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Temperature dependence of high strain-rate impact fracture behaviour in highly filled polymeric composite and plasticized thermoplastic propellants

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The effect of temperature and strain-rate on the fracture behaviour during high strain-rate ($\sim 10^3\,\text{sec}^{-1}$) impact of two highly filled polymeric composite propellants (containing segmented polyurethanes based on hydroxy-terminated polybutadiene (HTPB) or glycidyl azide polymer (GAP) filled with ammonium perchlorate (AP) particles) and a plasticized thermoplastic (cast double base (CDB) nitrocellulose–nitroglycerine) propellant have been examined over a wide temperature range encompassing the "brittle–ductile" transition. In the "elastic" region of the load–displacement curve, the yield stress and fracture toughness is highest for GAP/AP and lowest for HTPB/AP. In the "elastic" and post-yield "ductile" regions CDB is more fracture-resistant than GAP/AP and HTPB/AP over the temperature range −20 to 50° C, but below −40° C, where both CDB and GAP/AP are brittle, GAP/AP is more fracture-resistant than CDB (as observed in the "elastic" region). Although all the propellants are known to develop small cracks in the "elastic" and post-yield "ductile" regions of the load–displacement curve, the overall fracture behaviour is largely governed by viscoelastic properties (because the cracks close up in compression). The good mechanical properties of CDB, above the "brittle–ductile" transition temperature, can be attributed to the presence of a large β-transition loss peak. In the composites, the fracture behaviour is also influenced to a lesser extent by the degree of filler–binder interactions. Dynamic mechanical analysis indicates that GAP/AP has a slightly higher degree of filler–binder interactions than HTPB/AP. A temperature–strain rate reduction has been obtained for the yield stress and the composite curve can be expressed by the equation $\sigma_y = K_1 + K_2 \log(\dot{\varepsilon} a_T)$ where K_1 and K_2 are constants and a_T is a shift factor. K_2 is a material constant which reflects the temperature and strain-rate sensitivity.

1. Introduction

The impact and ignition sensitivities of a rocket propellant charge to high-velocity fragment attack depend on the chemical, physical and mechanical properties of the propellant. In service, the rocket motor is often required to operate over a wide range of temperature which can cause significant changes in the physical and mechanical properties of the propellant.

Little detailed information is available on the mechanical behaviour of polymeric materials measured under dynamic conditions of loading, which is expected to differ markedly from that measured under static conditions. The mechanical properties of some propellants [1] and plastic-bonded explosives [2] under dynamic compressive loading have been examined and it was found that these materials are very sensitive to changes in strain rate, due to their viscoelastic characteristics.

The temperature dependence of the mechanical properties of thermoplastics and composites under high strain-rate impact testing has not been reported before, to the best of our knowledge, although there have been several studies at low strain-rates [3, 4]. It is well known, for a wide range of thermoplastics under low strain-rate testing, that the largest and most important change in impact strength occurs over a relatively narrow temperature range where the type of fracture changes between brittle and ductile. This brittle–ductile transition depends on several factors such as the rate of testing and the chemical structure of the polymer, and may or may not correlate with a dynamic mechanical damping peak such as the glass transition or secondary relaxations [4].

We have previously investigated the impact sensitivity under high strain-rate conditions, at ambient temperature, of a series of composite propellants and found that the fracture behaviour is directly related not only to viscoelastic properties, but also to filler–binder interactions [7]. In low strain-rate testing, the crucial factors in determining the strength and stress–strain behaviour of composites are probably

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TABLE I Propellant compositions

Propellant type	Binder prepolymer/polymer matrix	Curative
Composite (binder/oxidizer)		
GAP/AP	Glycidyl azide polymer $HO{-}[\underset{CH_2N_3}{CH}{-}CH_2{-}]{-}O{-}CH_2CH_2{-}[O{-}CH_2{-}\underset{CH_2N_3}{CH}{-}]_n{-}OH$	Hylene W
HTPB/AP	Hydroxy-terminated polybutadiene $HO{-}[CH_2{-}CH{=}CH{-}CH_2{-}]_n{-}OH$	Dimeryl diisocyanate (DDI)
Double base		
CDB	Nitrocellulose–nitroglycerine (42:46 wt %)	

the nature of the filler–matrix interface and the degree of interfacial interaction. The cause of brittleness in composites has been attributed to weak interfacial bonding between filler and matrix [5]. This is expected to be less important in compression testing at high strain-rate because the compressive stresses will tend to close up the cracks resulting from debonding of the filler from the matrix.

In the present work, the temperature and strain-rate dependence of the yield stress and fracture toughness in high strain-rate impact compression testing of two highly filled rubbery polymeric composite propellants (HTPB/AP and GAP/AP) are examined and compared with a plasticized thermoplastic propellant (cast double base, NC/NG), over a temperature range encompassing the brittle–ductile transition.

2. Experimental procedure

2.1. Materials

The composite propellant types, cast double base propellant (CDB), and their compositions are listed in Table I. The CDB propellant was made from a casting powder (1 mm diameter cylinders of 1 mm length) comprising 60% nitrocellulose (NC) and 30% nitroglycerine (NG) and a casting liquid comprising 76% NG and 23% glycerol-triacetate. The composite propellants were manufactured with the same binder to oxidizer (ammonium perchlorate) weight ratio (17:83). The binder was prepared by curing the hydroxy-terminated prepolymer with an isocyanate curative (NCO:OH = 1:1). The propellants were made by standard processing techniques and were kindly supplied by Mr B. Hamshere and Mr N. Ayres.

