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DOI:[10.1063/1.5044871](https://doi.org/10.1063/1.5044871)**Document Version**

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)**Citation for published version (APA):**

Whiteman, G., Millett, J. C. F., Brown, E., Gray, G. T., & Bourne, N. (2018). The Response of a Commercial Fluorinated Tri-Polymer to 1-D Shock Loading. In *AIP Shock Compression of Condensed Matter 2017* [090014] <https://doi.org/10.1063/1.5044871>

Published in:

AIP Shock Compression of Condensed Matter 2017

Citing this paper

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The Response of a Commercial Fluorinated Tri-Polymer to 1-D Shock Loading

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Abstract. The response of simple polymers to shock loading is governed by a number of factors such as the complexity of the polymer chains and nature of the atoms attached to the main carbon-carbon backbone. In the case of polyethylene based materials such as polyethylene, polypropylene and polytetrafluoroethylene the competing effects of inter chain tangling (tacticity) and electrostatic repulsion between adjacent polymer chains have been shown to have a profound effect on shock velocity, release velocity and shear strength development. In this work, we apply these considerations to a commercially available fluoro-tripolymer, Viton-B, where all these molecular features are present.

INTRODUCTION

Given the wide range of structures that can be adopted by polymeric materials (thermoplastics such as polyethylene, cross linked thermoset resins including epoxies and elastomers such as polychloroprene), it is not surprising that the shock response of these materials can often be a complex issue. Despite this, over the past decade, we have made a systematic effort to study the effects of simple molecular changes such as increasing the size of dangling side groups (polyethylene – PE, polypropylene – PP and polystyrene – PS) [1] or changing the number of fluorine atoms attached to the main carbon-carbon backbone (PE, polyvinylidene difluoride – PVDF and polytetrafluoroethylene – PTFE)[2]. More recently, we have extended these studies to materials such as polyvinylchloride – PVC (the replacement of a hydrogen in PE with a chlorine atom) and polychlorotrifluoroethylene (the replacement of a fluorine atom in PTFE with a chlorine) [3, 4]. These studies have led us to the hypothesis that the shock response of polymers is governed in the main by three factors. Firstly, by tacticity, whereby adjacent polymer chains become entangled as the shock front drives them together. This results in increasing shear strength behind the shock front and increased shock velocity and reduced release velocity. Most polymers display this sort of behavior, either due to the open nature of the polymer (PE) or large side groups increasing polymer chain interactions (PP, PS). In contrast, heavily fluorinated polymers such as PTFE has a low shock speed and high release speed, combined with a near constant shear strength behind the shock front. This was explained in terms of the highly electronegative fluorine atoms surrounding the carbon backbone giving a high degree of electrostatic repulsion between chains that resists compression during the shock and enhances release, whilst reducing interchain tangling and hence reducing the level of strengthening behind the shock as the chains can move past each other with greater ease. A final point worth noting concerns PVDF. Here it was noted that the shock and release speeds were closer to those of PE than PTFE, whilst the shear strength was greater than both. It was suggested that the alternating CH₂-CF₂ groups could result in local changes in charge density along the polymer chain which could increase attraction between chains, whilst corresponding effects on shock response.

The polymers discussed above can be considered ‘pure’ materials. However, in industrial environments, properties can be optimized to the required level by manipulating the nature of the material itself. In the case of metals, this is done via alloying with small amounts of different elements. In the case of polymers, an analogous process uses

different monomer units to make up the ultimate polymer chain. In the case of Viton-B. Viton-B is a tripolymer consisting of the monomer units ($\text{CF}_2=\text{CH}_2$ -vinylidene difluoride; VDF), ($\text{CF}_2=\text{CF}_2$ -tetrafluoroethylene; TFE) and ($\text{CF}_2=\text{CF}-\text{CF}_3$ - hexafluoropropylene; HFP) with a net fluorine content of 68 wt%. It finds application in the automotive and aerospace industries where resistance to temperature and chemical attack is required. From the nature of the basic monomer units, it can be seen that the effects discussed above (chain tacticity, electrostatic repulsion and charge density variations) are all present within this material.

