High Energy Binders: Glycidyl Azide and Allyl Azide Polymer

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Summary: Hydroxy-terminated azido polymers such as poly(glycidyl azide), poly bis(azidomethyl oxetane) and poly(azidomethyl methyloxetane) have been investigated in the past in propellent formulations and as fuels in rocket technology. The high energy released upon the decomposition of the azido group is responsible for their specialized application as high-energy binders. The present paper describes the synthesis and characterization of new low molecular mass azido polymer i.e. poly(allyl azide). The curing reaction was carried out by using 1,3-cyclic dipolar addition reaction. The dipolarophiles, such as dimethylene glycol dimethacrylate (EGDMA) and addition polyimides (bismaleimides, bisnadimides and bisitaconimides) were used for curing of azido polymers. The curing reaction was monitored by FT-IR and differential scanning calorimetry. Curing was carried out at 40°C for 16 h (EGDMA) or 2 days (bismaleimide) and then at 60°C by using different phr of dipolarophiles. The heat of exothermic transition, due to decomposition of azide groups and thermal polymerization of addition polyimides, was very high and an improvement in thermal stability of cured resins was observed.

Keywords: bismaleimides; cycloaddition; ethylene glycol dimethacrylate; poly (allyl azide); poly (glycidyl azide)

Introduction

High-energy solid rocket propellants are composite materials having a binder [hydroxy terminated polybutadiene (HTPB)], and high-energy additives [e.g. ammonium perchlorate (AP)] and pyrolants (metallic powder). HTPB is an inert binder, which has been used in cast-cure propellant systems. Substitution of HTPB by more energetic binders may lead to an enhancement in performance of such propellants. Azido polymers have attracted researchers attention for the past two decades and compatible propellants with acceptable physical properties could be formulated from azide-containing ingredients.[1-4] The polymeric azides include poly (glycidyl azide) (GAP) and its copolymers, poly (*bis*-azidomethyl oxetane) [poly (BAMO)] and its copolymers, and poly (azidomethyl methyl oxetane)[poly (AMMO)]. [3] Although extensive studies have been reported on glycidyl azide polymers, no studies on poly (allyl azide) (PAA)

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have been carried out. In this paper we report the synthesis, characterization, curing behaviour and thermal stability of poly (allyl azide).

The hydroxyl-terminated azido prepolymers are cured by reacting with isocyanates. There are certain problems associated while using isocyanates as curing agents for hydroxy- terminated binders. An alternative approach is the use of cycloaddition reaction with appropriate dipolarophiles. Curing of glycidyl azide polymers with multifunctional acrylic or acetylenic esters has been reported in the literature. [5,6] In this paper we present the results of our studies on curing of poly(allyl azide) using ethylene glycol dimethacrylate and addition polyimides such as bismaleimides, bisitaconimides or bis (*endo*-5-norbornene-2,3-dicaroximide) (bisnadimide) end-capped resins.

Experimental

Titanium tetrachloride (anhydrous) (Spectrochem. Pvt. Ltd); aluminum 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.

Poly (allyl azide)[7] and bismaleimides[8-10] i.e. 4,4'- bis(maleimidodiphenyl) ether (BE), 4,4'-(bismaleimidodiphenyl) sulphone (BS), and 1,6- bismaleimido hexane (BH) were synthesized according to the method reported earlier. The m.pt of the bismaleimides- BE, BS and BH were 174-175°C, 252°C and 138°C respectively. Synthesis of PAA was carried out by first preparing the poly(allyl chloride) followed by azidation.

The curing behaviour of poly (allyl azide) with varying amounts (10-30 phr) of bismaleimides or ethylene glycol dimethacrylate (5-45 phr) was evaluated by using TA 2100 thermal analyzer having 910 DSC module. A heating rate of 5-10°C/min in static air atmosphere and a sample mass of 4±1 mg were used. The exothermic transition observed in the temperature range of 150-280°C was characterised by determining the temperatures of (a) onset of exotherm (Ti), (b) extrapolated onset (To), (c) end of exotherm (Te) and exothermic peak temperature (Tp). Heat of the reaction (ΔH) was determined from the area under the exothermic transition.

Studies on isothermal curing of PAA with bismaleimides was also carried out in an air oven at 40°C (2 days) or 16 h with EGDMA and 60°C for several days. DSC was used for the evaluation

of changes in the exothermic transition in these samples after heating at 40°C for two days and then after keeping at 60°C for 0-6 days.

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). A sample mass of 5-6 mg was used and the rate of heating was 5-10 °C/min. 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.

Characterisation Techniques

FT-IR spectrometer (Bio-Rad Digilab FTS-40/ Nicolet 5PC) was used for recording the IR spectra of PAC and PAA. 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.

Structural changes taking place in the polymer during isothermal curing were studied by FT-IR. 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. FT-IR spectra were recorded at regular intervals of time for 5 days.