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

2.2. Measurements

For the modified Hopkinson bar [6] tests, the specimens were conditioned for at least 1 h at the required temperature, quickly removed and fixed to the output stationary bar (connected to strain gauges to measure applied loads) by grease. A moving input bar was then fired (using a commercial gas gun) at the specimen which was compressed between the two bars. The stress–strain data were collected using a Nicolet 4094 four-channel digital oscilloscope and an HP 9826 computer and the results analysed as described previously [7]. The specimens were tested in triplicate at −60, −40, −20, 0, 10, 20, 40 and 50° C with impact velocities varying from 6 to 30 m sec^{-1}.

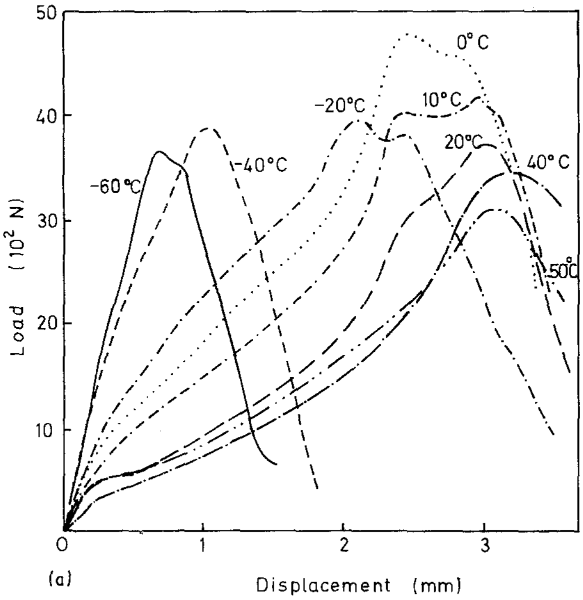
Dynamic moduli (Young's and shear) and loss tangent (tan δ) values were measured using a Polymer Laboratories Dynamic Mechanical Thermal Analyser, interfaced to an HP 9826 computer for data acquisition. The analysis was done over the temperature range −130 to 160° C at a scan rate of 2° C min^{-1} with test frequencies of 0.33, 3 and 30 Hz.

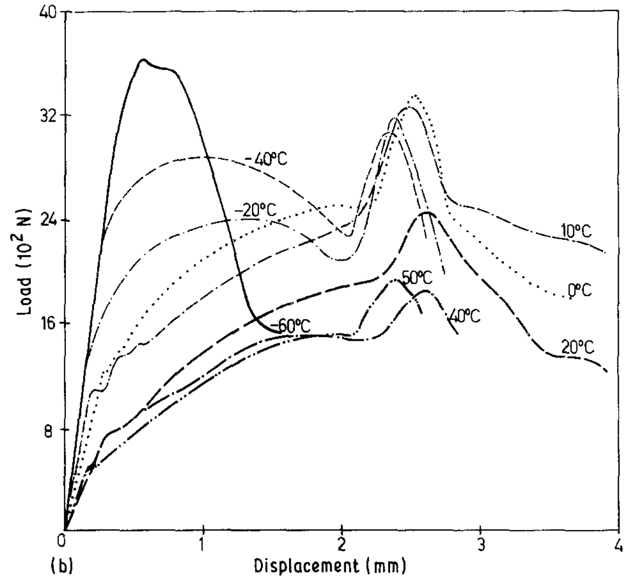
3. Results and discussion

The load–displacement plots at the various temperatures, measured at an impact velocity of 12 to 14 m sec^{-1}, for the CDB, GAP/AP and HTPB/AP propellants are shown in Figs 1a, b and c, respectively. Yielding occurred in the high strain-rate compression tests at all temperatures. The initial "linear" region of the load–displacement curve is only a psuedo-elastic event [7] as there is evidence that small cracks are formed in this portion of the load–displacement curve. SEM examination (Figs 2 and 3) of the surface of the side of the samples which had been compressed at low velocity and at low temperature, in which the load–displacement curve consists mainly of the initial "linear" region, showed that cracks were formed before or during yielding. SEM of the filled composites (Fig. 3) shows debonding and cracking around the filler–binder interface region. In the CDB propellant, the cracks run around the NC/NG grains.

The fracture process occurring in the post-yield "ductile" region of the curve is less clear than that 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 difficult. However, the errors caused by the input bar slowing down and the change in area of the specimen is likely to be small at strains up to and before the maximum stress. The load–displacement plots up to the maximum stress are reproducible to within ±30%. The analysis in this study has been divided into two regions: the "elastic" region and the "elastic" and post-yield "ductile" regions (Fig. 4).

Figs 1a, b and c show that "brittle" fracture occurred at around −40° C for CDB and between −40 and





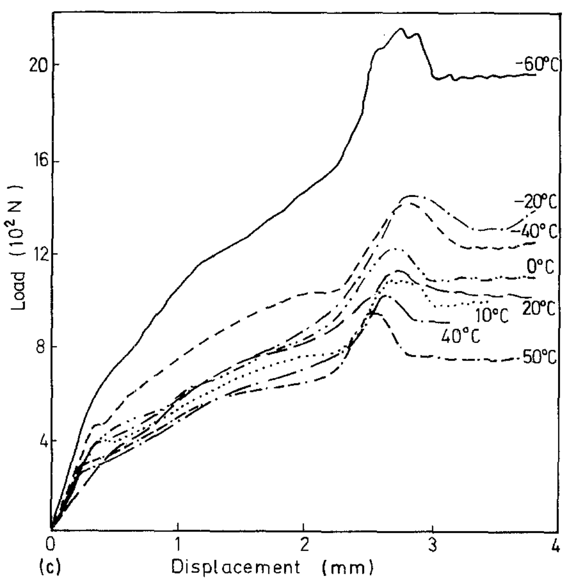


Figure 1 Load–displacement at various temperatures for (a) CDB, (b) GAP/AP and (c) HTPB/AP, at the impact velocity 12 to 14 m sec^{-1}.

