The Effects of Changing Chemistry on the Shock Response of Basic Polymers

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| Abstract | The shock response of four common semicrystalline thermoplastic polymers—polyethylene (PE), polyvinylchloride (PVC), polytetrafluoroethylene (PTFE) and polychlorotrifluoroethylene (PCTFE)—have been studied in terms of their Hugoniots, release velocities and shear strengths. Through the variations in behaviour caused by changes to the attached atoms to the carbon backbone, it has been possible to suggest that there are two main factors in play. The first is an electrostatic repulsion between adjacent polymer chains. Where this force is large, for example in PTFE with highly electronegative fluorine atoms, this results in this force dominating the shock response, with low shock velocities, high release velocities and little if no hardening behind the shock front. In contrast, in materials such as PE, this force is now weaker, due to the lower electronegativity of hydrogen, and hence this force is easier to overcome by the applied shock stress. Now the main factor affecting shock behaviour is controlled by the shape of the polymer chain allowing inter chain tangling (tacticity). This results in higher shock velocities, lower release speeds and significant hardening behind the shock front as the chains are forced together. This is prevalent in materials with a relatively open structure such as PE and is enhanced with the presence of large side groups or atoms off the main polymer chain. |

| Footnote Information | |

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The Effects of Changing Chemistry on the Shock Response of Basic Polymers

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D. C. Wood[4] · G. Appleby-Thomas[4]

Abstract The shock response of four common semicrystalline thermoplastic polymers—polyethylene (PE), polyvinylchloride (PVC), polytetrafluoroethylene (PTFE) and polychlorotrifluoroethylene (PCTFE)—have been studied in terms of their Hugoniots, release velocities and shear strengths. Through the variations in behaviour **AQ1** caused by changes to the attached atoms to the carbon backbone, it has been possible to suggest that there are two main factors in play. The first is an electrostatic repulsion between adjacent polymer chains. Where this force is large, for example in PTFE with highly electronegative fluorine atoms, this results in this force dominating the shock response, with low shock velocities, high release velocities and little if no hardening behind the shock front. In contrast, in materials such as PE, this force is now weaker, due to the lower electronegativity of hydrogen, and hence this force is easier to overcome by the applied shock stress. Now the main factor affecting shock behaviour is controlled by the shape of the polymer chain allowing inter chain tangling (tacticity). This results in higher shock velocities, lower release speeds and significant hardening behind the shock front as the chains are forced together. This is prevalent in materials with a relatively open structure such as PE and is enhanced with the presence of large side groups or atoms off the main polymer chain.

Introduction

Interest in the response of polymeric materials to high strain-rate and shock loading conditions is driven by a number of factors, chief amongst them is their role as binder phases in energetic materials [1–4] and inert structural composite systems [5–7]. In addition, materials such as neoprene have found application in earthquake protection of buildings [8]. Detailed programmes on the shock response of polymers have until recently been relatively sparse when compared to other materials. Polymethylmethacrylate (PMMA), an amorphous transparent thermoplastic also know as acrylic, Plexiglas, Lucite, or Perspex, has received a deal of attention due to its use as a window material for interferometric measurements [9], whilst thermosetting epoxy based resins have been studied as they are often used as adhesives in the manufacture of target assemblies [10–12]. However, it should be appreciated that polymers have an extremely wide range of structural variation at the molecular level, and thus it is often difficult to identify trends and common features that describe their response to shock loading. Despite this, some common features *have* been identified; for example in plotting the shock velocity (U_S) against particle velocity (u_p), whilst the majority of polymers display a linear response of the form,

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$$U_S = c_0 + S u_p, \tag{1}$$

where c_0 and S are empirically derived constants [13], it has been observed that unlike simple metals, the value of c_0 does not equate with the measured value of bulk sound speed (c_B), but rather is significantly higher. Indeed in many polymers it was observed that it lay above the ambient pressure longitudinal sound speed (c_L) [11, 14–16]. In some polymers such as PMMA [9] and polyvinylidene difluoride (PVDF) [17], a non-linear U_S-u_p response, with shock velocity dropping at lower particle velocities was observed. It has been subsequently suggested that this may be a more typical polymeric response [18], although rarely observed since the minimum particle velocity measured may have been above the non-linear part of the Hugoniot. Particulate composites with a hard particle in a soft binder, for example glass beads in hydroxyterminated polybutadiene (HTPB) [19] or the explosive RDX, also in HTPB [1, 20] have been observed to behave in a similar way, prompting Bourne and Milne [20] to suggest that this was due to a transition from elastic to plastic behaviour in the hard particles. Bourne et al. [18] went on to suggest that as many polymers are semi-crystalline in nature, a similar effect was taking place between the crystalline and amorphous regions within the polymer microstructure. In-situ neutron diffraction measurements of the elastic moduli in polytetrafluoroethylene (PTFE) [21] indicated that the modulus along the carbon–carbon backbone was of the order 220 GPa, whilst in the amorphous phase it was much lower at ca. 0.38 GPa. Another feature of the shared shock behaviour of polymers lies in a change in slope of the U_S-u_p curve above 20 GPa (precise values varying from polymer to polymer). Carter and Marsh [14] suggested that this be due to a re-ordering of the bonding within the polymer molecules from a predominantly two dimensional configuration to a more three dimensional situation due to the breaking and reformation of carbon–carbon bonds.

As stated above, the large variation in molecular chemistry displayed by polymer molecules can make a systematic investigation somewhat difficult. However, matters can be simplified if a molecular feature is 'fixed', for example the carbon–carbon backbone. In a previous article [15], the complexity of the monomer unit was systematically increased by changing the nature of a single side group, starting with polyethylene (PE), moving to polypropylene (PP) with a dangling methyl side group and finally to polystyrene (PS) with a dangling benzene ring. It was observed that the Hugoniots in longitudinal stress (σ_x) particle velocity space increased from PE to PS, but more significantly the differences between the calculated hydrodynamic pressure (P_{HD}) where,

$$P_{HD} = \rho_0 U_S u_p, \tag{2}$$

with ρ_0 the ambient density, and the measured longitudinal stress. As this is defined in terms the hydrostatic pressure (P) and the shear strength (τ), via,

$$\sigma_x = P + \frac{4}{3}\tau, \tag{3}$$

this is an indication that the shear strength is increasing with pressure. Further, at a fixed particle velocity of 0.8 mm μs^{-1}, this difference was seen to increase from PE to PP, with PS being the largest, corresponding to an increase in size of the dangling side group. This was later confirmed by direct measurement of the shear strength in the three materials [22] where it was suggested that increasing the size of the side group increased the degree of tangling between adjacent polymer chains, and hence increase the forces required to move those chains closer.

