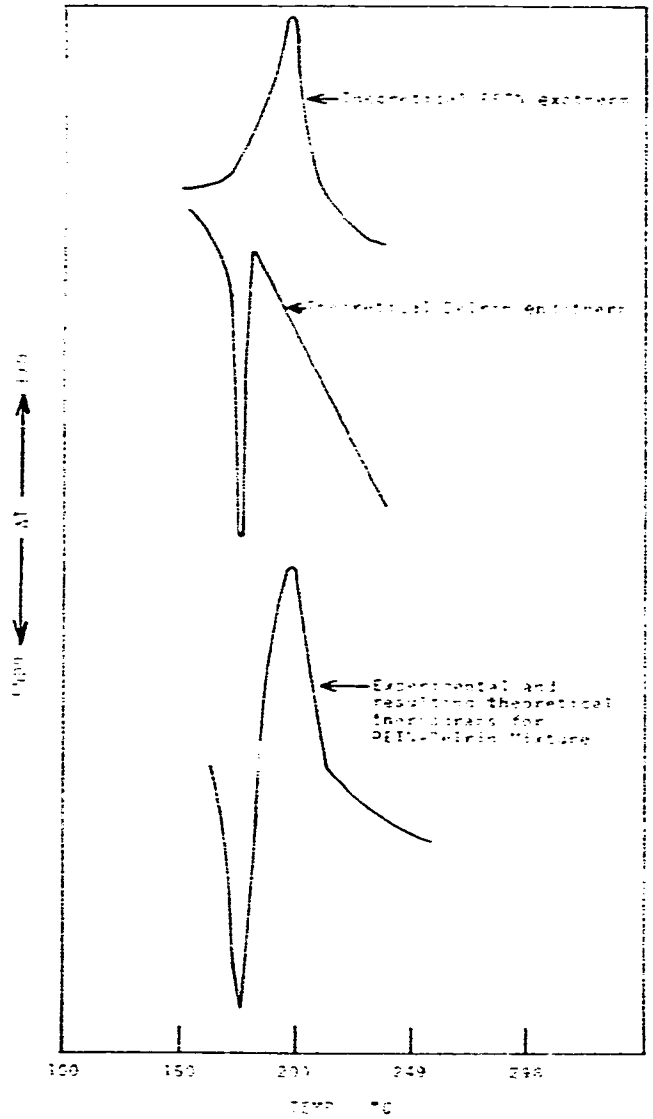

Fig. 2. Algebraic addition of ΔT's for theoretical PETN exotherm and Delrin endotherm to obtain theoretical PETN–Delrin thermogram which is superposable on the experimental thermogram.

of PVP. In regard to the value of $E = 59 \pm 3$ kcal mole^{-1} obtained in this work for PETN, it may be mentioned that a range of E values has been reported[2,12], i.e., 39–60 kcal mole^{-1} (the lower values are generally from the initial portions of isothermal curves whereas, the higher values were deduced from the autocatalytic stages).