$-60°$ C for GAP/AP, but HTPB/AP remained "ductile" even at $-60°$ C. The "brittle–ductile" transition temperature obtained from the stress–strain data is related to the glass-transition temperature determined from DMA (see Table II). The high temperature of the glass-relaxation process of CDB compared to GAP/AP and HTPB/AP suggests that it is the more "brittle" of the three propellants. HTPB/AP is still "ductile" at $-60°$ C, consistent with its low T_g (soft segment) value and the presence of a β-relaxation peak at around $-85°$ C [7] (see Figs 9a, b and c below).

Figs 5 and 6 show the temperature and strain-rate dependence of the yield stress and fracture toughness in the "elastic" and post-yield "ductile" regions (total fracture toughness). These plots can be divided into two regions: (i) above and (ii) below the "brittle–ductile" transition temperature. For the GAP/AP and CDB propellants, two different fracture mechanisms must be involved in view of the change in slope of the yield stress against temperature plots (which reflects temperature dependence of fracture in these regions). The temperature dependence of the yield stress and of the total fracture toughness is similar at the various strain-rates, except that the maximum of the total fracture toughness against temperature plot is shifted to a higher temperature when the strain-rate is increased.

TABLE II Transition temperatures of propellants

Propellant type	T_α (°C)	T_β (°C)	T_γ (°C)
HTPB/AP	−58 (soft segments) 50 (hard segments)	−85	–
GAP/AP	−28 (soft segments) 45 (hard segments)	–	–
CDB	11	−35	−100

3.1. Initial "elastic" region of load–displacement curve

The yield stress against temperature plots for the three propellants (Fig. 7) show that above the temperature where the "brittle–ductile" transition occurs (below $-60°$ C for HTPB/AP, around $-40°$ C for CDB and between -40 and $-60°$ C for GAP/AP, at the impact velocity 12 to 14 m sec^{-1}), the yield stress decreases almost linearly with increasing temperature. The effect of temperature on the strain at yield stress (in the initial "linear" region) is small in all cases (1 to 5%).

The GAP/AP propellant has a higher yield stress than the HTPB/AP and CDB propellants. This is related to its high modulus compared to the other propellants. In the same temperature range, HTPB/AP has the lowest yield stress.

Below the "brittle–ductile" transition temperature of CDB and GAP/AP, the yield stress of these propellants increases with decreasing temperature as expected in brittle materials.

The fracture toughness against temperature plots for the initial "elastic" region, at the impact velocity of 12 to 14 m sec^{-1}, are shown for the three propellants in Fig. 8a. They do not show the same features as the

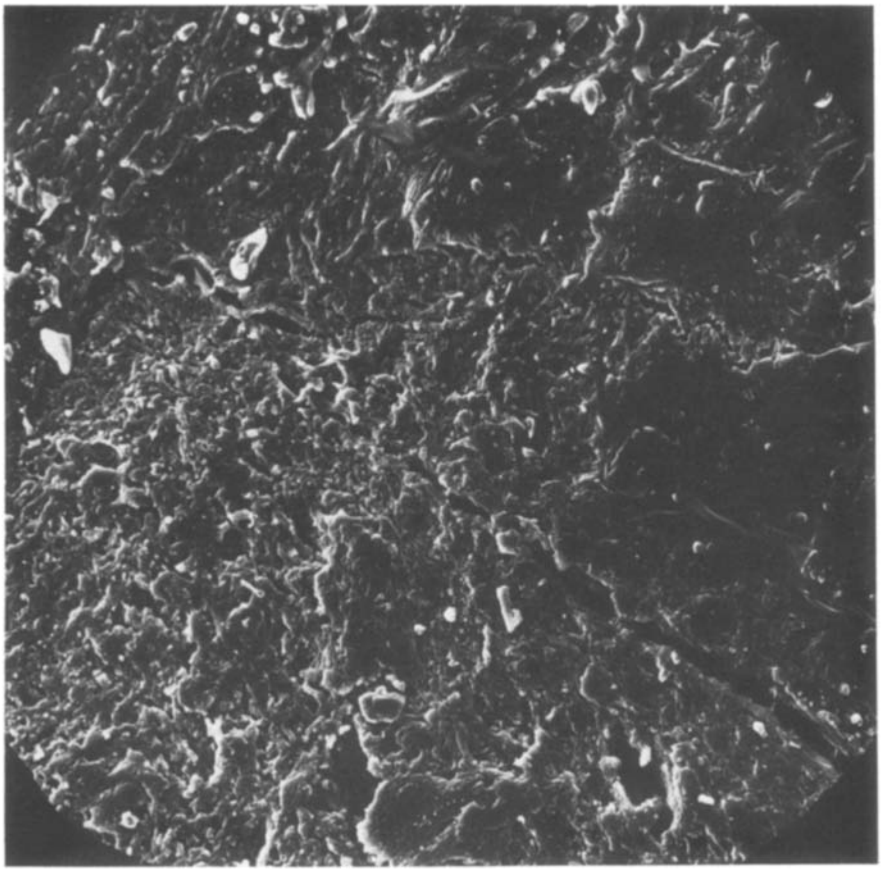


Figure 2 SEM of CDB after compression testing.

total fracture toughness (i.e. "elastic" and post-yield "ductile") against temperature plots (Fig. 8b) because of the relatively small strains involved in the initial "linear" region. The errors in the fracture toughness in the "elastic" region are large due to the small strains. In the "elastic" region of the load–displacement curve, GAP/AP has a higher fracture toughness than CDB and HTPB/AP.