In a similar series of experiments, the effects of fluorine additions to the basic polyethylene molecule were investigated, using the materials polyethylene, polyvinylidene difluoride (PVDF—two hydrogen atoms per monomer unit replaced by fluorine) and polytetrafluoroethylene (PTFE—Teflon—all hydrogen replaced by fluorine) [18]. Increasing the levels of fluorine resulted in a reduction in shock speed, with PE having the highest and PTFE the lowest. However, due to a corresponding increase in density, the Hugoniot steepens with added fluorine. Interestingly, it was also noted that the release speed in PTFE was anomalously high, both here and in a previous article [23]. Although not stated explicitly in that work, it should be noted that PTFE undergoes a phase transition at approximately 0.5 GPa, see for example the work of Champion [24], Nagao et al. [25], Bourne et al. [26], Resnyansky et al. [27] and Rae et al. [28]. This has been identified as a phase II (a helical rotation over 13 CF_2 units in a hexagonal array) to phase III (a planar zig-zag confirmation in an orthorhombic lattice). Recovery experiments on PTFE by Brown et al. [29] showed that below the II-III phase transition decreases in crystallinity, Young's modulus and yield strength occurred, whilst above, the converse occurred, again indicating that significant microstructural changes occur at the phase transformation. Although not stated explicitly, it is possible therefore that these high release speeds may in fact be due to the high-pressure phase.

Materials

It is clear that even small alterations in the basic monomer unit can have a profound effect upon the shock response of even similar materials. Having observed the effects of side

161 group size [15, 22] and degree of fluorination [18], we now
162 turn our attention to the effects of a chlorine addition to the
163 monomer. We have chosen two materials to act as a
164 baseline; polyethylene $(CH_2–CH_2)_n$ and PTFE $(CF_2–CF_2)_n$,
165 and replaced one hydrogen to produce polyvinylchloride—
166 PVC $(CH_2–CHCl)_n$ and one fluorine with chlorine to pro-
167 duce polychlorotrifluoroethylene—PCTFE/KelF-81 $(CF_2–$
168 $CFCl)_n$. The basic conformation of the polymer molecules
169 are displayed in Fig. 1.
170   The materials under investigation in this report were
171 mostly obtained as commercial Stock of the Shelf (SoTS).
172 However, some of the PTFE was also was from pedigreed
173 sources, manufactured from pressed and sintered PTFE
174 powders under the names DuPont PTFE 7A and DuPont
175 PTFE 7C. Further details can be found in references [28, 30,
176 31]. The polyethylene investigated in this report was the high
177 density form, studied in previous papers [15, 18, 22, 32].
178 Relevant materials properties data are presented in Table 1.

Experimental

180 All shots were carried out using single stage gas guns
181 (50 mm bore, 5 m long barrel and 51 mm bore, 6 m barrel)
182 at Cranfield University [33]. Two sets of experiments were
183 performed; equation of state experiments to investigate the

184 Hugoniot and release response and strength measurements
185 to probe the variation of shear strength, both with impact
186 stress and time behind the shock front. In the former, a
187 manganin stress gauge (MicroMeasurments type LM-SS-
188 025CH-048) was embedded between plates (of known
189 thickness) of the material of interest or supported on the
190 rear surface with either a thick block of the target material
191 or a 12 mm block of PMMA. This was to prevent releases
192 from the rear of the target assembly interfering with
193 releases from the rear of the flyer plate as it crossed the
194 gauge location. A second gauge was supported on the front
195 of the target assembly (the 0 mm position) with a 1 mm
196 thick plate of either aluminium alloy 6061-T6 (Dural) or
197 copper, and matched to the material of the flyer plate. In
198 this way, both gauges would experience the Hugoniot
199 stress generated by the impactor and through impedance
200 matching the corresponding particle velocity, but also due
201 to the temporal separation of the gauge traces (Δt) along
202 with the known physical separation of the gauges $\Delta w)$, the
203 shock velocity could be determined through $U_S = \Delta w/$
204 Δt. Gauge calibrations were according to Rosenberg et al.
205 [34] The second series of experiments was designed to
206 investigate the strength response of these materials. 10 mm
207 thick samples were sectioned in half and a manganin stress
208 gauge (MicroMeasurements type J2 M-SS-580SF-025)
209 was introduced 4 mm from the impact face (2 mm in the
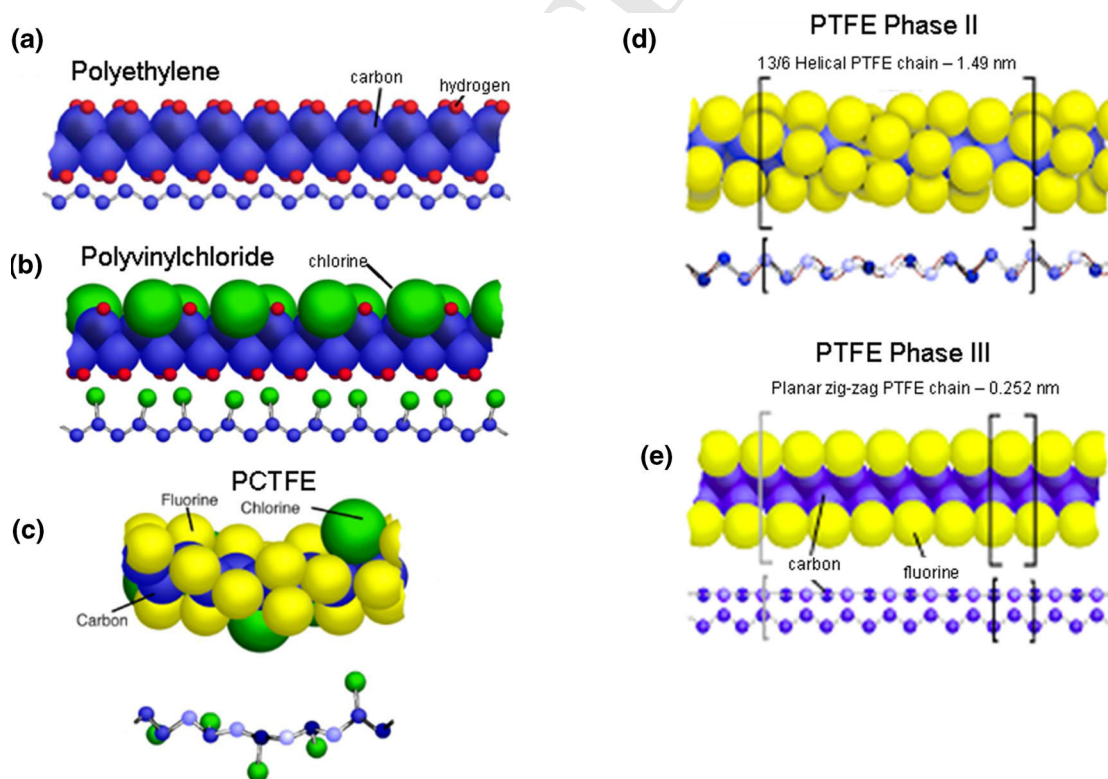
Fig. 1 The molecular structures of **a** polyethylene, **b** polyvinylchloride, **c** polychlorotrifluoroethylene, **d** polytetrafluoroethylene phase II, **e** polytetrafluoroethylene phase III