In Table 1, it was noted that Celcon and Delrin polymers decompose in the same PETN decomposition temperature range (cf. Fig. 1). Therefore, values of E and n were not reported in this table. Nevertheless, an estimate of compatibility for these polymers was made in general as follows: If there is no interaction between polymer and PETN then algebraic addition of ΔT's for theoretical thermograms of the neat PETN and neat polymer should afford a theoretical composite thermogram which should be superposable on the experimental thermogram from the mixture of polymer and PETN. The theoretical thermogram for neat PETN could be constructed using experimentally obtained values of E and n (cf. Table 1). Thus, in Fig. 2 is shown the resulting experimental thermogram for a mixture of PETN and Delrin. A trial-and-error attempt was then made to obtain a theoretical thermogram of the mixture which would be superposable on the experimental thermogram. To this end, a theoretical PETN exotherm was constructed ($E = 56$ kcal mole^{-1} and $n = 0.91$) as depicted in Fig. 2 and a theoretical endotherm was also drawn, based on experimental endotherms. Algebraic addition of ΔT's was then carried out using average baselines where necessary. The resulting theoretical thermogram could be superposed on the experimental thermogram (cf. Fig. 2) indicating that Delrin was compatible with PETN. It should be noted that T_m would be relatively unaffected by this treatment so that T_m (exptl.) should be nearly the same as T_m (PETN), as observed. (Vacuum stability tests on mixtures of PETN and Delrin at 100° indicated compatibility.) A similar treatment as in the preceding was carried out for mixtures of PETN and Celcon. As previously noted, Celcon alone lost only ca. 25% by weight when heated up to 290°C. However, in the presence of PETN, the Celcon weight loss was ca. 90% at 165°C indicating that PETN was catalyzing the decomposition of Celcon (probably due to acidic or basic residues). In Fig. 3 is depicted a theoretical curve for PETN ($E = 58$ kcal mole^{-1} and $n = 1.1$). This thermogram was constructed using the experimental data for a mixture of PETN and Celcon to the right of the peak maximum ($> T_m$) since at these higher temperatures all the Celcon had decomposed and, therefore, the PETN curve for this temperature range should be similar to that for PETN alone. The theoretical Celcon endotherm in this figure was drawn based on experimental endotherms for this material. Using algebraic addition, a theoretical curve could be constructed (solid lines on the right hand side of Fig. 3). This curve was only partially superposable on the experimental curve (dotted lines on right-hand side of Fig. 3). Thus, the experimental curve was narrower than the theoretical curve. This discrepancy was attributed to the fact that in the presence of PETN the degree of Celcon decomposition increased so that the Celcon endotherm depicted in Fig. 3 should be broader. A broader Celcon endotherm would narrow the theoretical PETN exotherm depicted thereby making experimental and theoretical thermograms more superposable. (Again, as for Delrin,

