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THERMAL BEHAVIOUR OF POLY(ALLYL AZIDE)

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Abstract

The paper describes the synthesis of low molecular mass poly(allyl chloride) (PAC) (M_n= 856–3834 g mol^{-1}) using Lewis acid ($AlCl_3$, $FeCl_3$, $TiCl_4$) and Al powder. Branching in PAC was indicated on the basis of elemental analysis and ^{1}H-NMR spectroscopy. Azidation of PAC could be carried out at 100°C by using NaN_3 and DMSO as solvent. Curing of poly(allyl azide) (PAA) by cyclic dipolar addition reaction with EGDMA (ethylene glycol dimethacrylate, 5–45 phr) was investigated by differential scanning calorimetry and structure of cured polymer was confirmed by FTIR. A two-step mass loss was exhibited by uncured and cured PAA in nitrogen atmosphere. A mass loss of 20–28% (155–274°C) and 50–61% (330–550°C) was observed.

Keywords: curing studies**,** dipolarophiles, poly(allyl azide), poly(allyl chloride), thermal behaviour, triazole

Introduction

The application of azido polymers {e.g. poly(glycidyl azide), poly(azidomethyl methyloxetane) and poly(bisazidomethyl oxetane)} as binders and fuels in rocket technology is well documented in the literature [1–2]. The high-energy release upon the decomposition of the azide group of these polymers is responsible for their specialised application as a high-energy binder in composite solid propellants. The traditional method used for propellant formulation is to mix low molecular mass, hydroxy-terminated azido polymers (M_n<3000) with curing agent (diisocyanates) and chain extender (trimethylol propane) [3], high-energy additives (ammonium nitrate or ammonium perchlorate) and pyrolant (metallic powder) [4].

These propellants in addition to being fuel rich liberate large amounts of hydrogen, carbon monoxide and hydrocarbons on their burning in the primary chamber and are greatly insensitive to impact and provide high burn rates.

Although extensive studies have been reported on glycidyl azide polymers, no studies on poly(allyl azide) (PAA) have been carried out. In this paper we report the synthesis, characterization, curing behaviour and thermal stability of poly(allyl azide).

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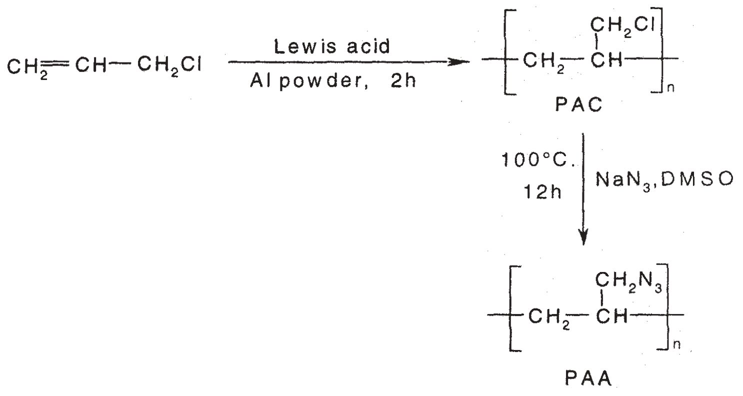
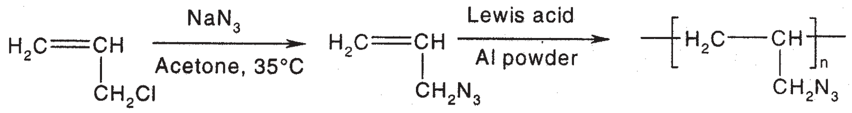
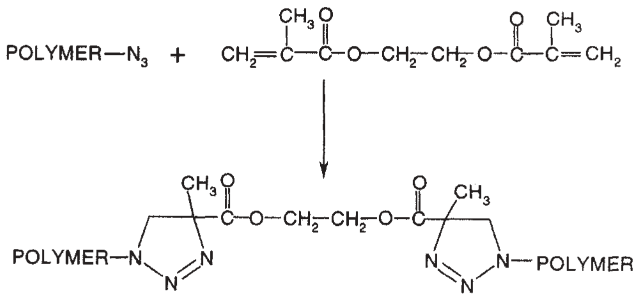


