Correlation between fracture properties and dynamic mechanical relaxations in composite propellants

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The fracture behaviour of a series of composite propellants (containing segmented polyurethanes based on hydroxy-terminated polybutadiene (HTPB) or poly(ether glycols) or glycidyl azide polymer, filled with ammonium perchlorate (AP) particles) during impact has been measured on a modified Hopkinson bar and correlated with viscoelastic properties measured by dynamic mechanical thermal analysis (d.m.t.a.). Results from Fourier analysis of the impact pulse give direct evidence that molecular relaxation processes responsible for the binder soft-segment α-transition govern the fracture property of these composite polymers. However, fracture also depends on other factors such as filler–binder interactions and impact temperature. Evidence is given for filler–binder interactions at the filler–binder interface. Propellants containing glycidyl azide polymer as binder are less sensitive to impact than comparable propellants with HTPB or poly(ether glycol) as binder. The chemical structure of the polymeric binder appears to have little influence on the impact sensitivity whereas physical properties are important.

(Keywords: segmented polyurethanes; hydroxy-terminated polybutadiene; glycidyl azide polymer; fracture properties; dynamic mechanical relaxation; filler–binder interactions)

INTRODUCTION

A current major emphasis in rocket propulsion technology is to lower the sensitivity of the propellant charge in rocket motors to fragment or bullet attack without compromising ballistic performance. The resistance of the propellant grain to fracture or cracking under high (impact) strain rates is an important aspect in determining the sensitivity. The fracture behaviour of composite propellants (in particular, the effects of the physical and mechanical properties of the polymeric binder) are examined in this study.

The fracture properties can be expected to be related to the magnitude of the various mechanisms by which the material can dissipate the impact energy and thus to relaxation processes that contribute to energy dissipation of the impact blow. Although it is well documented that various correlations exist between mechanical relaxations and impact behaviour in bulk polymers[1–3], there has been comparatively little work published on composite propellants containing an elastomeric polymer binder and an oxidizer (which also acts as the filler).

Matuszak *et al.*[4] found a rough correlation between impact sensitivity (measured by the drop height test) and loss factor or glass transition temperature (measured by dynamic mechanical analysis) of composite propellants. However, little work has been done to identify the relaxation processes responsible for the energy dissipation, or to investigate the relationship between impact strength and the dynamic mechanical energy dissipation mechanism at the temperature and frequency of the impact. The importance of comparing impact properties and viscoelastic energy losses at the same temperature and frequency has been reported by several workers for bulk polymer systems[5–7]. In the present study, the fracture properties of a series of composite propellants are related to their linear viscoelastic properties and mechanical relaxation processes at the temperature and timescale of impact loading.

The dynamic mechanical property of filled polymers is not only dependent on the nature of the polymer and filler but is often strongly influenced by the character of the polymer–filler interface[8–10]. Polymer–filler interaction between the filler particle surface and the polymeric binder matrix has not been previously investigated for composite propellants under high-strain-rate conditions. Evidence for interactions at the filler–binder interface in composite propellants is provided in this study.

EXPERIMENTAL

Materials

The composite propellant types and their principle binder ingredients are listed in *Table 1*. Ammonium perchlorate (AP) was used as the oxidizer in all samples, except for the PBG/PETN,RDX propellant where pentaerythritol tetranitrate (PETN) and cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) were used. The same binder-to-oxidizer weight ratio (17:83) was used for all propellants studied. The binder NCO/OH ratio was 1:1. The propellants were made by standard processing techniques and were kindly supplied by Mr B. Hamshere.

The processed propellants were machined into 8 × 8 mm pellets for the Hopkinson bar test, 30 × 6 × 2 mm bars for dynamic mechanical thermal analysis (d.m.t.a.) in the single cantilever mode and 5 × 2 mm discs for d.m.t.a. in the shear sandwich mode.