Table 1 Properties of materials under investigation

	ρ_0 (g cm^{-3})	c_L (mm μs^{-1})	c_S (mm μs^{-1})	c_B (mm μs^{-1})	v	K (GPa)	μ (GPa)	T_g (°C)	T_m (°C)
PE	0.95	2.36	1.01	2.05	0.388	3.99	0.98	−100	110
PVC	1.42	2.28	1.11	1.89	0.345	5.07	1.74	87	212
PTFE	2.15	1.23	0.41	1.14	0.437	2.77	0.36	−73	327
PCTFE	2.13	1.74	0.77	1.50	0.378	4.77	1.26	45	216

ρ_0 ambient density, c_L, c_S and c_B longitudinal, shear and bulk sound speed, v Poisson's ratio, K bulk modulus, μ shear modulus, T_g glass transition temperature, T_m melting temperature

case of PCTFE) before reassembly, during which the sample was held in a special jig for a minimum of 12 h to allow the epoxy adhesive to cure. After this the impact face was lapped flat to within 5 optical fringes from a monochromatic light source. In the case of PCTFE, a second gauge was supported on the front of the target assembly with a 1 mm plate of either Dural or copper, matched to the flyer plate material. This was used to determine the longitudinal stress, otherwise it was calculated using the Hugoniot data measured in the previous experimental series. Lateral gauge data were analysed using the methods of Rosenberg et al. [35], taking into account the fact that the shape of the gauge will influence the result at low shock pressures. Schematic representations of the target assemblies are shown in Fig. 2.
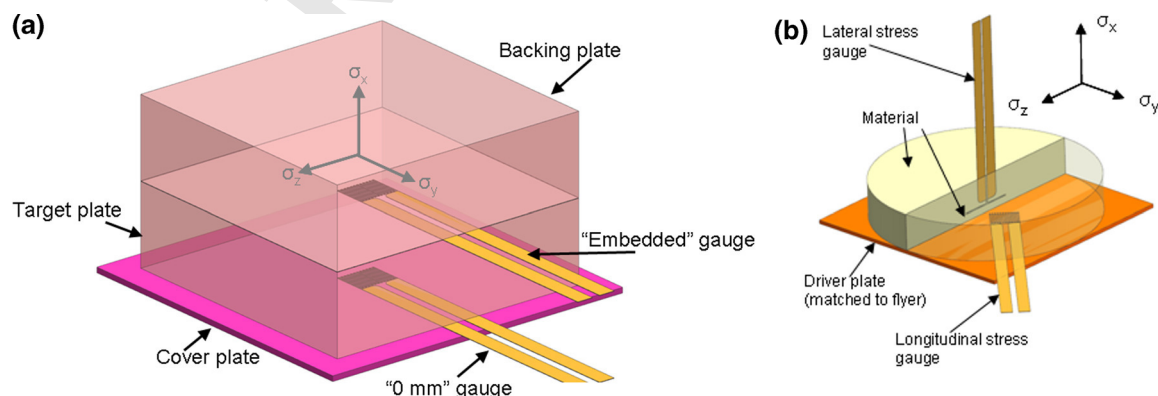
The lateral stress gauge target was used to determine shear strength by measuring the lateral component of stress (σ_y). By assuming that the hydrostatic pressure during shock loading is the average of the three orthogonal components of stress,

$$P = \frac{\sigma_x + \sigma_y + \sigma_z}{3}, \tag{4}$$

and that the two non-longitudinal stresses are equal, substituting Eq. 4 into Eq. 3 and re-arranging, shear strength can be determined thus,

$$2\tau = \sigma_x - \sigma_y. \tag{5}$$

Results

A typical set of results from a longitudinal gauge experiment is presented in Fig. 3, in this case from PCTFE, with the back surface gauge supported with 12 mm of PMMA.