Scheme 1 Preparation of poly(ally azide) by azidation of poly(ally chloride)



Scheme 2 Polymerisation of allyl azide



Scheme 3 Curing of PAA using EGDMA

Poly(allyl azide) can be conveniently prepared by (a) azidation of low molecular mass poly(allyl chloride) (Scheme 1) or (b) polymerisation of allyl azide (Scheme 2).

In our studies we used Scheme 1 for the synthesis of poly(ally azide). The curing of PAA to obtain a cross-linked network was done by employing 1,3-cyclic dipolar addition reaction [5], with ethylene glycol dimethacrylate (EGDMA), according to Scheme 3.

Experimental

Materials

Titanium tetrachloride (anhydrous) (Spectrochem. Pvt. Ltd); aluminium chloride (anhydrous) (Spectrochem. Pvt. Ltd); ferric chloride (anhydrous) (S.d. fine chem. Ltd); aluminium powder (Loba Chemie Co.); sodium azide (CDH); dimethyl sulphoxide

(Merck); chloroform (Qualigens) and ethylene glycol dimethacrylate (EGDMA) (Merck) were used as such. Allyl chloride, *b.p.*=44–48°C (Lancaster) was distilled before use.

Synthesis of poly(allyl chloride) (PAC)

Allyl chloride (0.5 mol) was polymerized using Lewis acids such as anhydrous $TiCl_4$/$FeCl_3$/$AlCl_3$ and aluminium powder [6]. The concentration of the catalyst was varied from 0.7–4.2 mol% of the monomer. The quantity of aluminium powder was kept constant (2 g). The reaction was carried out by placing allyl chloride and Al powder in a 500 mL four-necked reaction kettle having a thermometer pocket, water condenser, nitrogen inlet and a mechanical stirrer. The contents were stirred at 0°C in nitrogen atmosphere and then Lewis acid was introduced. The stirring was continued for 45 min and the temperature was raised gradually to 5°C (in $AlCl_3$), 10°C (in $FeCl_3$) and 20 or 30°C (in $TiCl_4$). Stirring was continued for 2 more h at this temperature. Brown coloured viscous polymer formed was dissolved in chloroform. Aluminium powder was separated from the product by filtration. Neutralisation was done with 10% $NaHCO_3$ solution, followed by washing with distilled water and finally with petroleum ether. Polymer was then dried in an air oven at 60°C.

Synthesis of poly(allyl azide) (PAA)

5 g of poly(allyl chloride) and 5 g of sodium azide were dissolved in dimethyl sulphoxide (20 mL) and the solution was stirred in a reaction kettle at 100°C for 12 h on an oil bath. The contents were then cooled to room temperature. The reaction mixture was washed with hot distilled water to remove sodium chloride and unreacted sodium azide. The polymer was recovered after filtration. It was washed repeatedly with methanol and dried in an air oven at 60°C.

Characterisation techniques

FTIR spectrometer (Bio-Rad Digilab FTS-40/ Nicolet 5PC) was used for recording the IR spectra of PAC and PAA. Bruker AC 300 MHZ FT-NMR spectrometer was used to record the ^{1}H-NMR. $CDCl_3$ was used as solvent and tetramethyl silane as an internal standard. Molecular mass of the polymers was determined using Knauer vapor pressure osmometer K-7000 and benzil as calibration standard. A 2% polymer solution in chloroform was used for molecular mass determination.

Curing of poly(allyl azide)

The curing behaviour of poly(allyl azide) samples with varying amounts (5–45 phr) of EGDMA was evaluated by using TA 2100 thermal analyzer having 910 DSC module. A heating rate of 10°C min^{-1} in static air atmosphere and a sample mass of 2–3 mg were used. For curing studies, the samples were prepared by thoroughly mixing PAA and requisite quantities of EGDMA in teflon boats.