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Table 1 Propellant composition

Propellant type (binder/oxidizer)	Binder prepolymer	Curative
HTPB/AP	Hydroxy-terminated polybutadiene	Dimeryl diisocyanate (DDI)
PBG/AP	Poly(butylene glycol)	Isophorone diisocyanate (IPDI)
PBG/PETN,RDX	Poly(butylene glycol)	Isophorone diisocyanate (IPDI)
Teracol/AP	Teracol	Hexamethylene diisocyanate (HMDI)
PPG/AP	Poly(propylene glycol)	Hexamethylene diisocyanate (HMDI)
GAP/AP	Glycidyl azide polymer	Hylene W

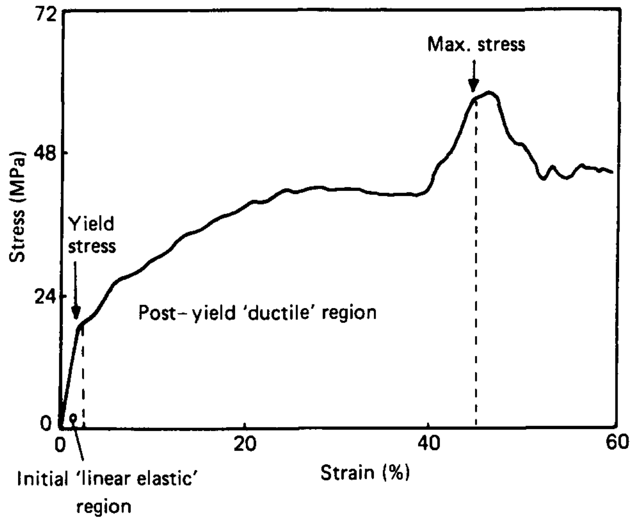

Figure 1 Load vs. displacement for the GAP/AP propellant at an impact velocity of 19.8 m s^{-1}

Figure 2 SEM of HTPB/AP after compression testing

Measurements

Dynamic moduli (Young's and shear) and loss tangent (tan δ) values were measured using a Polymer Laboratories dynamic mechanical thermal analyser, interfaced to an HP9826 computer for data acquisition, in the single cantilever or shear sandwich mode. The analysis was made over the temperature range -130 to 160°C at a scan rate of 2°C min^{-1} with test frequencies of 0.33, 3 and 30 Hz.

The fracture properties of the composite propellants were assessed on a modified Hopkinson bar[11,12] (where the sample is impacted and compressed by a high-velocity projectile—input bar) which measures mechanical properties at high strain rates. The surface of the impact end of the specimen was lightly greased to minimize friction. Stress–strain data were collected using a Nicolet 4094 two-channel digital oscilloscope and an HP9826 computer. The specimens were tested in triplicate at ambient temperature (20°C) and impact velocities varied from 6 to 30 m s^{-1}.

The frequency spectrum of the impact stress pulse was obtained by discrete Fourier transform analysis, utilizing the '4094 Waveform Analysis' software package for the Nicolet oscilloscope, which allows the data captured on the digital CRO to be truncated so that only the initial linear region or the initial and post-fracture region of the load vs. time plot is analysed.

RESULTS AND DISCUSSION

Fracture properties

Figure 1 shows a typical stress vs. strain curve for the propellants studied in this work. The observed stress vs. strain curves may be explained by compression of the sample on impact by the moving input bar, resulting in what appears to be an initial 'linear elastic' region followed by a yield point and further post-yield compression. However, the initial linear region of the stress–strain curve is only a pseudo-elastic phenomenon, since there is good evidence that small cracks do occur in the sample during this portion of the stress–strain curve. Evidence for the formation of small cracks before the yield point comes from the low-impact-velocity tests performed at low temperatures ($\sim$0°C), in which the stress vs. strain curve consists mainly of the initial linear region with a yield point. Small cracks were observed but the sample was not grossly fragmented. Scanning electron microscopy of the samples (*Figure 2*), after impact, show debonding and cracking around the filler–binder interface region. This 'initial' elastic region is a very small region and can only be used to predict behaviour accurately for a very narrow regime of conditions, i.e. at very small strains where the material has 'brittle' characteristics'. The fracture process occurring in the post-yield 'ductile' region of the curve is less clear than in the initial 'elastic' region. Viscoelastic/plastic deformation, further crack propagation and other secondary deformation mechanisms contribute to this portion of the curve. Furthermore, the velocity of the input bar may have slowed down slightly in this region and the area of the specimen may have changed on compression, making interpretation of the data more difficult than in the initial linear region. However, the errors caused by these changes are likely to be small at strains up to and before the maximum stress. The stress–strain plots up to the maximum stress are reproducible to within ±30%.