3.2. "Elastic" and post-yield "ductile" regions of load–displacement curve

The total fracture toughness against temperature plots

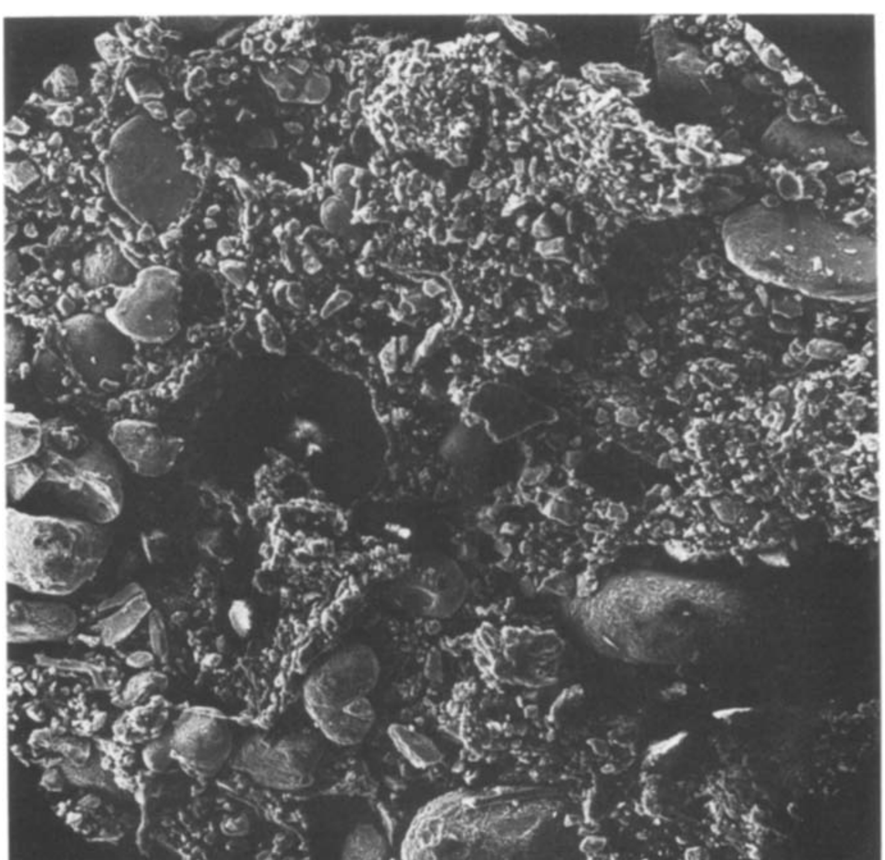


Figure 3 SEM of HTPB/AP after compression testing.

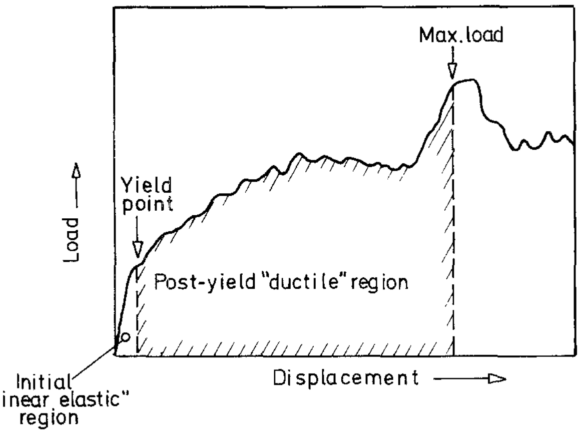


Figure 4 Schematic load–displacement curve defining the parameters used in this study.

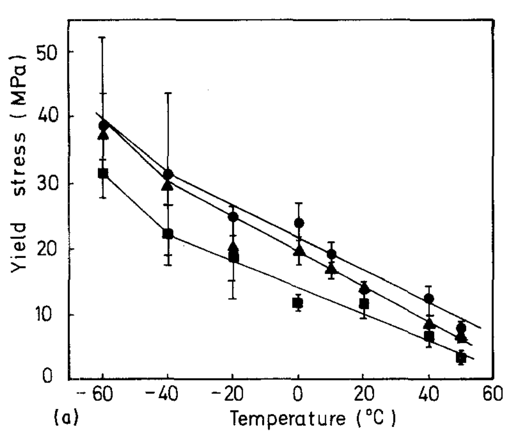
(Fig. 8b), above the "brittle–ductile" transition temperatures of the various propellants, show that the total fracture toughness is highest for CDB and lowest for HTPB/AP. The high total fracture toughness of the CDB propellant can be attributed to the presence of a large β-transition loss peak observed in the DMA spectrum (Fig. 9a). The high fracture toughness of some thermoplastic polymers at room temperature have been attributed to low-temperature secondary relaxations [8, 9]. There is, however, a second important difference between CDB and the composite propellants that may contribute significantly to the better fracture behaviour observed for CDB (above the "brittle–ductile" transition temperature). The CDB propellant does not contain particulate filler and fracture of the polymer requires considerable energy, whereas fracture of the interfaces present in filled composites usually requires very little energy (especially when there is poor adhesion between the polymer matrix and filler). In addition, the mismatch of properties, such as moduli and coefficients of thermal expansion, of the two components in the composite propellants introduces stresses at the interface which may result in debonding or in the formation of cracks during temperature conditioning which tend to reduce their impact strength.