The exothermic transition associated with curing/decomposition of azido group was characterised by determining T_i (kick-off temperature), T_0 (temperature of onset of exotherm), T_p (temperature of peak position of the exotherm), T_f (temperature of the end of the exotherm) and ΔH (heat of curing reaction/heat of decomposition).

Activation energy for the curing reaction of PAA with 20 phr of EGDMA was determined using multiple heating rate method (5, 10, 15, 20°C min^{-1}) of Ozawa [7]. The assumption made in this method is that, the peak maximum represents a point of constant conversion for each heating rate and the temperature dependence of the reaction rate constant obeys Arrhenius equation. Activation energy of curing reaction was calculated from the slope of log of heating rate *vs.* $1/T_p$ plot.

Studies on isothermal curing of PAA with EGDMA were also carried out in an air oven at 40 and 60°C for several days. DSC was used for evaluation of residual cure in these samples after regular intervals of time.

Structural changes taking place in the polymer during isothermal curing were studied by FTIR. For this purpose, poly(allyl azide) was mixed with 20 phr of EGDMA and a thin film was coated on KBr disc, which was then heated in an air oven at 60°C for several days. FTIR spectra were recorded at regular intervals of time for 5 days.

Thermogravimetric analysis

A TA 2100 thermal analyser having 951 TG Module was used for thermal characterisation of isothermally cured poly(allyl azide) in nitrogen atmosphere (flow rate 60 mL min^{-1}). A sample mass of 5–6 mg was used and the rate of heating was 5°C min^{-1}. Isothermally cured samples for this purpose were prepared by thoroughly mixing requisite quantities of EGDMA (5–45 phr) with PAA and placing them in a teflon boat in an air oven at 40°C for 16 h. The temperature was then raised to 60°C and the samples were heated at this temperature for 48 h. The samples containing up to 20 phr of EGDMA were flexible while samples having higher content of EGDMA were brittle in nature. The relative thermal stability of these samples was estimated by comparing initial decomposition temperature (*IDT*), final decomposition temperature (T_f), temperature of maximum rate of mass loss (T_{max}) and char yield at 600°C.

Results and discussion

Polymerisation of allyl chloride

In order to study the effect of reaction parameters on the molecular mass and conversion of allyl chloride, several polymer samples were prepared by changing the catalysts and their concentration (Table 1).

The yield varied from 28 to 45%, when $AlCl_3$ or $FeCl_3$ were used whereas lower conversion was observed with $TiCl_4$. However, the concentration of $TiCl_4$ used was significantly lower than $AlCl_3$ or $FeCl_3$. The number average molecular mass (M_n) values varied from 856 to 3834 g mol^{-1}. M_n increased with the increasing concentration of Lewis acid. Generally an increase in catalyst concentration leads to a decrease in M_n but a reverse trend is observed in the present work.

Table 1 Polymerization of allyl chloride. Effect of reaction parameters on % conversion and molecular mass (M_n) (Al powder=2 g in all samples)