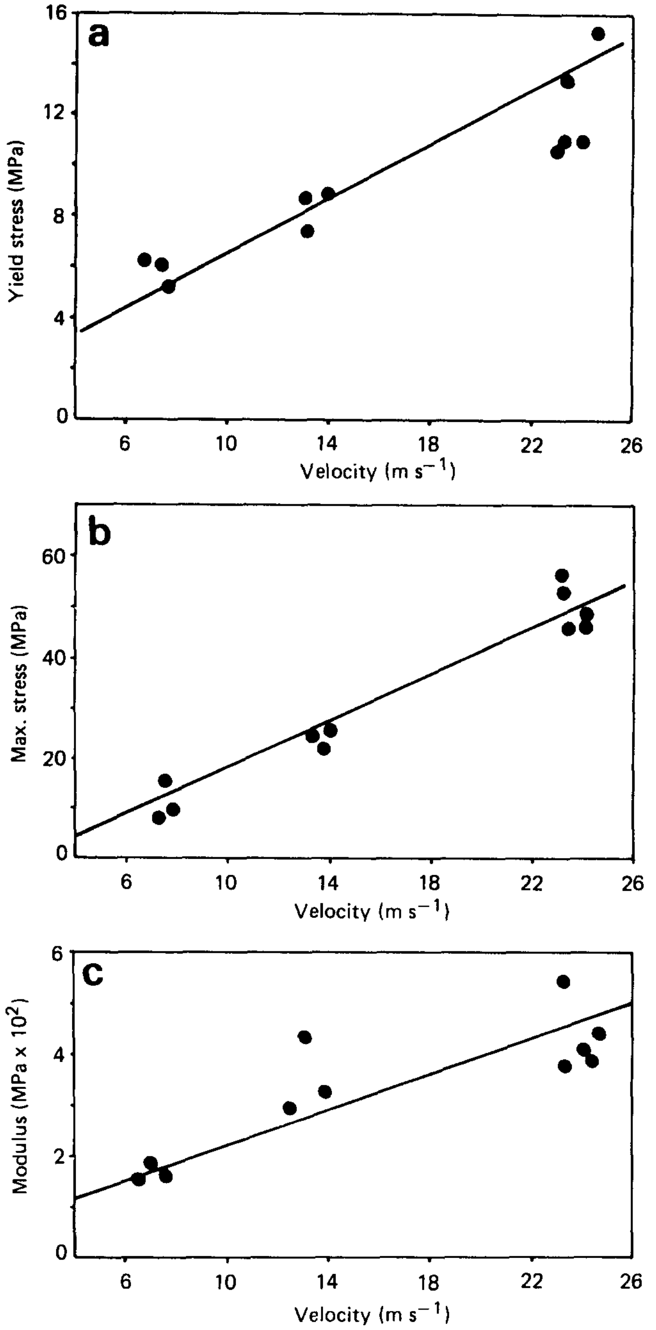

Figure 3 Dependence of (a) yield stress, (b) maximum stress and (c) modulus on velocity for the PPG/AP propellant

The fracture properties are dependent on the impact velocity (*Figure 3*). For all the samples studied, good linear plots were otained for the yield stress, maximum stress and fracture toughness. Thus, interpolation to obtain these values at a given velocity is valid when comparing impact properties between different propellant samples. Alternatively, the slopes of these plots can be utilized for comparison purposes. A linear relationship between modulus and velocity is also obtained for some of the composite propellants studied. However, the errors involved in the determination of the modulus are iarge (~ ±80%) and this would explain the deviation from linearity for the other samples.