EXPERIMENTAL

All shots were performed using a 50 mm bore, 5 m long single stage light gas gun [5]. Two sets of experiments were undertaken to probe the Hugoniot and shock induced shear strength. In the former, a manganin stress gauge (MicroMeasurements type LM-SS-125CH-048) were placed between a 12 mm thick plate of Viton-B (machined flat and parallel to $\pm 5 \mu\text{m}$) and a 12 mm plate of PMMA using a low viscosity epoxy adhesive. In this way, the gauge would measure the longitudinal stress (σ_x) and used to infer the particle velocity (u_p) from impedance matching with the velocity and known shock response of the flyer plate material. A second gauge was supported on the front of the target assembly with a 1 mm thick plate of either copper or aluminium alloy 6082-T6 (Dural), matched to the material of the flyer plate. The temporal spacing between the gauges, along with their known physical separation could then be used to determine the shock velocity (U_s). Gauge calibrations were according to Rosenberg *et al.* [6]. Shock loading was induced by 5 and 10 mm plates of copper or Dural impacting onto the target assembly in the velocity range 295 to 885 m s^{-1} . In the second series of experiments, a single plate of Viton-B 50 mm x 50 mm by 11 mm was sectioned in half, and manganin stress gauge (MicroMeasurements J2M-SS-380-SF-025) introduced 4 mm from the impact surface. The targets were reassembled using a low viscosity epoxy and held in a special jig for a minimum of 12 hours. In this configuration, the gauge is sensitive to the lateral component of stress (σ_y), and through knowledge of the longitudinal stress from the impact conditions, the shear strength (τ) can be determined through the relation,

$$2\tau = \sigma_x - \sigma_y \quad (1)$$

Gauge data were reduced to lateral stress using the methods of Rosenberg *et al.* [7] Impact stresses in the range 0.63 to 5.64 GPa were generated by 5 mm flyer plates of either Dural or copper, at impact velocities of 202 to 891 m s^{-1} . Schematic diagrams of the target assemblies are shown in Figure 1.

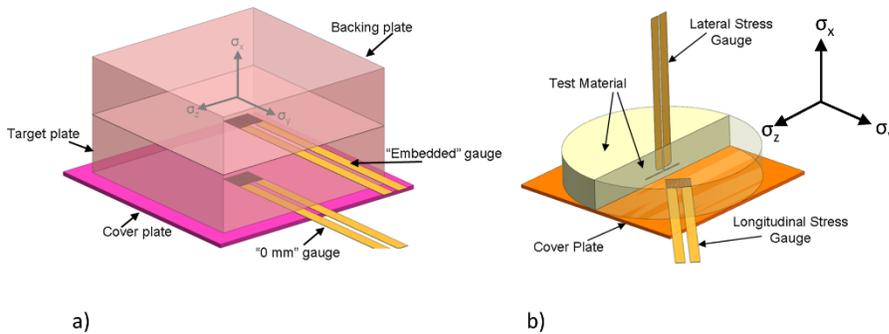


FIGURE 1. Schematic diagrams of target configurations a) longitudinal stress and b) lateral stress.

RESULTS

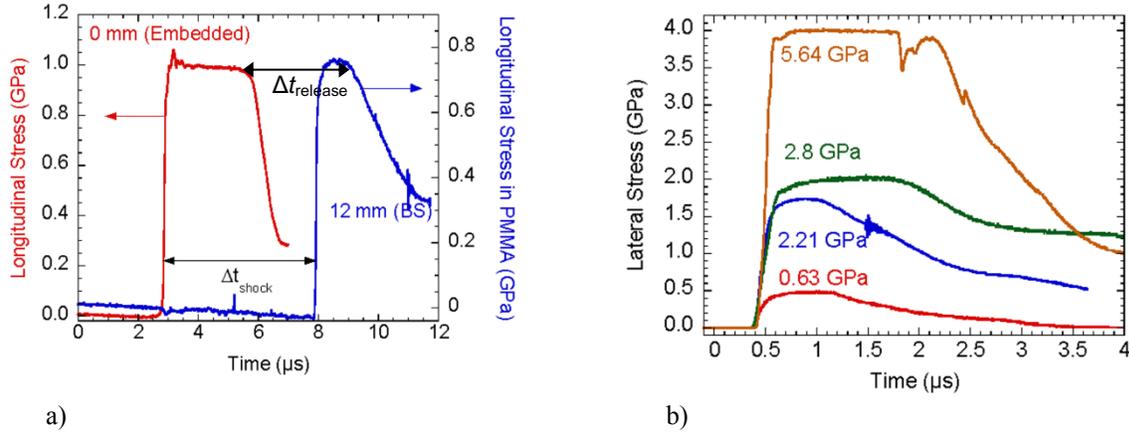


FIGURE 2. Representative stress gauge traces from Viton – B a) longitudinal stress and b) lateral stress