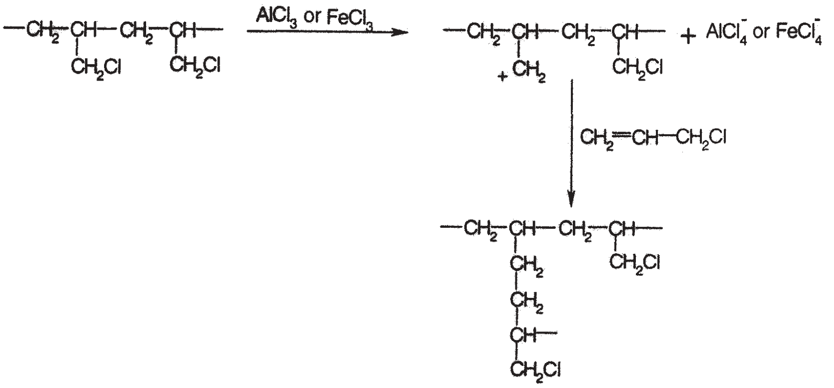
Sample designation	Catalyst system		T/°C	Conversion/%	M_n/g mol^{-1}
	Lewis acid	Amount/ mol% of monomer			
PAC-1	$AlCl_3$	2.9	5	35.2	1230
PAC-2	$FeCl_3$	4.2	10	38.9	1334
PAC-3	$FeCl_3$	3.2	10	45.0	1292
PAC-4	$FeCl_3$	2.8	10	28.5	1152
PAC-5	$TiCl_4$	1.2	20	16.5	3834
PAC-6	$TiCl_4$	0.9	20	26.0	1872
PAC-7	$TiCl_4$	0.7	30	33.2	856

Table 2 Elemental analysis of poly(allyl chloride) samples. The theoretical values for C, H and Cl content of linear poly(allyl chloride) are 47.05, 6.53 and 46.05% respectively

Sample designation	C/%	H/%	Cl/%
PAC-1	52.69	8.39	39.43
PAC-2	55.71	6.26	–
PAC-3	50.79	8.24	40.43
PAC-4	51.21	7.15	–
PAC-5	54.65	6.92	35.5
PAC-6	53.45	6.71	35.71

Structural characterisation of PAC samples was done by FTIR, ^{1}H-NMR and elemental analysis. The results of elemental analysis are given in Table 2. Percentage of chlorine in PAC samples was found to be in the range of 35–40 and was much lower than the theoretical value (46.05%). On the other hand, carbon content was higher than the expected value. A discrepancy in chlorine and carbon content of the polymers can be explained on the basis of side reaction. It is quite likely that in the presence of Lewis acid, chloride ion is abstracted from the side chain, thereby leading to branch formation. This will result in an increase in carbon content and a decrease in chlorine content (Scheme 4). In the FTIR spectra of various PAC samples, the absorption peak at 736 cm^{-1} due to –CH_2Cl stretching was present. A decrease in the intensity of alkene double bond absorption peak at 1639 cm^{-1} indicated the polymerisation of allyl chloride (Fig. 1a).

^{1}H-NMR spectrum of polymer sample is shown in Fig. 1b. The chloromethyl protons in poly(allyl chloride) were observed at 4.03 ppm. The vinylic protons resonance signals of allyl chloride at 5.22, 5.32 and 5.94 ppm were absent in poly(allyl chloride). Additional resonance signals were observed at 0.88–2.27 ppm. The integration of the resonance signals in this region does not correspond to the number of methine (1H) and methylene (2H) protons in the polymer backbone for a linear-chain polymer. The loss of chlorine, as indicated by elemental analysis results (Table 2) also suggests the formation of a branched polymer. Therefore, on the basis of elemental analysis and ^{1}H-NMR it can be concluded that the synthesised poly(allyl chloride) was a branched polymer.



Scheme 4 Probable side reaction during the synthesis of poly(allyl chloride)

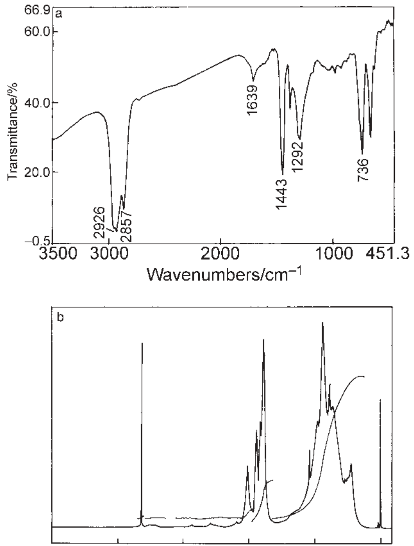


Fig. 1 Poly(allyl chloride) a – IR spectrum; b – ^{1}H-NMR spectrum

In most of the azido binders (e.g. glycidyl azide polymer) used in solid propellants the M_n is around 2000 g mol^{-1}. A very low molecular mass azido polymer (M_n<1000) is useful as a plasticiser while a high molecular mass polymer is used as an elastomer. Therefore, using the synthesised sample PAC-6 we carried out further studies on azidation, curing behaviour and thermal stability.