Table 2 shows the slopes of the yield stress, maximum stress and fracture toughness vs. velocity plots for the various propellants studied. Fracture toughness in the 'elastic' region and the total fracture toughness were obtained from the area under the stress–strain curve in the initial 'linear elastic' region and in the initial 'linear elastic' and post-yield 'ductile' regions, respectively. At ambient temperature, the general conclusions drawn from this study are not affected by whether the fracture toughness in the 'elastic' region or the total fracture toughness was used in this analysis.

The results show that the glycidyl azide polymer (GAP) propellant is more resistant to impact than the other propellants, as indicated by the higher yield stress, maximum stress and fracture toughness. Propellants with hydroxy-terminated polybutadiene (HTPB) and poly(ether glycol) binders have comparable impact sensitivities. This suggests that slight variations in the chemical structure of the polymeric binder do not influence the impact strength—the oxygen atom in the main chain of the polymeric binder does not appear to affect the impact sensitivity of the propellant. However, the physical properties of the polymeric binder are important. Preliminary studies show that temperature has a marked effect on the impact sensitivity (particularly at low impact temperatures where the propellant is brittle)[13].

There is little difference between the poly(butylene glycol) (PBG) propellants with AP and those with PETN or RDX oxidizers, suggesting either that the type of oxidizer has little effect on the impact sensitivity or that the AP oxidizer exerts a similar effect on the sensitivity as the RDX and PETN oxidizers. Further studies on the contribution of the oxidizer to fracture properties will be reported in a later paper[13].

Dynamic mechanical thermal analysis

The relaxation behaviour of the HTPB/AP propellant is illustrated in *Figure 4*. Similar plots are observed for the other propellants studied. The loss tangent plots show two major relaxations corresponding to the two phases

Table 2 Impact sensitivity of propellants

Propellant type	Yield stress/velocity (MPa/m s^{-1})	Max. stress/velocity (MPa/m s^{-1})	Fracture toughness in elastic region/velocity (Pa mm/m s^{-1})	Total fracture toughness/velocity (MPa mm/m s^{-1})
HTPB/AP	0.65±0.02	1.9±0.2	13	22±1
PBG/PETN,RDX	0.8±0.1	2.8±0.3	9±2	39±12
PBG/AP	0.8±0.1	3.0±0.2	9±5	41±6
Teracol/AP	0.64±0.06	2.0±0.2	12	28±7
PPG/AP	0.74±0.03	2.4±0.2	14	42±5
GAP/AP	1.3±0.1	4.18±0.04	29±2	60±10

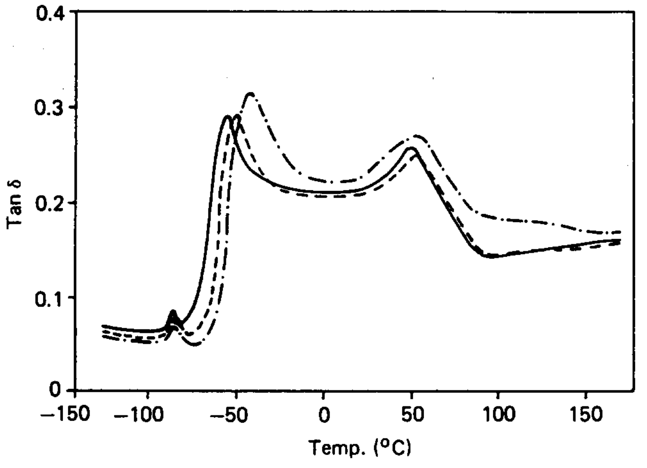

Figure 4 Temperature dependence of tan δ for the HTPB/AP propellant: (———) 0.33 Hz, (-----) 3 Hz, (–·–·–) 30 Hz