Representative gauge traces in Viton-B are presented in Figure 2. In 2a, the 0 mm gauge shows a square stress pulse but is otherwise featureless. This is due to the fact that the shock has passed through only 1 mm of copper in this example. The gauge at 12 mm (labelled BS) is more revealing as it has passed through 12 mm of Viton-B. The main feature is the much shorter pulse width. Given the thick PMMA plate backing the target assembly, the release will have come from the rear of the flyer plate, and hence the traces can be used to determine the release velocity (U_R). As well as this, the shock velocity can also be determined through the temporal separation of the traces (Δt_{shock}). These are calculated via,

$$U_S = \frac{w}{\Delta t_{shock}} \text{ and } U_R = \frac{w}{\Delta t_{release}} \left[1 - \frac{u_p}{U_S} \right] \quad (2)$$

where w is the physical separation between gauges and the calculation of the release velocity has to take into account the strain imposed by the passage of the shock. In figure 2b, lateral stress gauge traces for impact stress from 0.63 to 5.64 GPa are shown. It can be seen that the traces themselves are near flat behind the shock front, in contrast to most other polymers where the same measurement has been made [8-11]. This implies that the shear strength itself is near constant behind the shock front, and is discussed in more detail later in paper.

We present both sets of values below in figure 3, along with equivalent values for the related polymers, PTFE and PVDF[2].

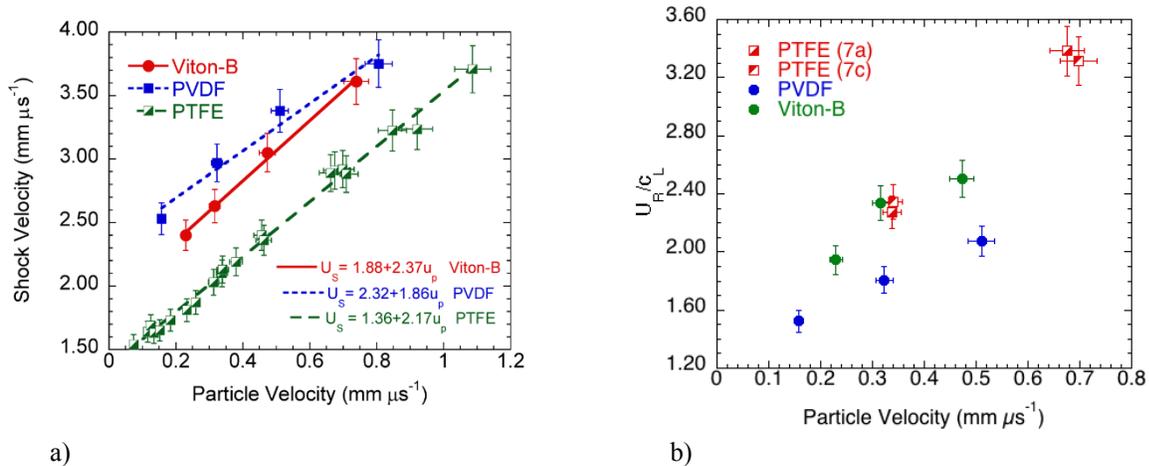


FIGURE 3. Shock and relative release velocities of Viton-B and the related materials, PTFE and PVDF[2], a) U_S - u_p and b) relative release velocities.

In terms of shock velocity, Viton-B appears to be closer to PVDF rather than PTFE. However in the case of the release velocities, Viton-B is closer in nature to PTFE. Note that we have normalized the release speed by the ambient longitudinal sound speed. We have done so on the basis that the head of the release fan will be travelling at the longitudinal sound speed at the shock pressure.

In Figure 4a, we have plotted the Hugoniot of Viton-B in stress – particle velocity space, along with the equivalent data for PTFE and PVDF. Note that the data has been curve fitted according to the hydrodynamic pressure (P_{HD}) calculated from

$$P_{HD} = \rho_0 U_S u_p, \quad (3)$$

where ρ_0 is the ambient density (1.96 g cm^{-3}).

Note that the agreement between measured shock stress and calculated hydrodynamic pressure is good at lower pressures, but begins to diverge as pressure increases (especially for PVDF and Viton-B) with stress being the higher. This may be an indication that the shear strength behind the shock front is increasing with pressure, and this issue to explored further in figure 4b.