In the FTIR spectrum of PAA (Fig. 2a) the intensity of 736 cm^{-1} absorption band due to –CH_2Cl decreased whereas a strong band due to –CH_2N_3 appeared at 2095 cm^{-1}. The ^{1}H-NMR spectrum of PAA (Fig. 2b) shows the disappearance of resonance signals due to chloromethyl group at 4.03 ppm and appearance of a proton resonance signal at 3.3 ppm due to azidomethylene protons.

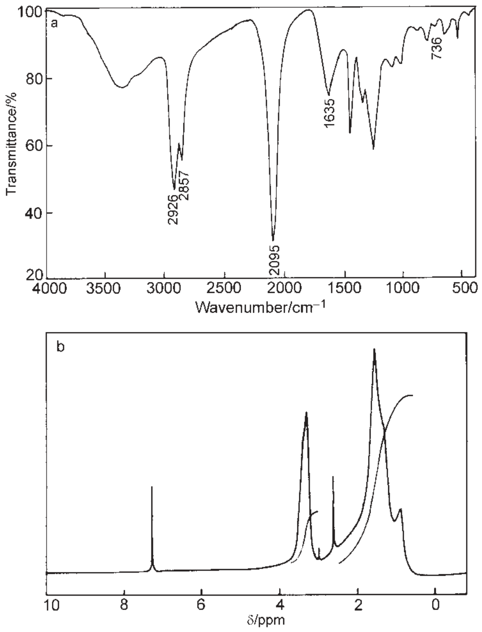


Fig. 2 Poly(allyl azide) a – IR spectrum; b – ^{1}H-NMR spectrum

Thermal behaviour of poly(allyl azide)

The DSC scan (Fig. 3a) of poly(allyl azide) showed an exothermic transition in the temperature range of 155–274°C, with exothermic peak temperature at 231°C. The energy liberated was 1099 J g^{-1}. The TG trace of poly(allyl azide) (Fig. 3b) showed an initial mass loss of 7%, which may be attributed to the moisture and low molecular mass oligomers. The main decomposition proceeded in two stages of mass loss. The first step of the decomposition occurred in the temperature range of 160–322°C, which was in good agreement with the temperature range of exothermic transition in the DSC scan. A mass loss of 28.3% was observed. The exothermic transition observed in DSC accompanied by a mass loss (28.3%) can be attributed to breakdown of azido group according to the following reaction scheme (Scheme 5), which is similar to the one proposed earlier for poly(glycidyl azide) [8–10].

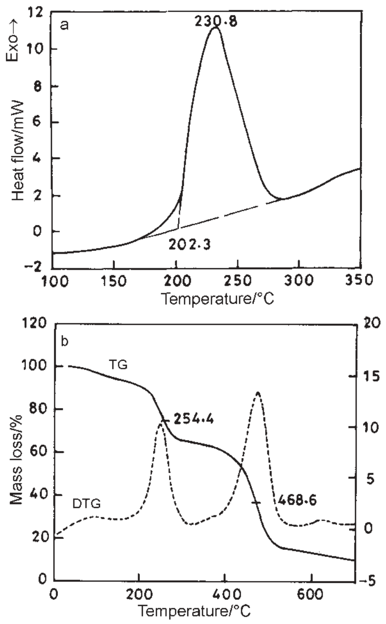
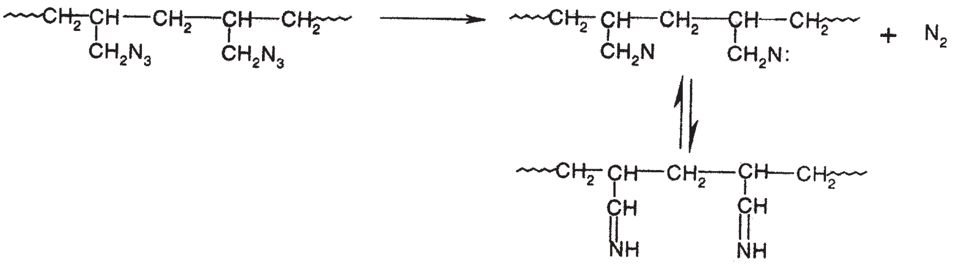