Results and Discussion

Polymerisation of allyl chloride

Poly(allyl chloride) (PAC) with different molecular masses could be obtained by changing catalyst and monomer concentration. A PAC sample having molecular mass of 1872 was used for carrying out further studies. 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.

Thermal behaviour of poly (allyl azide)

The DSC scan 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 (Fig. 1a). The TG trace of poly (allyl azide) 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. The first step of 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 (Fig. 1b). The exothermic transition observed in DSC accompanied by a mass loss (28.3 %) has been attributed to breakdown of azido group, by a mechanism reported earlier for glycidyl azide polymer. [11-12]

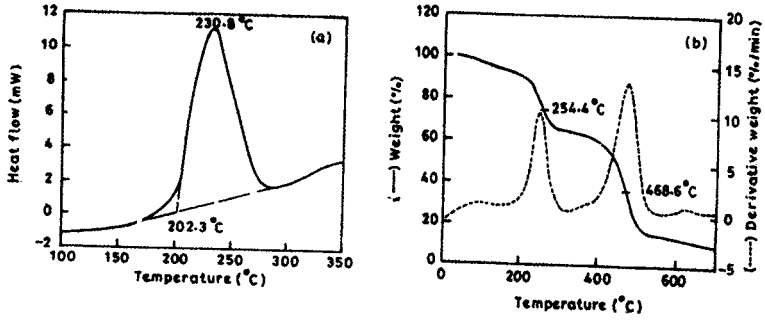


Figure 1. DSC and TGA Traces of poly(allyl azide)

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 of the polymer. 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. A char residue of 12.5 % at 600°C and 7 % at 800°C was obtained and, may be due to the formation of cross-linked structure. [10]

Curing studies

Poly (allyl azide) and EGDMA

Samples of PAA containing upto 25 phr of EGDMA were flexible. A further increase in EGDMA content resulted in a brittle product. In the DSC scans of PAA cured in presence of 25/

45/ 75 phr of EGDMA, 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 Ti values were 70.4, 93.4 and 100°C and the peak exothermic temperatures (Tp) 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 with the increase in the EGDMA content.

An exotherm was observed after the curing exotherm and this may be due to decomposition of residual azido groups in the samples. The ΔH for the decomposition exotherm of neat PAA was 1099 J/g, while for PAA containing 45 phr of EGDMA, it was 181.1 J/g.

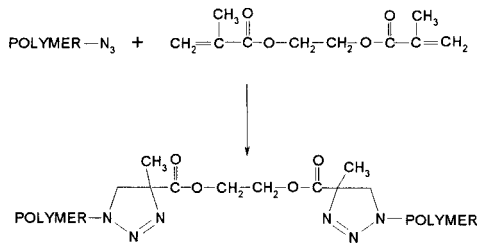
Monitoring of residual cure in isothermally cured samples

The DSC scans of EGDMA (20 phr) and PAA were recorded after isothermal curing. A significant decrease in heat of curing was observed on increasing the duration of isothermal curing. The heat of curing at 40°C changed from 128.6 to 47.2 J/g in 12 days whereas at 60°C after 7 days (ΔH = 13.4 J/g) 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.

Structural changes during curing

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. This shift indicates the removal of the double bond, (which was conjugated with the carbonyl group) by the formation of triazoline ring. A new absorption peak was observed at 1135 cm^{-1} and can be attributed to the ring breathing vibrations of 1,2,3-triazolines. [13] 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 triazoline ring even at higher ratio of EGDMA at 60°C.



Scheme 1. Curing of PAA using EGDMA

Poly (allyl azide) and bismaleimides

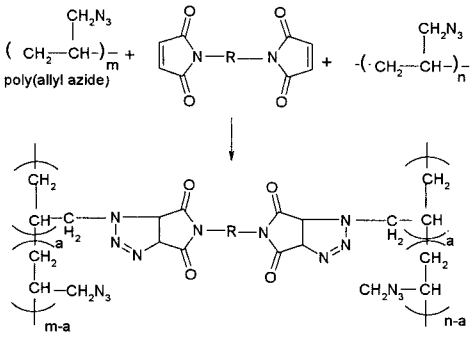
The curing of PAA was done with three different bismaleimides containing (a) flexible aliphatic units (hexamethylene) (BH), (b) aromatic rings having flexible ether (BE) linkage or (c) a strong electron withdrawing group sulphone (BS) as the bridging units between maleimide end caps. The bismaleimide content was varied to evaluate the effect of concentration on curing (10-30 phr). This corresponds at 10 phr to an azide:maleimide ratio of 1:0.06, 1:0.47 and 1:0.02 for BH, BE and BS respectively. Thus, azide groups were much higher in concentration than maleimide under investigation. This will control the cross-link density of the cured product.