The higher fracture resistance of GAP/AP compared to HTPB/AP (Fig. 8b) can be attributed to two factors [7]: (i) the high tan δ value of the soft segment α-transition of GAP/AP (Fig. 9b) and (ii) the higher degree of filler–binder interaction of GAP/AP compared to HTPB/AP as indicated by the larger T_g shift, and smaller-than-predicted decrease in the tan δ value in the presence of filler. The expected damping of a composite, if there are no additional damping mechanisms provided by the filler, is given by

$$\Delta = \Delta_1 \phi_1$$

where Δ_1 is the damping of the unfilled polymer and ϕ_1 is its volume fraction [10, 11]. Thus, the reduced damping, $\Delta/\Delta_1\phi_1$, is greater than unity if there are additional damping mechanisms such as filler–matrix interactions and agglomeration of the filler particles (where frictional heat generated by the movement of one particle against another adds to the total damping of the system). The calculated reduced damping for GAP/AP is 1.7 compared to 1.3 for HTPB/AP. The oxidizer was well mixed into the propellant before casting and SEM of the propellants did not show any evidence of agglomeration. Thus, the additional damping may be attributed mainly to filler–binder interactions. The degree of filler–binder interaction in GAP/AP is only slightly higher than that in HTPB/AP, as suggested by the reduced damping. The higher degree of filler–binder interaction observed in GAP/AP is as expected, since GAP is a relatively polar binder compared to HTPB and would interact more strongly with AP which is highly polar and hydrophilic. Thus, the larger tan δ value of the α-transition in GAP/AP is largely responsible for its higher fracture resistance compared to HTPB/AP.

Above 40° C, the fracture toughness of all three



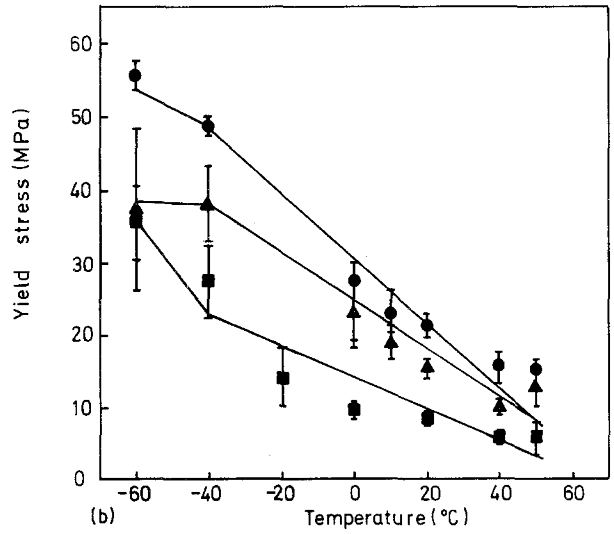
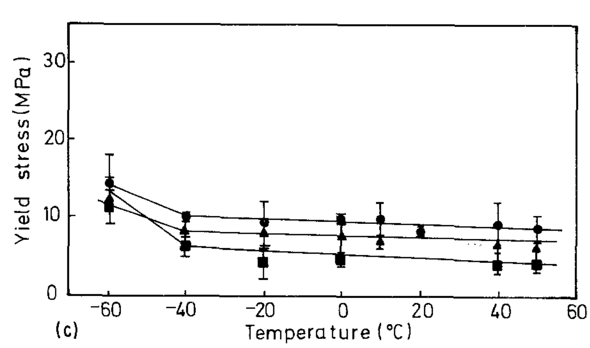
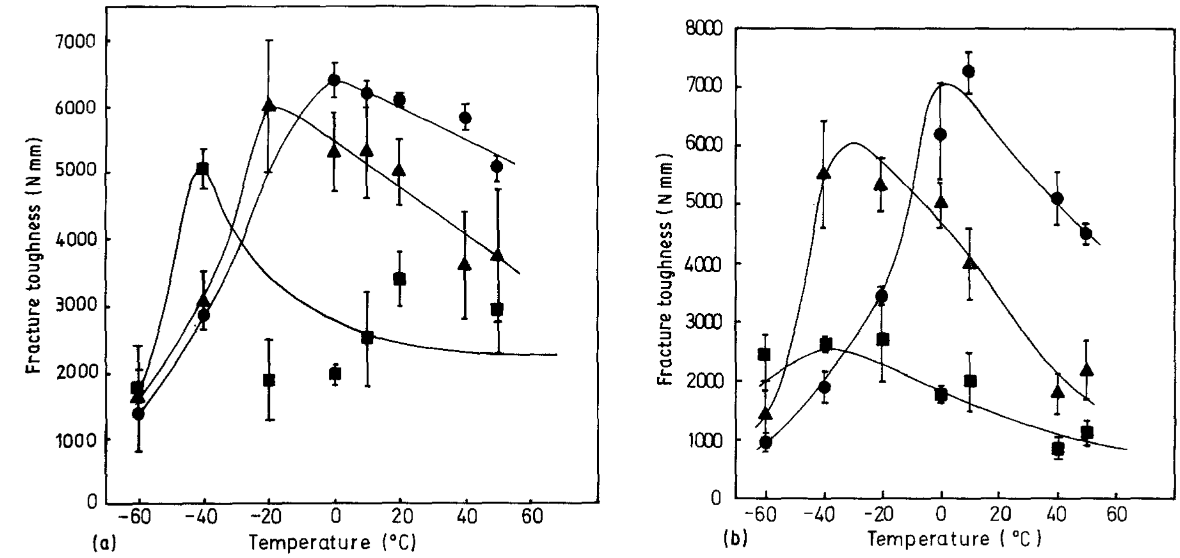


Figure 5 Yield stress against temperature, at various impact velocities for (a) CDB, (b) GAP/AP and (c) HTPB/AP (●) 16 to 18 m sec^{-1}, (▲) 12 to 14 m sec^{-1}, (■) 6 to 8 m sec^{-1}.