present in the polymeric binder. The observation of two glass transition temperatures (T_g), associated with relaxation of the hard segment (composed mainly of sequences of isocyanate reacted with the extender) and of the soft segment (composed primarily of the prepolymer), and the incompatibility of the hard and soft segments and subsequent phase separation into separate domains, have been documented for block copolymers and segmented polyurethanes[14–16]. The T_g values of the propellants studied, determined at 0.33 Hz from the tan δ peaks, and activation energies for the transitions are given in *Table 3*. T_g occurs at around −40°C for the binder soft segment and at around 40°C for the hard segment, for all the propellants studied. Activation energies for the soft-segment α-transition are in the range 160–240 kJ mol^{-1}, appropriate to molecular motion within the main chain[17]. The activation energy does not appear to influence the impact sensitivity (see *Tables 2* and *3*).

A small peak is also observed at −85°C for the HTPB/AP propellant. This β-transition can be attributed to molecular motion of segments of the HTPB polymer chains. Mathew *et al.*[18] observed loss peaks at −103°C for *cis*-polybutadiene and at −63°C for *trans*-polybutadiene and assigned these to the β-transition process.

The presence of filler (oxidizer) in the composite propellants caused an increase in the T_g values (4–7°C for the soft segment and around 10°C for the hard segment), compared to the binder without filler. Although the filler content is high (~83 wt %), the intensities of the tan δ peaks are only slightly lower than those of the binder without filler (especially in the high-temperature region). The relatively small decrease in damping (a larger decrease would be expected from the high filler content[19,20]) and the shift in T_g to higher temperatures, in the presence of filler, indicate the presence of filler–binder interactions. The increased damping has generally been seen to be an interfacial effect, caused by particle–polymer friction[21]. A shift in T_g has also been reported to give some indications of interface interactions[22]. Interactions at the interface between filler and polymer in composite systems have been reported by a few workers[21,22,24,25], and the adhesive bonds between filler particles and the polymeric matrix can cause an increase in mechanical performance. This interface region has important implications in the fracture mechanism of the composite propellants—if debonding occurs at the interface or if adhesion is low, cracks will initiate and propagate around the filler–binder interface.

Comparison of the intensities of the loss peaks with impact properties (*Table 2*) shows that the magnitude of the hard-segment loss peak has no correlation with impact sensitivity. However, the soft-segment loss peak shows good correlation with the impact sensitivity (*Figure 5*). This is as expected from theory, as the soft segment has more rubbery characteristics compared to the hard segment, and would be more efficient at dissipating the impact energy. Only the HTPB/AP propellant does not lie on the straight-line plot of tan δ vs. fracture toughness in the elastic region. This may be attributed to the lower T_g of the HTPB binder compared to the other binders and/or to the presence of a β-transition loss peak which can result in a high impact strength.

The larger T_g shift of the hard segment, in the presence of filler, compared to the soft segment suggests that the sites of filler–binder interaction are mainly at the hard segment. Thus, although fracture is dominated by the intensity of the soft-segment damping peak, the hard segment (indirectly) also exerts a smaller effect.

Table 3 T_g behaviour of composite propellants

Propellant type	T_g(soft) (°C)	T_g(hard) (°C)	Activation energy of soft-segment α-transition (kJ mol^{-1})±5%
HTPB/AP	−58	40	180
PBG/AP	−41	45	150
PBG/PETN,RDX	−37	45	240
Teracol/AP	−48	45	240
PPG/AP	−27	55	220
GAP/AP	−28	45	180