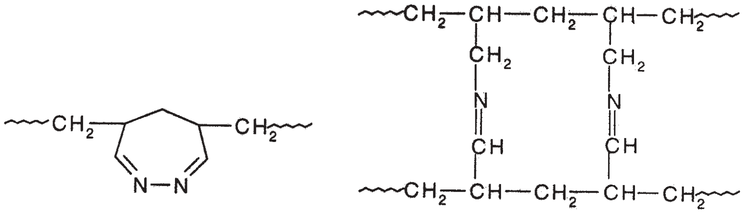
Fig. 3 Poly(allyl azide) a – DSC curve in air atmosphere; b – TG curve in nitrogen atmosphere



Scheme 5 Reaction sequence depicting decomposition of PAA

Theoretically the decomposition of the azido group in a linear PAA should have resulted in a mass loss of 33.7%. The poly(allyl azide) thus had lower azido content. This may be due to the branched structure of poly(allyl chloride), which resulted in lower chlorine content, and since poly(allyl azide) was prepared by azidation of PAC therefore the azido content will be decreased.

Major mass loss was observed above 400°C (~59%) and is due to breakdown of the polymer backbone leading to the formation of hydrogen, carbon monoxide, carbon dioxide, methane, ammonia, hydrogen cyanide gas and other higher hydrocarbons [11]. A char residue of 15% at 600°C and 7% at 800°C was obtained and, may be due to the formation of cross-linked structure by reaction of imine intermediate (inter- as well as intra-molecular) (Scheme 6) [10].



Scheme 6 Intra- and inter-molecular reactions of imino groups

Curing studies

Dynamic DSC scans

Typical dynamic DSC scans for the curing of PAA using 25/45/75 phr of EGDMA are given in Fig. 4. An exothermic transition was obtained above 70°C and may be due to cycloaddition reaction of EGDMA with PAA and thermal polymerisation of EGDMA. The T_i (kick-off) temperatures were 70.4, 93.4 and 100°C and the peak exothermic temperatures (T_p) were 148.5, 149.1 and 151.4°C for samples containing 25, 45 and 75 phr of EGDMA respectively. The heat of curing also increased from 136.5 to 212.4 J g^{-1} with the increase in the EGDMA content.

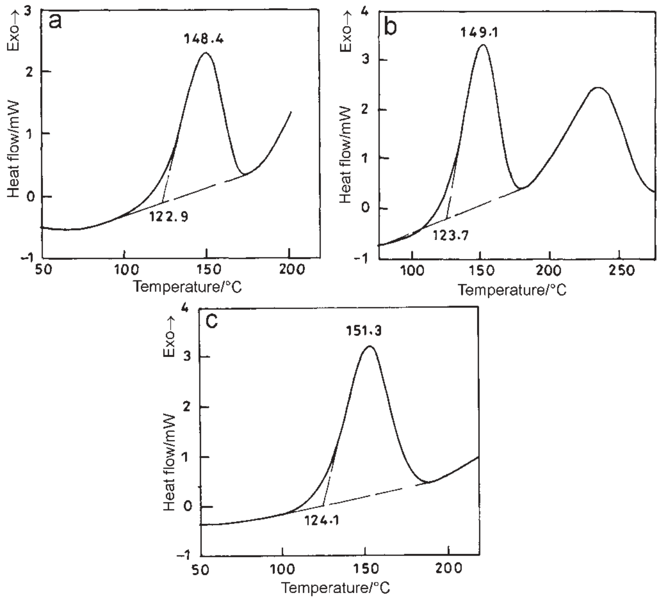


Fig. 4 DSC scans of PAA curing with a – 25; b – 45; c – 75 phr of EGDMA (heating rate 10°C min^{-1})