The blends of PAA and bismaleimide were initially sticky mass irrespective of the composition of blends. Isothermal heating at 40°C for 2 days resulted in a marginal change in physical characteristics. When isothermal heating was done at 60°C for several days, the sticky mass converted to a non-sticky elastic product.

The PAA blends with bismaleimides BH, BE or BS have been designated as PH, PE and PS respectively. The phr of the bismaleimides is indicated by writing A (10 phr), B (15 phr) and C (30 phr) after the letter designation of concerned blend. The duration of isothermal curing i.e. 0, 1, 5 days etc are indicated by writing the number after letter designation of the formulation. Thus, a blend of PAA and BE (10, 15, 30 phr) and cured for 5 days is designated as PEA-5, PEB-5, and PEC-5, respectively. The 1,3- cyclic dipolar addition with bismaleimides can be depicted according to the scheme 2.

The exothermic peak position of PAA was 231°C but addition of structurally different bismaleimides reduced it by 20-30°C. The ΔH was 1099 J/g for PAA but in most blend samples ΔH value was either equal to or higher than this value. Slightly lower values were observed only

in PEC-6, PEB-0, PHC-1 and PHC-5 samples. The observed exotherm in PAA bismaleimides samples arises due to two reactions- (a) loss of N_2 from PAA to yield nitrenes and (b) curing of bismaleimides. The ΔH values of bismaleimides (150-200 J/g) are lower than the heat evolved during decomposition of azide groups.



Scheme 2. Curing of Poly (allyl azide) with Bismaleimides

These results thus indicate that only few azide groups had reacted with bismaleimides at 60°C and a large proportion was available for decomposition of these energetic binders. Bismaleimide did not act as an inert material (as in case of isocyanates) but contributed towards the heat of curing in the same temperature range in which azide group undergoes decomposition. Thus the over all heat evolved in the temperature range of 150-277°C was either equal to neat PAA or greater than that.

The results of TG studies are summarized in Table 1. A two-step decomposition was observed. A mass loss of 18 – 23% was observed in temperature range 150- 280°C. In comparison to pure PAA, a reduction in mass loss of about 5-10 % is observed. Curing of bismaleimides is an addition reaction without evolution of any volatiles whereas PAA eliminates N_2 in this temperature range. Increase in phr of bismaleimides reduced the mass loss in this temperature region. The second step decomposition was observed in the temperature range of 290-310°C with a mass loss of 57-64 %. Compared to PAA, the char residue at 600°C was higher in these resins. This is due to the network formation of cured bismaleimides, which favour condensation and char formation at high temperatures.

Table 1. Thermal behaviour of isothermally cured PAA with BH resin (heating rate 10°C/min)

Sample designation	IDT (°C)	T_{max} (°C)	T_f (°C)	Mass loss (%)	Y_c (%, 600°C)
PHA-1	155.4	209.4	280.0	22.0	23.4
	297.7	482.1		63.2	
PHA-5	153.5	201.5	271.4	27.6	22.5
	296.4	459.8	610.7	57.5	
PHB-1	124.4	213.8	291.1	22.0	14.8
	300.0	477.0	600.0	63.2	
PHB-5	144.4	210.3	291.1	21.9	20.0
	304.4	468.3	555.6	58.5	
PHC-1	142.8	221.5	275.0	18.2	21.6
	289.3	466.5	628.6	58.4	
PHC-5	132.1	194.0	264.3	18.1	20.7
	282.1	461.8	600.0	60.3	
PEA-1	135.6	211.8	286.7	24.2	13.5
	295.6	472.4	580.0	62.5	
PEA-6	125.0	210.0	282.1	22.7	19.4
	292.8	459.3	610.7	59.5	
PEB-1	128.9	220.8	297.8	24.5	15.2
	297.8	467.6	573.3	60.3	
PEB-5	135.7	207.7	282.1	20.4	22.0
	285.7	463.6	607.1	60.0	
PEB-1	111.2	203.4	302.1	18.7	25.8
	311.0	464.2	635.5	59.2	
PEB-6	142.8	202.7	282.1	18.7	21.6
	292.8	460.7	592.9	62.6	
PSB-1	124.4	213.8	291.1	22.0	14.8
	300.0	477.0	600.0	63.2	
PSB-5	146.5	212.9	275.5	22.0	19.4
	297.7	460.6	532.2	62.3	

Conclusion

Curing of poly(allyl azide) can be carried out under mild conditions using bismaleimides (10-30 phr) as the dipolarophiles. The cured resins were flexible and retained their elastic behaviour for several weeks. The ΔH value for the exothermic decomposition of azido groups was significantly high. This may be due to exothermic curing of bismaleimides and the decomposition of azido groups in almost same temperature range. In contrast to isocyanates, which are generally used for curing of hydroxyl-terminated azido polymers, bismaleimides do not act as inert curing agents. An increase in char residue of cured resin at 600°C was also observed.

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