Note that there are two gauge traces. The first, labelled '0 mm' comes from the Dural cover plate/PCTFE interface. The shape of the trace will be influenced by passage through ca. 1 mm of Dural, and as a consequence, it is relatively featureless, although its amplitude will give the longitudinal stress within the PCTFE, as dictated by the impact conditions, and by extension, the particle velocity, determined by standard impedance matching techniques. The second gauge, labelled 'Back Surface' is more revealing as the shock front has now travelled through ca. 10 mm of PCTFE, and hence its shape will have been modified by the properties of the PCTFE. The main feature to draw from here is the significantly reduced pulse width, indicating that PCTFE has an extremely high release wave speed, although this is explored further later in the text. The temporal spacing between traces, along with the physical spacing of the gauges themselves has been used to generate shock velocity [as indicated by the double arrow labelled Δt(shock)], and the release speeds by the double arrow labelled Δt(release).

The calculated shock velocities have been plotted against particle velocities and the results presented in Fig. 4a.

Fig. 2 Schematic diagrams of longitudinal and lateral stress gauge assemblies. **a** Longitudinal stress **b** lateral stress
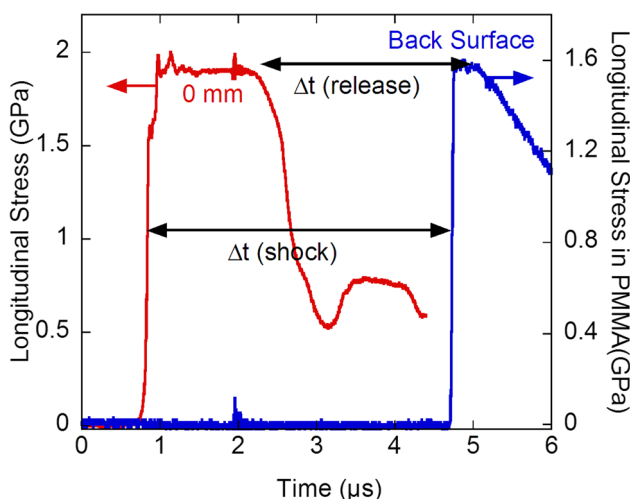
Fig. 3 Representative longitudinal stress gauge traces from a 10 mm PCTFE plate, with the back surface gauge supported with 12 mm of PMMA. The flyer plate was 5 mm of dural at 495 m s^{-1}

262   All four polymers under investigation have a linear
263 relationship between shock velocity and particle velocity,
264 in common with many other materials [13]. Although a
265 slight cusp can be observed in the Hugoniot of PTFE near
266 0.2 mm μs^{-1} due to the phase II to III transition [27].
267 Simple linear fits according to Eq. 1 have been fitted, and
268 the results summarised in Table 2.
269   It should be noted that the values quoted in the above
270 table are generated from a number of combined sources
271 (see references). The values of c_0 and S are simple
272 empirical constants, although attempts have been made to
273 give them physical significance; c_0 has been related to the
274 bulk sound speed (c_B), whilst S has been related to the first
275 pressure derivative of bulk modulus [40]. In the case of
276 simple metals such as copper, these assumptions have
277 been seen to hold true [13]. However, with the polymers
278 discussed in this report, it can be seen from Table 2 that c_0
279 clearly exceeds c_B, indeed in the case of PTFE and
280 PCTFE, it is greater than the longitudinal sound speed as
281 well. In the case of PTFE, this might be due to the fact of
282 a phase transformation at a stress of ca. 0.6 GPa [24].
283 However, in the case of PCTFE, no such phase transfor-
284 mation occurs, and as such another explanation is
285 required. As all measurements in this investigation were
286 made using stress gauges, the Hugoniot in terms of shock
287 stress and particle velocity were also determined, and
288 presented in Fig. 4b. Unlike the shock velocities, where
289 clear differences can be seen, the Hugoniots are much
290 more closely grouped, with PE having the shallowest
291 curve, whilst the two fluorinated materials have a stiffer
292 response, and PVC being placed somewhere between
293 these two groups. Note that in Fig. 4b, the data has been
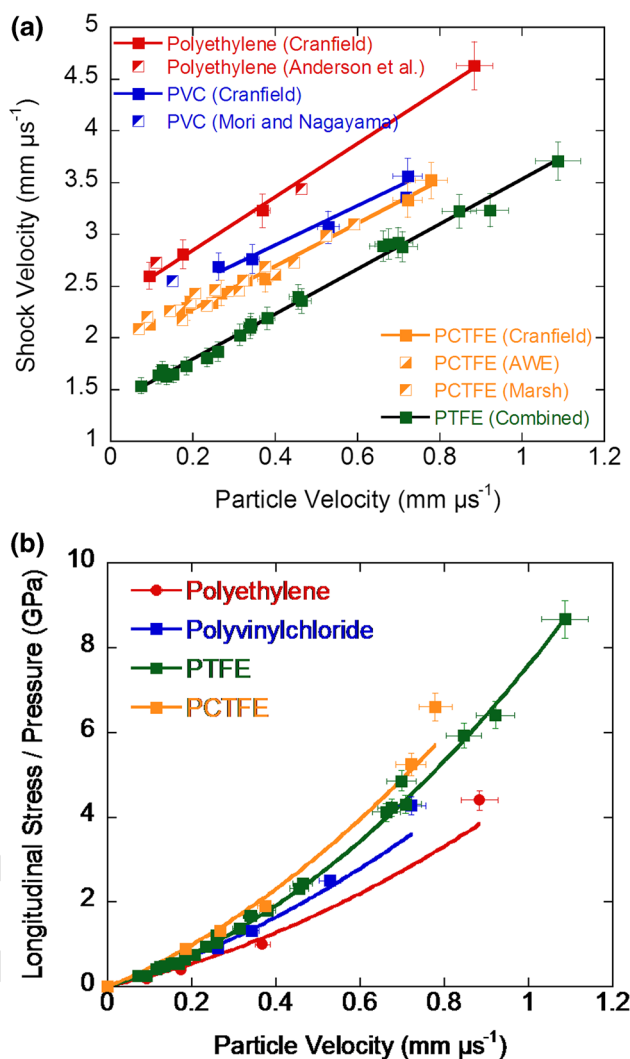
Fig. 4 Hugoniots of polymers under investigation. **a** Shock velocity–particle velocity. **b** Stress–particle velocity

fitted with Eq. 2, using the values of c_0 and S quoted in 294
Table 2. Note that in all materials (apart from PTFE), 295
there is a divergence between measured longitudinal 296
stress and calculated hydrodynamic pressure at higher 297
particle velocities with stress being the greater. This is 298
likely to be a first indication that these materials have 299
increasing shear strength with shock stress (see Eq. 3). 300
PTFE may also show this behaviour, but at higher stresses 301
than explored in this paper. 302
    From Fig. 3, the design of the target assemblies has 303
allowed us to determine the velocity of the head of the 304
release fan. These have been calculated using the known 305
spacings of the gauges, taking into account that the mate- 306
rial has been shock compressed, thus, 307

$$U_R = \frac{\Delta w}{\Delta t(release)}\left(1 - \frac{u_p}{U_S}\right). \tag{6}$$