An exotherm was observed after the curing exotherm and this may be due to decomposition of residual azido groups (Fig. 4b) in the samples. The ΔH for the decomposition exotherm of neat PAA was 1099 J g^{-1}, while for PAA containing 45 phr of EGDMA, it was 181.1 J g^{-1}.

Using Ozawa method [7], $\log\beta$ (programme rate) was plotted *vs*. reciprocal of peak temperature and from the slope obtained by regression analysis, the activation energy and frequency factor for the curing reaction of PAA with 20 phr of EGDMA was found to be 98 kJ mol^{-1} and $1.2\cdot10^{12}$ min^{-1}, respectively.

Monitoring of residual cure in isothermally cured samples

The DSC scans of EGDMA (20 phr) and PAA were recorded after isothermally heating the samples at 40 or 60°C for several days. A significant decrease in heat of curing was observed on increasing the duration of isothermal curing (Table 3). The heat of curing at 40°C changed from 128.6 to 47.2 J g^{-1} in 12 days whereas at 60°C after 7 days (ΔH=13.4 J g^{-1}) extent of cure was much higher thereby resulting in a significant decrease in the residual cure. The exothermic peak temperature also decreased marginally. Gradual curing of poly(allyl azide) can therefore be carried out with EGDMA at 40°C by keeping the samples for several days whereas one can accelerate the curing process by carrying out the reactions at 60°C.

Table 3 Monitoring of residual cure by DSC in isothermally cured PAA using EGDMA (20 phr) at 40 and 60°C (heating rate 10°C min^{-1})

Duration/h	T_p/°C		ΔH/J g^{-1}	
	40	60	40	60°C
0	146.5	146.5	128.6	128.6
2	142.2	–	95.6	–
4	141.1	–	75.6	–
5	–	144.1	–	37.3
6	141.7	–	63.7	–
7	–	154.3	–	13.4
9	142.3	–	52.6	–
12	141.1	–	47.2	–

Structural changes during curing

Only marginal changes in the IR spectra of isothermally cured PAA/EGDMA (20 phr) samples were observed. A shift in the absorption peak due to ester carbonyl of EGDMA from 1721 to 1740 cm^{-1} was observed after 24 h of heating at 60°C (Fig. 5). This shift indicates the removal of the double bond, (which was conjugated with the carbonyl group) by the formation of triazole ring. A new absorption peak was observed at 1135 cm^{-1} and

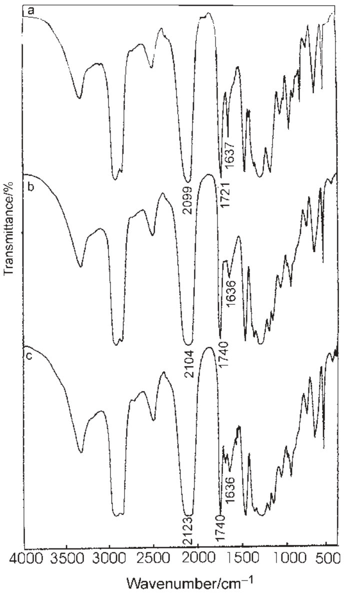


Fig. 5 FTIR of PAA containing 20 phr of EGDMA after heating at 60°C for a – zero h; b – 24 h; c – 120 h

can be attributed to the ring breathing vibrations of 1,2,3-triazoles [12]. These studies thus confirm the cyclic dipolar addition reaction of PAA with EGDMA.