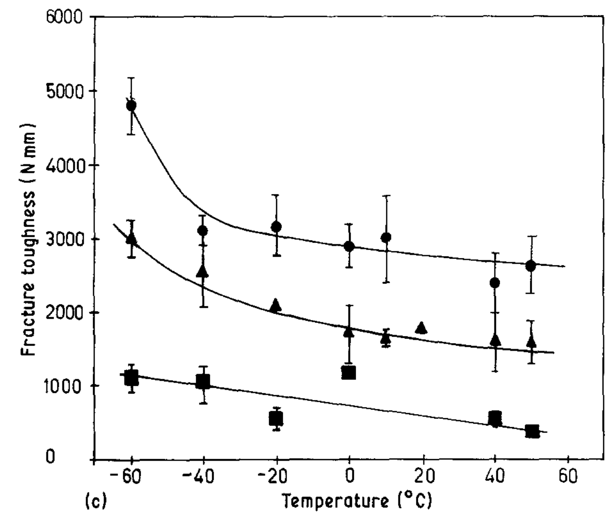


Figure 6 Total fracture toughness ("elastic" + post-yield "ductile") against temperature, at various impact velocities for (a) CDB, (b) GAP/AP and (c) HTPB/AP. (●) 16 to 18 m sec^{-1}, (▲) 12 to 14 m sec^{-1}, (■) 6 to 8 m sec^{-1}.

propellants decreases to low values. This high-temperature region where the propellant becomes soft is extremely important, as mechanical properties become poor and high pressure build-up on compression can cause an increase in ignition sensitivity. Results from preliminary experiments show that the ignition probability above 40° C is high for all three propellants.

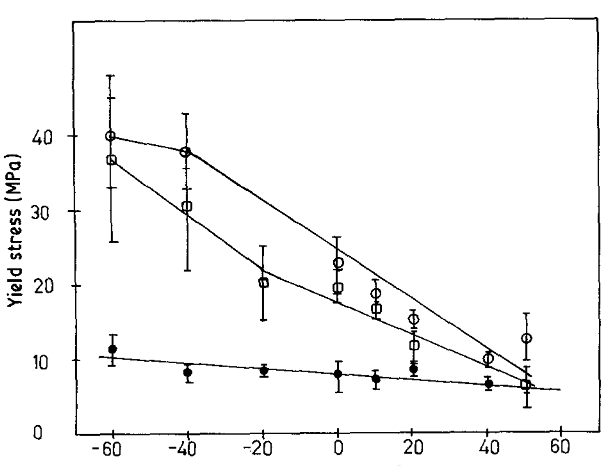


Figure 7 Yield stress against temperature for the various propellants, at the impact velocity 12 to 14 m sec^{-1}. (○) GAP/AP, (□) CDB, (●) HTPB/AP.

Below the "brittle–ductile" transition temperature of CDB and GAP/AP, the total fracture toughness of these propellants increases on increasing the temperature as the compliance of the material increases. HTPB/AP is still "ductile" at −60° C, and has a higher total fracture toughness than CDB and GAP/AP below −40° C.

In the temperature range below the "brittle–ductile" transition temperature of GAP/AP and CDB, GAP/AP has better mechanical properties than CDB as indicated by the total (i.e. "elastic" and post-yield "ductile" regions) fracture toughness against temperature plots. The better mechanical properties of GAP/AP in this temperature region may be due to the presence of toughening mechanisms which are common in filled composite polymer systems in the glassy state, where the modulus of the filler is higher than that of the polymer matrix. In these systems, the crack would not go through the hard filler particles but would travel round them, increasing the surface energy (and thus fracture energy) due to the increase in the crack length [5].

4. Temperature–strain-rate reduction

Plots of yield stress (σ_y) against logarithmic strain rate ($\dot{\varepsilon}$) at various temperatures for the three propellants gave linear relationships (Figs 10a, b and c). The lines at the various temperatures for the same propellant are approximately parallel, except at 40 and 50° C. Shifting the plots (below 40° C) along the log $\dot{\varepsilon}$ axis with respect to the values at 20° C resulted in a composite curve (as shown in the same figure), indicating that increasing (or decreasing) temperature has the same effect on the yield stress as decreasing (or increasing) strain-rate within the temperature and strain-rate ranges studied in this work.

The composite plots of σ_y against log ($\dot{\varepsilon}a_T$) can be expressed by the empirical equation