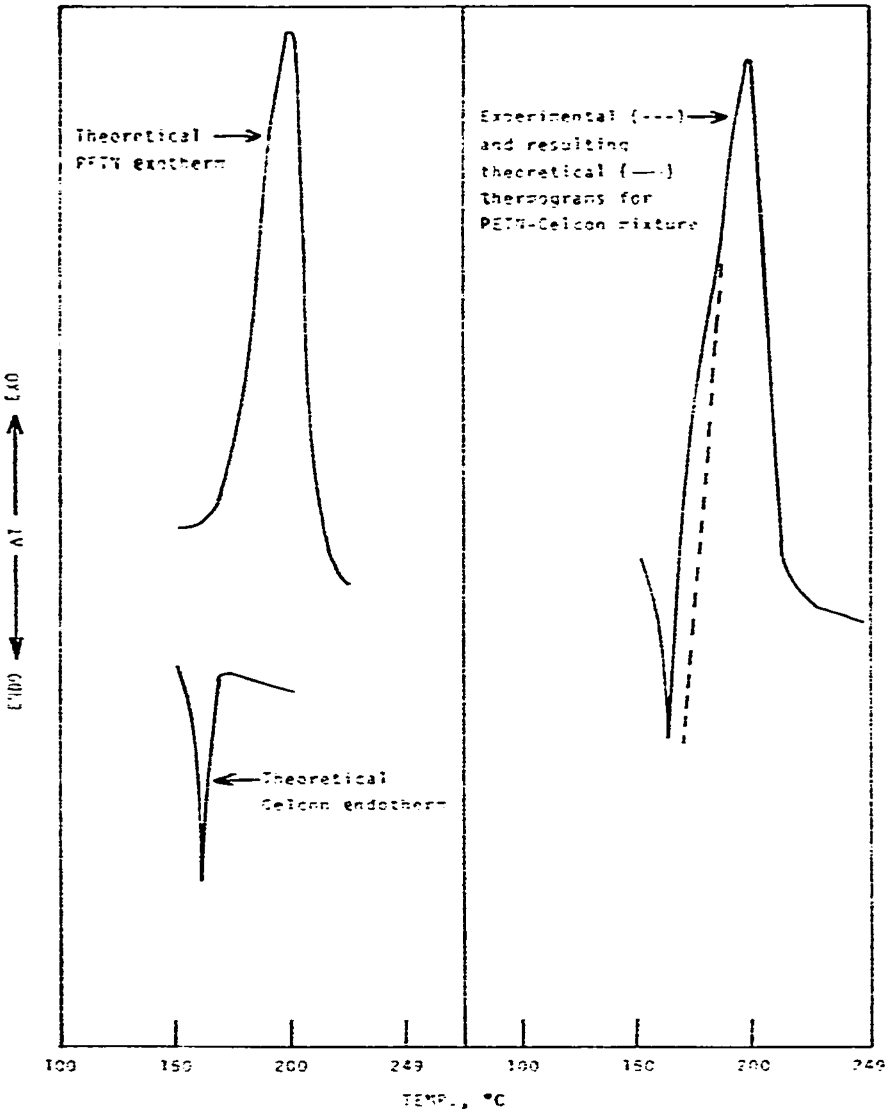

Fig. 3. Algebraic addition of Δ*T*'s for theoretical PETN exotherm and Celcon endotherm to obtain theoretical (——) PETN–Celcon thermogram in relation to experimental (— —) thermogram.

T_m (PETN) should be similar to T_m (exptl.) for the PETN–Celcon mixture, as observed.) In view of the preceding, the PETN–Celcon mixture was considered to be compatible. (Vacuum stability tests at 100°C indicated compatibility for such mixtures.)

Mixtures containing NGN

In Table 2 are summarized values of parameters for mixtures of NGN with various polymers. Average parameter values for NGN alone are based on four runs. These parameter values are fairly reproducible even though they represent melting