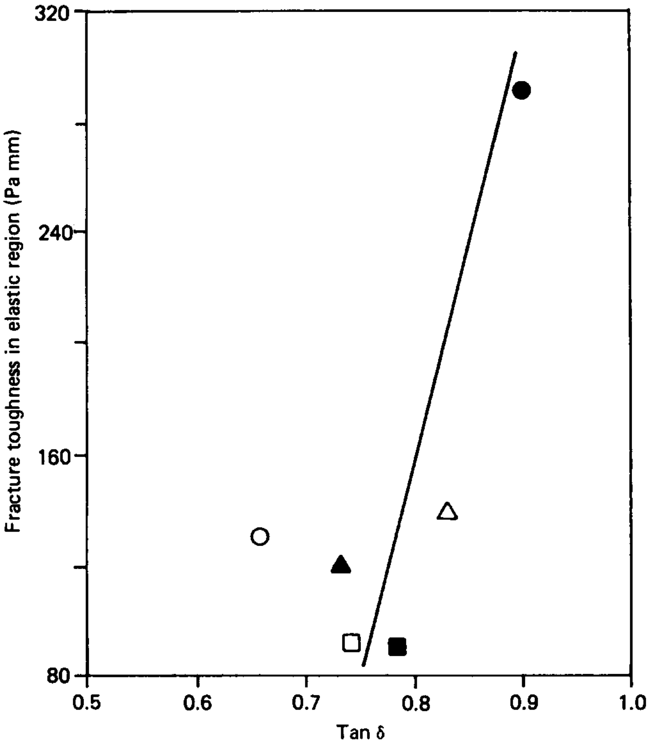

Figure 5 Loss tangent of soft-segment α-transition vs. fracture toughness in elastic region: (○) HTPB/AP, (●) GAP/AP, (△) PPG/AP, (▲) Teracol/AP, (□) PBG/PETN,RDX, (■) PBG/AP

Impact behaviour and viscoelastic energy losses at the same temperature and frequency

A dynamic mechanical loss process which occurs at a temperature well below that of the impact temperature may be operative to dissipate the impact energy, as the impact pulse corresponds to a high-frequency measurement and has the effect of raising the transition to a higher temperature. In this study, the fracture properties are related to the dynamic mechanical losses which exist in the temperature and frequency ranges of impact (and are thus capable of dissipating the impact energy) by (i) doing a Fourier analysis to obtain the frequency spectrum of the impact pulse and comparing this with (ii) the frequency spectrum at room temperature of the α-transition loss peak, calculated using a modified form of the WLF equation.

WLF calculations were performed using the time–temperature shift technique described by Townend[23]. The constants $C_1 = 13.5$ and $C_2 = 66.2$ at a frequency of 1 Hz were used. The experimental data have been verified to fit the WLF equation by calculating the temperature shift of peak tan δ with frequency (three experimental frequencies were used) and comparing this with the actual temperature shift.

The frequency distribution of the soft-segment α-transition at room temperature is shown in *Figure 6*. At room temperature, the spectrum of the loss peak is shifted to higher frequencies and over a broader frequency range with a maximum at around 9 MHz.

The load vs. time data collected on the digital oscilloscope were transformed to the frequency domain using the following discrete Fourier transform equations:

$$S_k(\text{real}) = 1/N\left(\sum_{i=0}^{N-1} x_i\cos(2\pi ik/N)\right)$$

$$S_k(\text{imaginary}) = 1/N\left(\sum_{i=0}^{N-1} x_i\sin(2\pi ik/N)\right)$$

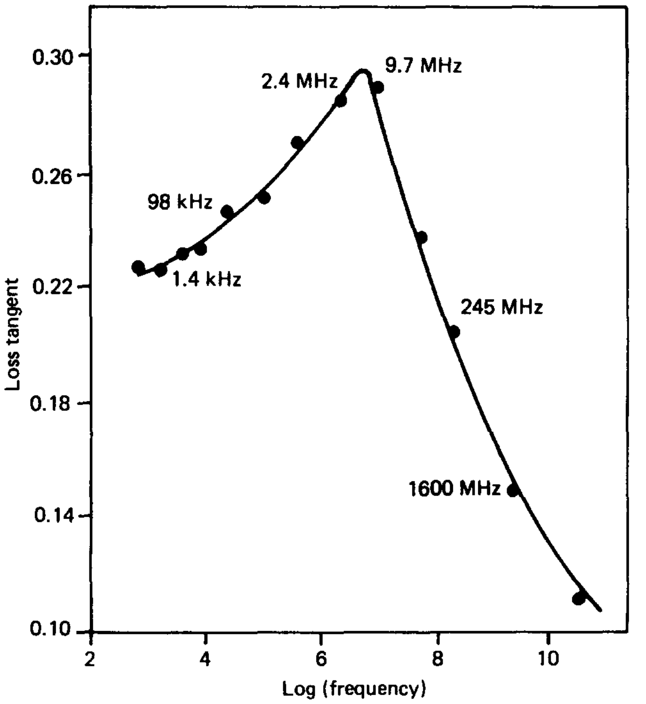

Figure 6 Frequency spectrum at room temperature of the α-transition loss peak of the binder soft segment, calculated from the measured d.m.a. spectrum

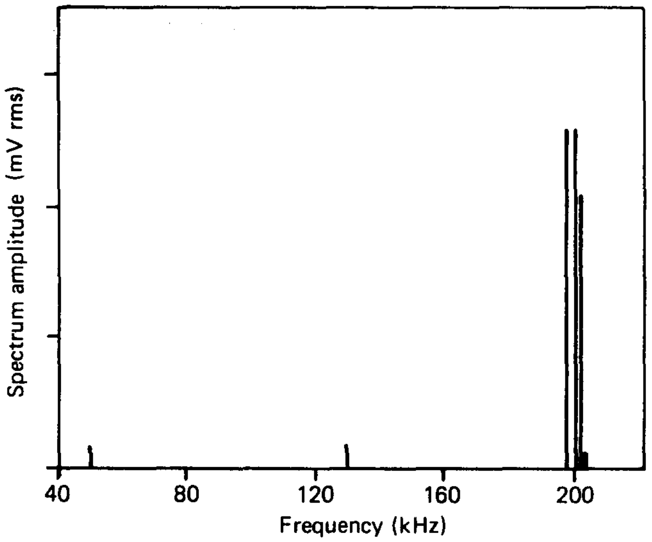

Figure 7 Frequency spectrum at room temperature of the impact pulse obtained by Fourier analysis

and

$$S(fx) = [S_k^2(\text{real}) + S_k^2(\text{imaginary})]^{1/2}$$

for $k = 0, 1, 2, \ldots, N\text{-}1$, where N = number of data points, x_i = time-domain component, S_k = resultant frequency-domain component and $S(fx)$ = Fourier amplitude.

A typical frequency spectrum of the impact pulse obtained by Fourier analysis is shown in *Figure 7*. The impact pulse occurs at very nearly the same frequency range as the binder soft-segment α-transition loss peak, calculated using the WLF equation. The maximum of the impact pulse occurs at around 200 kHz. This close correlation gives clear evidence that the soft-segment α-transition governs the fracture property of the composite polymers studied.

CONCLUSIONS

This study has shown that the fracture property of composite propellants can be related to the dynamic viscoelastic properties of the polymeric binder. The impact sensitivity of these polymers can be correlated with molecular motions ($E_a = 160$–$240\,\text{kJ mol}^{-1}$) responsible for the binder soft-segment α-transition, but also depends on other factors such as binder–filler interactions and impact temperature.

The shift in T_g to higher temperatures and the smaller-than-predicted decrease in damping, in the presence of filler, provide strong evidence for filler–binder interactions in the composite propellants studied.

Although GAP is a thermochemically energetic binder, GAP propellants are less sensitive to impact than comparable propellants with HTPB or poly(ether glycol) binders. Thus, propellants containing GAP as binder have low impact sensitivity properties at ambient temperature. The chemical structure of the polymeric binder appears to have little influence on the impact sensitivity whereas physical properties are important. There is little difference between the impact sensitivity of propellants containing AP as the oxidizer and those containing RDX or PETN.

The impact stress pulse spreads over a range of frequencies at room temperature with a maximum at ~200 kHz. At room temperature, the loss peak, assigned to the soft-segment α-transition, occurs over a frequency range which overlaps that of the impact pulse with a maximum at ~9 MHz. The close correlation gives direct evidence that the relaxation process associated with the soft-segment α-transition contributes to the fracture properties of composite propellants.

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