Table 2 Shock relations for the polymers under investigation

	ρ_0 (g cm^{-3})	c_0 (mm µs^{-1})	S	c_B (mm µs^{-1})
PE [14, 15, 18, 36]	0.95	2.37	2.49	2.05
PVC [37, 38]	1.42	2.25	1.64	1.89
PTFE [18, 24]	2.15	1.36	2.17	1.14
PCTFE [13, 39]	2.13	1.93	1.94	1.50

The results are presented in Fig. 5, both as basic release velocity (Fig. 5a) and normalised by the longitudinal sound speed (Fig. 5b).

It can be seen from Fig. 5a that the release velocity is linear in relation to particle velocity for all four materials under investigation, in common with a number of other polymers including polypropylene and polystyrene [15] and polycarbonate [41], and a glass fibre–epoxy composite
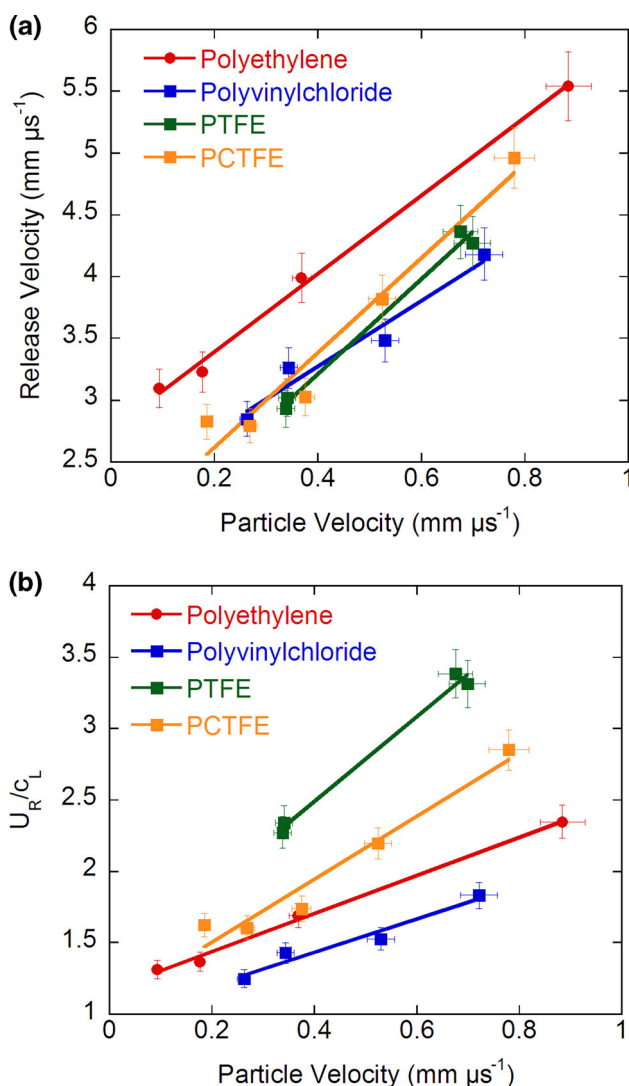
Fig. 5 Release response as a function of particle velocity. **a** Release velocity. **b** Normalised release velocity

[42]. However, given that the release response will be governed by the materials' properties and the shock response, it is difficult to identify trends from the basic release data. However, a previous article [18] made an attempt to normalise the release velocity by dividing by the shock velocity. This demonstrated that PTFE had an anomalously high release velocity when compared to either PE or PVDF, although no further explanation was given. In this work, we have modified this analysis slightly by normalising by the ambient longitudinal sound speed. The results are shown in Fig. 5b. Now a clearer picture emerges. PTFE has the highest relative release speeds, PE and PVC the lowest with PCTFE in the middle of the range. Further by assuming that relative release wave speed has a linear relationship with particle velocity of the form,

$$\frac{U_R}{c_L} = A + Bu_p, \tag{7}$$

It is possible to draw tentative conclusions about the materials response. The results are summarised below in Table 3.

In the majority of the materials in this investigation, the zero particle velocity intercept A appears to trend toward a value of one, the exception being PTFE. We have used this analysis on the assumption that the head of the release wave travels at the longitudinal sound speed at the applied shock pressure. Therefore if true, it would be unsurprising if the release wave speeds trend back towards the ambient longitudinal sound speed. That PTFE does not is likely due to the phase II to III phase transition experienced on shock.

The final set of experiments was designed to probe the shear strength of these materials under shock loading. Representative lateral stress gauge traces from each material are presented in Fig. 6.