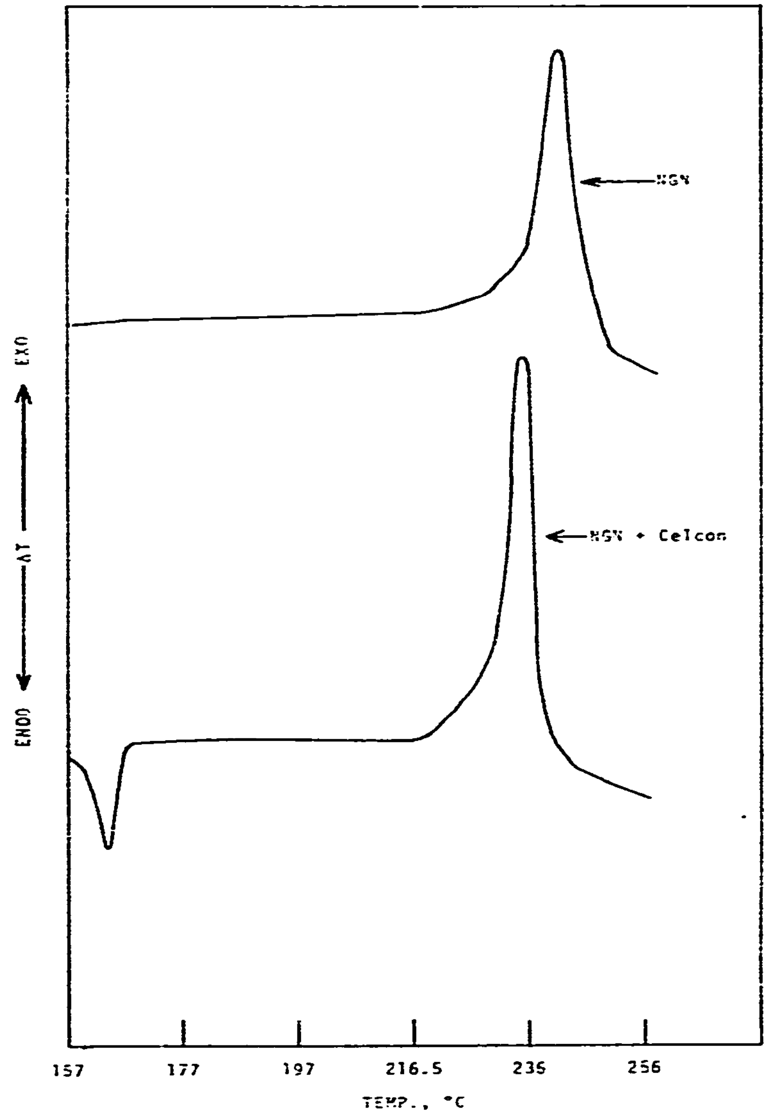

Fig. 4. DTA thermograms for NGN alone and for an incompatible mixture of NGN+Celcon.

and decomposition of NGN. Thus, it has been reported[7,13] that NGN decomposes immediately on melting, evolving ammonia and water vapor and forming solid products. This may in part account for the low fractional reaction order found for n. From Table 2, the following polymers are compatible with NGN: PE, PSt, parylene, and Epon 828 (BF_3-cured). The following show extreme incompatibility; CMC, Epon 828 (anh. cured), PIBM, PMMA, PVP, PEMA, PAA, and Celcon. For these materials, the values of E and n were exceedingly high. This may in part be attributed to the presence of a free amino group in NGN. Thus, the group may interact with the functional groups in the polymers, i.e., carboxymethyl, methacrylate, amide, and anhydride groups, which can result in incompatibility. For Gantrez (anhydride groups

TABLE 2

SUMMARY OF COMPATIBILITY DATA FOR NITROGUANIDINE (NGN)

Run no.	*HEM*	*Polymer*	*Wt. % HEM*	*Decomposition peak temp. (°C)*	*n*	*E (kcal mole^{-1})*
N-1	NGN	—	100	241±1	0.37±0.04	93±5
N-2	NGN	PSt	58	241	0.33	94
N-3	NGN	PE	47	241	0.32	93
N-4	NGN	Parylene	56	240	0.43	94
N-5	NGN	CMC	60[a]	236[a]	1.52±0.08[a]	137±1[a]
N-6	NGN	Celcon	58[a]	234[a]	0.53±0.08[a]	147±1[a]
N-7	NGN	Delrin	50[a]	227±3[a]	—[b]	—[b]
N-8	NGN	Epon 828 (BF_3-cured)	30[b]	242[b]	0.33±0.1[c]	91±9[c]
N-9	NGN	Epon 828 (anh. cured)	60	244	1.45	200
N-10	NGN	PIBM	49	241	0.89	141
N-11	NGN	PSF	42[a]	242[a]	0.21[a]	93±5[a]
N-12	NGN	Gantrez	62[a]	243[a]	0.27±0.02[a]	78±3[a]
N-13	NGN	PMMA	54	242	1.95	256
N-14	NGN	PVP	55	238	2.0	137
N-15	NGN	PEMA	40	243	1.0	136
N-16	NGN	PAA	36	238	2.0[b]	172[b]

[a] Averages of two runs. [b] This polymer decomposed in the NGN decomposition temperature range. [c] Averages of three runs.

present) and PSF (sulfone groups), although incompatibility was observed, the parameters for these materials did not change as much as for the preceding polymers. In the case of Delrin, the second endotherm for Delrin (cf. Fig. 1) was missing, indicating that NGN had catalyzed the Delrin decomposition. The resulting exotherm possessed a peculiar shape and $T_m = 227 \pm 3$. Because of this, values of E and n for NGN–Delrin mixtures were not calculated. In Fig. 4 are depicted thermograms for NGN alone and for an incompatible mixture of NGN and Celcon.

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