$$\sigma_y = K_1 + K_2 \log (\dot{\varepsilon}a_T)$$

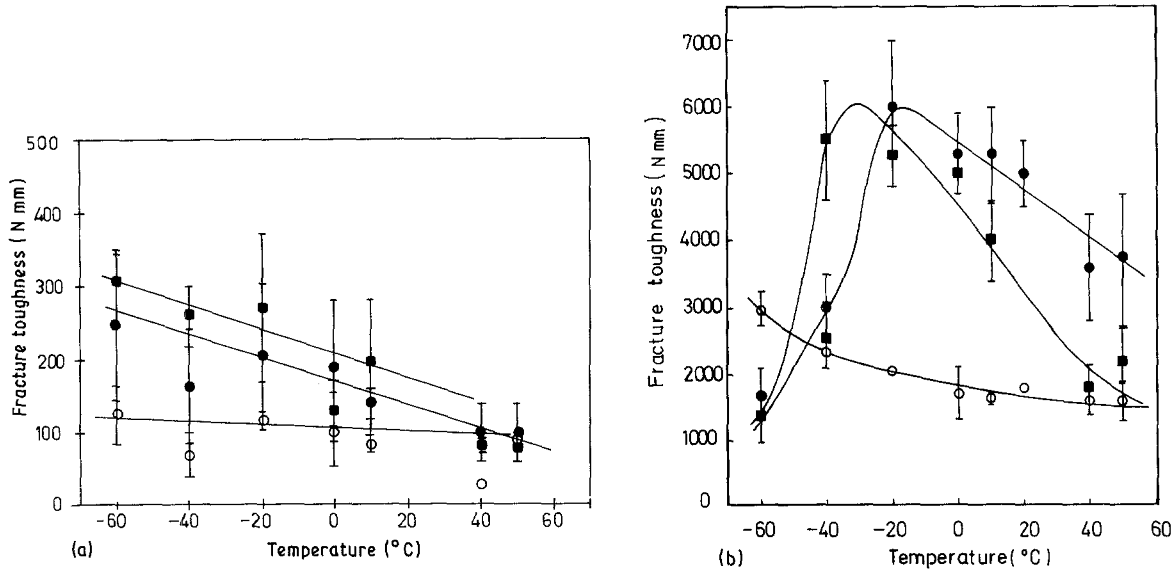


Figure 8 (a) Fracture toughnes in "elastic" region against temperature, (b) total fracture toughness ("elastic" + post-yield "ductile") against temperature for the various propellants, at the impact velocity 12 to 14 m sec^{-1}. (■) GAP/AP, (●) CDB, (○) HTPB/AP.

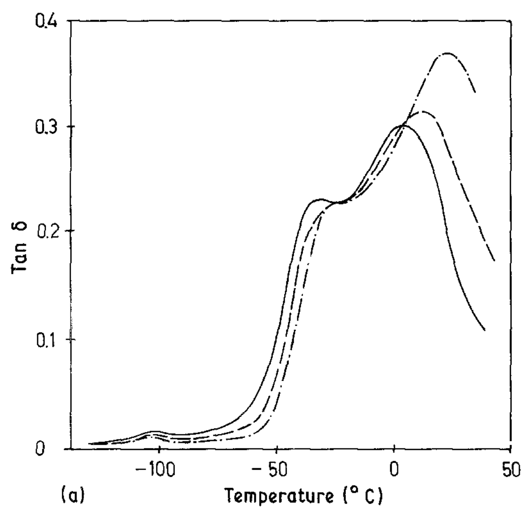
where K_1 and K_2 are constants and a_T is a shift factor. a_T is obtained empirically from Fig. 10 and is given by the equation

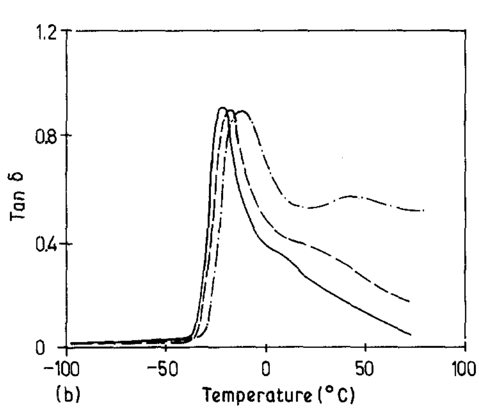
$$a_T = a + b(T - T_R)$$

where T is any given temperature, T_R is the reduced temperature (e.g. 20° C) and a, b are constants, obtained from a plot of a_T against $(T - T_R)$. Table III shows the K_1, K_2, a and b values, from the least-squares regression lines for the three propellants studied in this work.

The above equations provide in principle a means of (i) temperature and strain-rate conversion, so that the yield stress at a selected temperature over an extended strain-rate range can be predicted from the data determined over a restricted strain-rate range at a number of temperatures and vice-versa, and (ii) characterizing the propellant by their temperature and strain-rate dependence.

K_2, the slope of the composite plot, gives an indication of the sensitivity of the material to strain-rate and temperature. The high K_2 value of the GAP/AP propellant (see Table III) implies that the yield stress increases markedly with a decrease in temperature or an increase in strain-rate. HTPB/AP has a low K_2 value, suggesting that the yield stress is less sensitive to temperature and strain-rate compared to GAP/AP and CDB. K_2 appears to be related to the presence of loss peaks in the temperature range where the equation is applicable. HTPB/AP has no major loss





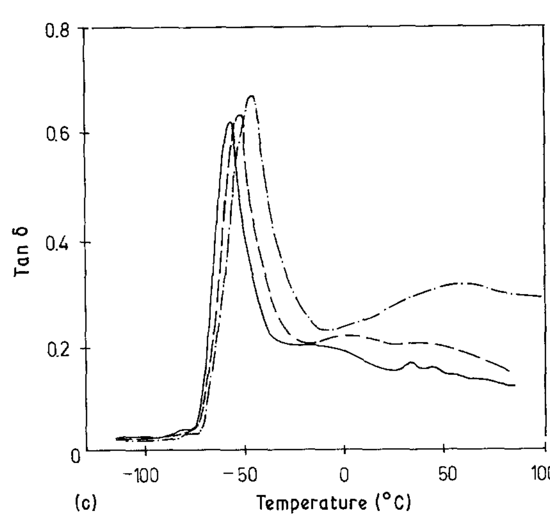
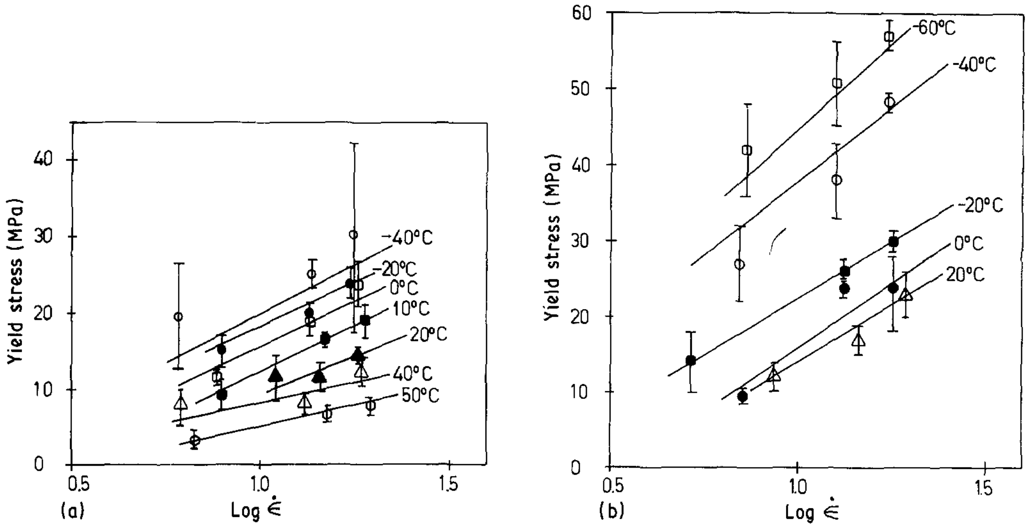