The basic form of these traces is a rapid rise to the peak lateral stress as the shock front crosses the gauge location, a near constant level of lateral stress behind the shock front

Table 3 Release characteristics

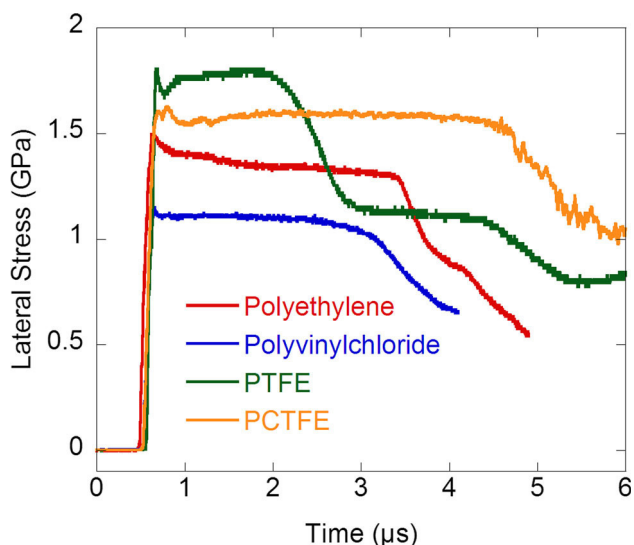| Material	A (mm µs^{-1})	B
Polyethylene	1.17	1.34
Polyvinylchloride	0.97	1.17
PTFE	1.30	2.98
PCTFE	1.06	2.21

Fig. 6 Lateral stress gauge traces

352 before releases enter the gauge location and the material is
353 returned to ambient conditions. The variation in pulse
354 widths are explained by differing flyer plates; 10 mm Dural
355 for PE and PVC, 10 mm copper for PCTFE and 5 mm
356 copper for PTFE. Also observe that in some for PE and
357 PVC, the lateral stress behind the shock front is not con-
358 stant, but rather decreases slightly over time, indicating an
359 increase in shear strength with time (Eq. 5). This has been
360 observed previously in a number of other polymers,
361 including PMMA [43, 44], polycarbonate [41] and PEEK
362 [16]. This has been quantified and is presented below in
363 Fig. 8. Before addressing this though, we consider the
364 shock induced shear strength as a function of longitudinal
365 stress, as presented in Fig. 7. These have been determined

366 using Eq. 5, although the following qualification must be
367 bourn in mind.
368 The lateral stress gauge traces from PTFE and PCTFE
369 are essentially flat behind the shock front (until releases
370 enter the gauge location), hence the calculation of shear
371 strength from the known longitudinal stress is trivial. The
372 situation with PE and PVC is complicated by the fact that
373 lateral stress behind the shock front decreases, thus indi-
374 cating an evolving (increasing) shear strength with time.
375 Therefore, the shear strength for these two materials pre-
376 sented in Fig. 7 have been determined *immediately* behind
377 the shock front. These results indicate that there is little
378 difference between the shear strengths of PE, PVC and
379 PTFE, and their variation with imposed shock stress. At
380 higher impact stresses, there does seem to be a strength-
381 ening in PCTFE, suggesting that modification of a pre-
382 dominately fluorinated polymer has a greater effect on
383 strength than similar modifications on a simple poly-
384 ethylene based polymer.
385 The final point we wish to discuss is the rate at which
386 lateral stress changes behind the shock front, giving an
387 indication of the kinetics of shock induced material
388 deformation in these materials. The results are presented in
389 Fig. 8.
390 As indicated by the lateral stress traces shown in Fig. 6,
391 the two fluorinated-materials have a largely flat response,
392 indicating zero change behind the shock front. In contrast,
393 PE and PVC both appear to harden behind the shock front,
394 with the level of that hardening increasing with imposed
395 shock stress. Further, it would appear that the degree of that
396 hardening is near identical between these two materials. In
397 previous works [22, 41] where this behaviour has been
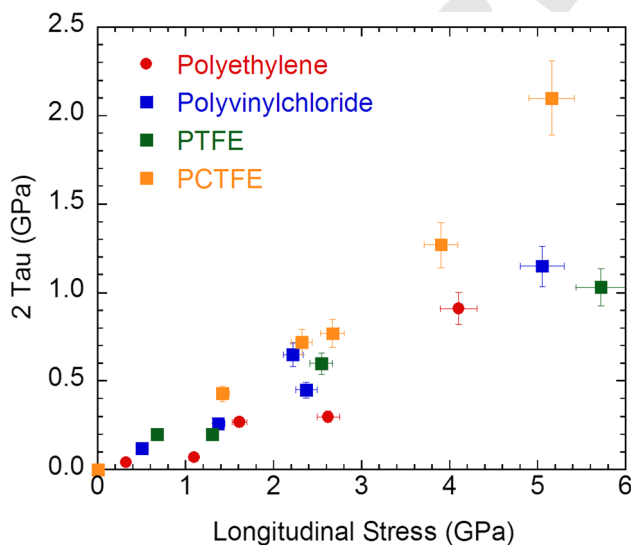398 observed, it has been suggested that this be due to steric

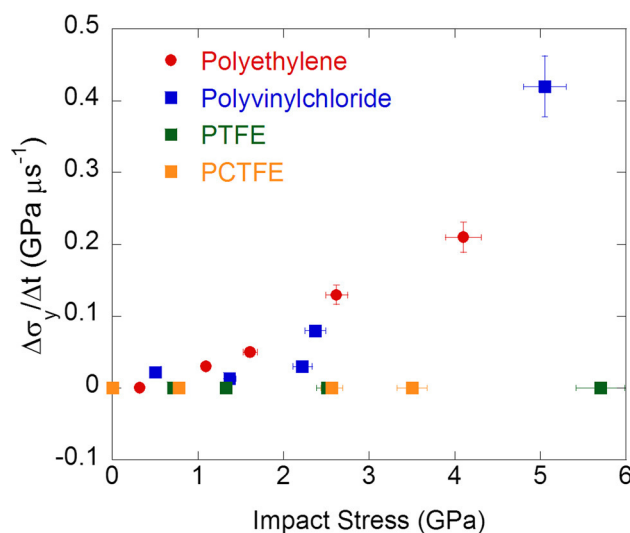**Fig. 7** Shear stress versus impact stress

Fig. 8 Lateral stress variation with impact stress

399 interference between adjacent polymer chains that is
400 responsible. In the case of fluorinated polymers, it was
401 proposed that the high electronegativity of the fluorine
402 atoms, combined with the sheathing effect of those atoms
403 around the carbon backbone allowed much easier passage
404 of the polymer chains past each other, thus resulting in a
405 flatter lateral stress response [18].