No appreciable decrease in the intensity of azido group at 2099 cm^{-1} was observed. This absorption peak shifted from 2099 to 2123 cm^{-1}. Increasing the phr of EGDMA did not affect the intensity of azido absorption band. This indicates a low conversion of azido group to triazole ring even at higher ratio of EGDMA at 60°C.

Table 4 Thermal behaviour of isothermally cured PAA with 5–45 phr of EGDMA (heating rate 5°C min^{-1})

EGDMA/phr	*IDT*/°C	T_{max}/°C	T_f/°C	Mass loss/%	Y_c/%, at 600°C
0	160.0 326.0	254.4 468.6	322.0 526.0	28.3 58.8	12.5
5	161.8 317.1	228.9 444.8	289.5 525.0	24.9 52.8	17.4
15	171.0 313.1	228.9 443.0	286.9 502.6	20.4 53.7	12.8
30	167.1 323.6	228.9 446.2	323.6 497.4	20.7 60.6	9.2
45	175.0 332.9	284.2 443.6	332.9 497.4	23.0 56.8	10.9

Decomposition behaviour of cured poly(allyl azide)

Results of the thermogravimetric analysis of isothermally cured samples of PAA with 5–45 phr of EGDMA are summarised in Table 4 (Fig. 6).

A mass loss of 0–13% was observed in all the isothermally cured samples due to moisture. The major decomposition occurred in two steps. A mass loss of 20–25% was observed in the temperature range of 161 to 324°C and may be due to the elimination of nitrogen from the azido group.

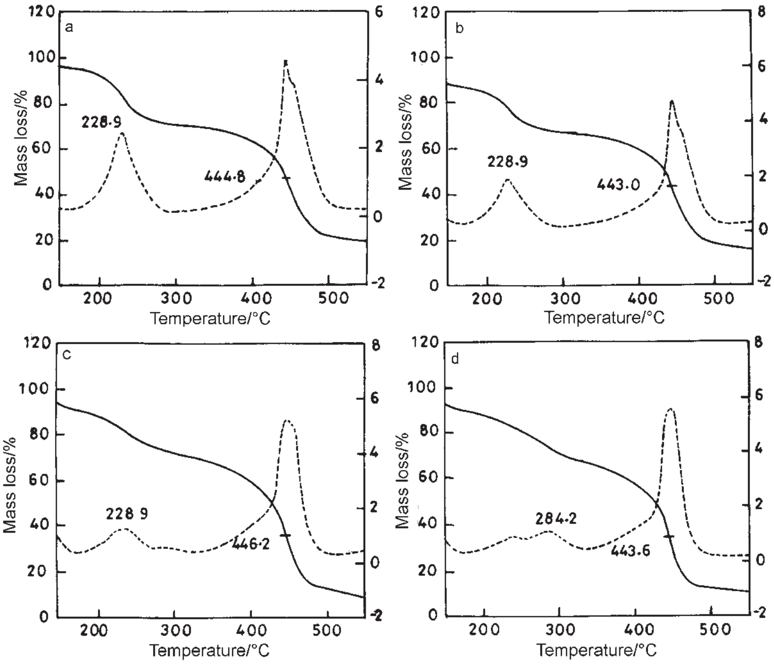


Fig. 6 TG curves of PAA cured at 40°C for 16 h and at 60°C for 48 h using different phr of EGDMA; a – 5; b – 15; c – 30; d – 45

The second stage decomposition was in the temperature range of 313–525°C accounting for the mass loss of 52–61%. This is due to the thermal degradation of the main chain along with triazole group formed by the cross-linking reaction. The char residue of 9–18 % was left at 600°C.

Conclusions

Our results thus indicate that matrix resins based on poly(allyl azide) curable by cyclic dipolar addition reaction release large amount of energy on heating and can be used as energetic-binders and fuels in rocket technology.

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