Figure 9 Temperature dependence of tan δ for (a) CDB, (b) GAP/AP and (c) HTPB/AP. (——) 0.33 Hz, (– – –) 3 Hz, (–·–·–) 30 Hz.



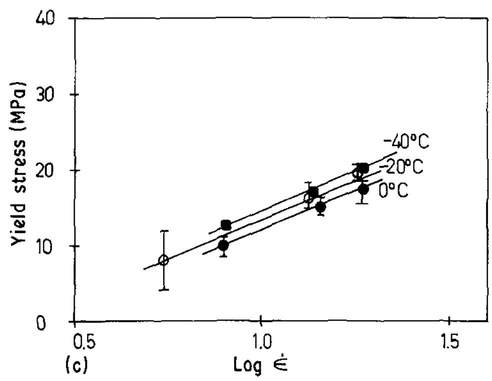


Figure 10 Yield stress against logarithmic strain-rate for (a) CDB, (b) GAP/AP and (c) HTPB/AP.

peaks over the temperature range -50 to $50°$ C compared to CDB and GAP/AP, which do have major loss peaks in this temperature range and would be expected to be less sensitive to temperature and strain-rate changes. If the relationship between K_2 and the loss peaks for the samples studied is valid, then the loss spectra of other materials similar to the samples studied here could be used as guides as to the usefulness of applying the above equation for σ_y to the materials in question.

The apparent K_1 values are negative for all three propellants and cannot be used to characterize the propellants, as no physical meaning can be attached to negative values of yield stress. Possible explanations for the negative K_1 values are: (i) this is an experimental artefact and/or (ii) the equation is not applicable at very low strain-rates and at high temperatures because the material would be in a different (rubbery) phase. The slope of the σ_y–log ($\dot{\varepsilon}a_T$) plot changes at low strain-rates and/or at high temperatures (above 40° C) so that extrapolation of the composite line may not be valid beyond these limits.

5. Conclusions

The temperature and strain-rate dependences of the impact sensitivity of two highly filled rubbery polymeric composite propellants have been examined and compared with a plasticized thermoplastic propellant, over a wide temperature range.

Analysis of the load–displacement curve has been divided into two regions: (i) the initial "elastic" region, which is a very small region and can only be used to predict behaviour for a very narrow regime of conditions (i.e. at very small strains where the material has "brittle" characteristics), and (ii) the post-yield "ductile" region. The data from this region are more difficult to interpret because they are due to contributions from several deformation mechanisms – viscoelastic/plastic deformation, extensive crack propagation and other secondary deformation processes. Errors in the analysis may also arise from the change in area of the specimen and the input bar slowing down, in this region of the curve. This casts some doubts on using the data from the post-yield "ductile" region, but using the "elastic" and post-yield "ductile" regions instead of the "elastic" region in the analysis gives only slightly different conclusions. However, the general conclusions drawn from the "elastic" and post-yield "ductile" regions do not contradict those from the "elastic" region because the initial "linear" region only predicts behaviour at very small strains.

Analysis of the data from the "elastic" region show that the yield stress and fracture toughness are highest for GAP/AP and lowest for HTPB/AP. In the "elastic" and post-yield "ductile" regions, CDB is more fracture-resistant than GAP/AP and HTPB/AP in the temperature range -20 to $50°$ C, but below $-40°$ C, where both CDB and GAP/AP are brittle, GAP/AP is more fracture-resistant than CDB (as observed in the "elastic" region).

Although all the propellants are known to have small cracks in the "elastic" and post-yield "ductile" regions, the overall fracture behaviour is largely governed by viscoelastic properties (because the cracks close up in compression). In the composites, the degree of filler–binder interaction also has some

TABLE III K_1, K_2, a and b values from the least-squares regression lines: $\sigma_y = K_1 + K_2 \log(\dot{\varepsilon}a_T)$ and $a_T = a + b(T - T_R)$

Propellant type	K_1	K_2	a	b
HTPB/AP	−5.5	10	1.2	−0.006
GAP/AP	−18	31	1.0	−0.05
CDB	−13	23	1.1	−0.02

effect, as indicated by the slightly higher reduced damping observed in GAP/AP.

A temperature–strain-rate reduction was obtained for the yield stress and the composite curve can be expressed by the equation

$$\sigma_y = K_1 + K_2 \log (\dot{\varepsilon} a_T)$$

Within the appropriate temperature and strain-rate ranges, this equation can be used for temperature–strain-rate conversion. K_2 is a material constant which can be used to characterize the temperature and strain-rate sensitivity of the propellant. From the limited data available in this study, K_2 appears to be related to viscoelastic properties of the material.

Acknowledgements

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