Discussion

407 The shock response of the four common polymers studied
408 in this investigation are in the main affected by two factors.
409 The first is an electronic component due to repulsion
410 between the constituent atoms as they approach each other
411 during shock compression. It would be expected that this
412 would be greatest in PTFE, where the carbon backbone is
413 sheathed by large (compared to hydrogen), strongly elec-
414 tronegative fluorine atoms. The second is due to the
415 physical interaction between adjacent polymer chains due
416 to their shape, in other words chain tangling or tacticity.
417 This would be expected to be greatest in a molecule where
418 a side group off a carbon atom disrupts the otherwise
419 regular ordering of the basic monomer unit, thus tangling
420 effects would be expected to be greater in PVC than PE,
421 and greater in PCTFE than PTFE. However, these effects
422 do not act in isolation, but rather in combination, and it is
423 the intention of this paper to indicate how these factors
424 affect the overall shock response.
425 The first point to consider is the equation of state, as
426 shown in Fig. 4 and Table 2. For the sake of clarity, we
427 reproduce the values of S along with the ambient condi-
428 tions bulk modulus in Table 4, ordered by decreasing value
429 of S.
430 Although the shock parameters c_0 and S are empirical
431 constants, c_0 has been related (in simple metals at least) to
432 the bulk sound speed [13, 40], whilst S has been linked to
433 the first pressure derivative of bulk modulus [40]. From
434 this, compressibility decreases from polyethylene, to PTFE
435 to PCTFE with PVC having the least compressibility. If we
436 take PE as the base line polymer, it would appear that any
437 degree of modification to the polymer chain has a stiffening
438 effect. Therefore PTFE is stiffer than PE due to the
439 repulsive effect of the highly electronegative fluorine

Table 4 Values of S and bulk modulus

	S	K (GPa)
Polyethylene	2.49	3.99
Polytetrafluoroethylene	2.17	2.77
Polychlorotrifluoroethylene	1.94	4.77
polyvinylchloride	1.64	5.07

440 atoms resisting the compression of adjacent polymer
441 chains. The chemically similar PCTFE has less com-
442 pressibility than PTFE, even though the additional chlorine
443 atom replacing a single fluorine atom will have minimal
444 changes to the repulsion between chains due to the simi-
445 larities between the electronegativities between chlorine
446 and fluorine. Therefore the stiffening effect is most likely
447 the result in the larger chlorine atom giving the polymer
448 chain some degree of tacticity, allowing a small degree of
449 increased resistance between polymer chains. The stiffest
450 material of all is PVC, with an S of 1.64. Given the
451 hypothesis given above, one would expect that the addition
452 of a single chlorine atom to the basic PE chain would only
453 have a small degree of repulsion between chlorine atoms,
454 and even with the additional tangling effects due to the
455 addition of the larger (compared to hydrogen) atoms, the
456 over all stiffening effect would not be great. However, an
457 additional effect lies in the alternating CH_2–$CHCl$ units in
458 the polymer chain. This will result in local changes in
459 charge density, which will effect how the polymer chains
460 interact. In a previous paper [18], a similar effect was noted
461 between PTFE and polyvinylidene difluoride (PVDF)
462 where alternating CH_2–CF_2 units were shown to signifi-
463 cantly affect the shock response. Finally we would also
464 point out that although the overall ranking of S appears to
465 agree with that of the ambient bulk modulus, the local trend
466 between PE and PTFE is reversed. Under ambient condi-
467 tions, PTFE has a lower bulk modulus than PE, suggesting
468 that it is more compressible. However, it should be noted
469 that PTFE undergoes a pressure induced phase change at
470 ca. 0.5 GPa [24, 45], and hence if the properties of PTFE in
471 its ambient phase II state and high pressure phase III state
472 are significantly different, it would explain this variation of
473 behaviour between bulk modulus and S.
474 Examination of the release behaviour (Fig. 5; Table 3)
475 also reveals the interplay between repulsion between
476 polymer chains and chain tangling. From Fig. 5b, it can be
477 seen that the ordering of relative release velocities (fastest
478 to slowest) is PTFE, PCTFE, PE with PVC being the
479 slowest. The same ordering can also be seen for slope of
480 the U_R/c_L–u_p curve, B. In the case of PTFE, the high
481 electronegativity of the sheathing fluorine atoms will drive
482 the adjacent polymer chains apart on release resulting in
483 the high release speeds observed in Fig. 5a. A similar
484 behaviour will affect PCTFE, where one would expect a
485 high release speed. From Fig. 5b and Table 3, it can be
486 seen that this is the case, although the overall release speed
487 is less than that of PTFE. We believe that this is due to the
488 influence of the replacement chlorine atom conveying a
489 small degree of tacticity, allowing adjacent chains a small
490 degree of resistance against electrostatic repulsion. With
491 PE, the degree of electrostatic repulsion will be minimal
492 and hence release speeds will be dominated by chain

tangling. As a consequence, the release speeds will be significantly lower as the chains resist coming apart. Finally, PVC has the lowest release speed and value of *B* of all four materials in this investigation. We believe two factors are in effect here. Firstly, the large chlorine atom (replacing a hydrogen) will increase the degree of chain tacticity compared to PE. Secondly, the highly electronegative chlorine atom will result in a variation of charge density along the PVC chain that will allow for additional localised attractive forces between adjacent chains, which will further reduce the release velocity.

The final side to this investigation was to examine the effects of additional chlorine atoms on the shock induced strength. As with many shock-loaded materials, there are two components to this response; a variation with time (behind the shock front) and a variation with pressure. Looking at the lateral stress gauge profiles in Fig. 6 and the quantified changes in lateral stress with respect to time (Fig. 8), it can be seen that the four materials under investigation can be split into two groups. PE and PVC show a *reduction* in lateral stress, and hence an *increase* in shear strength behind the shock front. From Fig. 8, it would appear that these changes with respect to impact stress are near identical. In contrast, both PTFE and PCTFE show a near constant lateral stress and hence shear strength behind the shock front, in common with a number of other fluorinated polymers such as KelF-800 (a bi-polymer between chlorotrifluoroethylene and vinylidene difluoride) [46] and Viton-B (a tri-polymer of tetrafluoroethylene, hexafluoropropylene and vinylidene difluoride) [47]. In the case of PTFE, we have suggested that the sheathing of the carbon backbone by large fluorine atoms has two effects; effectively making the polymer chain smoother, thus allowing easier movement between adjacent polymer chains, and high degree of electrostatic repulsion between chains due to the presence of the same strongly electronegative fluorine atoms. As a consequence, the chains will move relatively easily past each other, hence there will be little change in strength with time. In contrast, the relatively open nature of the PE molecule allows greater physical interaction between adjacent polymer chains (in other words tangling) and hence as tangling increases, the stresses required to move them together will increase with time. A similar response will occur in PVC where the addition of a single chlorine atom to the basic polyethylene monomer will enhance the propensity for adjacent polymer chains to tangle. From Figs. 6 and 8, it can be seen that PCTFE behaves in a similar way to PTFE. It would appear that any changes in tacticity due to the replacement of a fluorine atom by a chlorine atom are minimal, most likely due to the still strong electronegativity of the additional chlorine atom. However, the fact that other fluorinated polymers (KelF-800 and Viton-B) also display this

response, even though they have dangling side groups (chlorine atoms and trifluoromethyl) and alternating CF_2–CH_2 groups (Kelf-800 and Viton-B) would suggest that these materials should display a degree of tacticity resulting in a hardening response behind the shock front. The fact that they do not is an indication that the electrostatic repulsion between chains (when present) has a much stronger influence than chain tangling, operating at a greater inter chain separation that prevents physical interaction between chains from coming into effect. Finally, from Fig. 7 it can be seen that the strength of all four polymers under investigation increase with shock stress. Although there is a degree of scatter within the data, it would appear that the ordering (lowest strength first) is PE, PTFE, PVC and finally PCTFE with the highest strength. Therefore, the replacement of hydrogen with fluorine atoms has a strengthening effect due to the large increase in electrostatic repulsion between PE and PTFE, whilst the increase between PE and PVC is more likely to be due to an increase in polymer chain tacticity due to the addition of a single chlorine atom. PCTFE has the highest strength of all, suggesting that there is a cumulative effect between electrostatic repulsion and tacticity. Although Fig. 8 shows no evidence of hardening behind the shock front in PCTFE, the significant increase in overall shear strength at high stresses (compared to the other three materials under investigation) may be a first indication that chain tangling may be having a more significant role in the shock induced shear strength of PCTFE.

We therefore propose that the strength of polymers has two main components. Firstly, there will be an electrostatic repulsion between adjacent chains, the strength of which will depend on the precise chemistry of those chains. In the case of (mostly) hydrocarbon based polymer chains, this will be a relatively weak force that is readily overcome by the compression supplied by the shock. Conversely, where there are a large number of halogen atoms (principally fluorine) surrounding the basic carbon backbone, that interchain repulsive force will be much greater, and in many materials will actually dominate the materials mechanical response to shock loading. Secondly, there will be an effect due to the shape of the polymer, which allows adjacent chains to tangle as the shock pressure brings them closer together (tacticity). This will be more prevalent in materials with an open chain morphology (PE) or dangling side groups (PVC). This behaviour will operate at lesser distances than the electrostatic repulsion discussed above, and will only come into operation when this first force has been overcome. We hypothesis that at shock stresses greater than those employed in this study, heavily fluorinated polymers such as PTFE may begin to show hardening behaviour behind the shock front, similar to that displayed by PE at lower shock stresses. That PCTFE, of the four

materials discussed in this report, displays the greatest shear strength at the highest shock stresses could be a first indication of chain tacticity having a greater role in its shock response.

Conclusions

The effects of replacing either a hydrogen or fluorine atom in polyethylene and polytetrafluorethylene (to create PVC and PCTFE respectively) on the shock response has been investigated in terms of the Hugoniot, release velocities and shear strengths. The results from these shots have led us to suggest that there are two main factors affecting the shock response of simple polymers; an electrostatic repulsive force between adjacent polymer chains and a physical interaction due to tangling (chain tacticity). The former is dominant when the polymer chain is surrounded by highly electronegative atoms such as fluorine (PTFE) and/or chlorine (PCTFE). That these large (compared to hydrogen) atoms also has a sheathing effect upon the polymer chain, resulting in an over all smoother shape that allows easier passage of the polymer chains past each other during shock loading. Under such circumstances, this will result in a comparatively low shock speed, high release speed and a lack of hardening behind the shock front. In contrast, where inter chain tangling becomes dominant, the shock speed increases, the release speed reduces and hardening behind the shock front becomes significant. The addition of a single chlorine atom on either the PE (forming PVC) or PTFE chain (forming PCTFE) results in significant modifications of the basic shock response. PVC has a higher shock speed, lower release speed and reduced compressibility compared to PE. We believe that this is in part due to the large single chlorine atom on the base monomer unit increasing the likelihood of chain tacticity when compared to PE. However, we also suggest that the same chlorine atom will also result in localised changes in charge density along the chain, which could modify inter-chain interactions. In the case of PCTFE, the role of the additional chlorine atom also appears to result in an increase in shock-speed, reduction in release speed and an increase in shear strength at higher impact stresses. We therefore suggest that the shock response of these polymers is controlled by the interplay of these factors. As the shock pressure compresses the material, the initial behaviour is due to the electrostatic repulsion between chains. As pressure increases, the polymer chains move closer together and hence physical interaction between those chains, in the main due to tacticity but also due to charge distributions along the chains will become increasingly important. In heavily fluorinated materials such as PTFE and PCTFE, it is the repulsive forces that dominate. In contrast, in (predominantly) hydrocarbon polymers, the repulsive forces are weak, and hence inter chain tacticity becomes the dominant factor controlling shock response. It is likely that the hardening response behind the shock front displayed by PE and PVC would also be exhibited by PTFE and PCTFE at higher impact stresses, although at present these would be higher than the pressures investigated here.

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