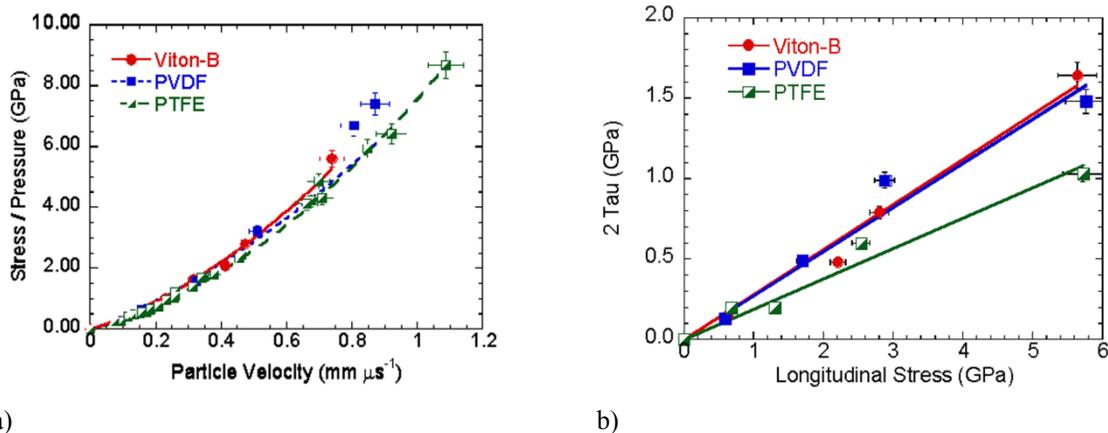


FIGURE 4. Hugoniot and shear strengths in Viton-B and related materials, a) Hugoniot stress and b) shear strength

The lateral stresses measured from these experiments have been used with the longitudinal stresses from the known experimental conditions to determine the shear strength behind the shock front using Equation 1,

It can be seen that Viton-B is stronger than PTFE, and has a shear strength that is near equal to that of PVDF.

DISCUSSION

The three monomer units in Viton-B (TFE, VDF and HFP) give the shock response a level of complexity not seen in related, but simpler materials. In the case of PTFE, the sheathing effect of the large (compared to hydrogen) fluorine atoms, in combination with their high electronegativity results in a reduced level of interaction between adjacent chains, leading to a low shock velocity, low strength and little change in shear strength behind the shock front. However, that high electrostatic repulsion between chains will also act to drive them apart during release, hence the high release speed. In contrast, PVDF has a significantly higher shock speed and shear strength, along with a small degree of hardening behind the shock front[2] and a low release speed. We would suggest that a combination of alternating $\text{CH}_2 \text{CF}_2$ sub units gives a degree of tacticity between chains, along with localized charge density along the chain will also increase attractive forces between chains, with the resultant changes in shock response in

comparison to PTFE. The addition of a monomer unit with a large dangling trifluoromethyl side group would be expected to lend a high degree of tacticity to the shock response, which can be seen from the high shock speed and shear strength. However, whilst the presence of the VDF monomer unit in the polymer chain would lead to a level of attraction between chains (as in PVDF), its effect would be limited to its effective dilution by the other two monomer units. The presence of the trifluoromethyl side group is also most likely responsible for the higher shear strength in Viton-B compared to PTFE, again due to interchain tacticity. However, it might also be expected to also result in a level of shear strength increase behind the shock front, when from Figure 2b, it clearly does not. This might in part be due to dilution effects again (the HFP monomer is only one of three monomer units in the polymer chain) but also note that it possesses six fluorine atoms, which will enhance the electrostatic repulsion effect between chains. In a previous article[3] we suggested that this effect may operate at longer length scales than either interchain tacticity or charge density attraction, and hence may be able to at least partially overcome the tacticity effects caused by the dangling side group, hence the high release speed and lack of shear strength increase behind the shock front. However, the increased tacticity also the shear strength in relation to PTFE.

CONCLUSIONS

The shock response of Viton-B, a tripolymer consisting of tetrafluoroethylene, vinylidene difluoride and hexafluoropropylene has been investigated in terms of its Hugoniot, release speeds and shock induced shear strength. Comparisons with the related but simpler polymers PTFE and PVDF. Results show that Viton-B shares common features with other heavily fluorinated polymers, including a high release speed and little or no hardening behind the shock front. It is believed that this is due to the high density of electronegative fluorine atoms around the carbon backbone reducing interchain interaction during shock loading. However, the presence of the trifluoromethyl side group does result in a higher degree of tacticity than in the simpler polymers, and hence leads to a higher shock induced shear strength.

ACKNOWLEDGMENTS

We would like to thank the staff of Cranfield University for their help in performing these experiments. British Crown Owned Copyright 2017/AWE. Published with permission of the Controller of Her Britannic Majesty's Stationery Office. "This document is of United Kingdom origin and contains proprietary information which is the property of the Secretary of State for Defence. It is furnished in confidence and may not be copied, used or disclosed in whole or in part without prior written consent of Defence Intellectual Property Rights DGDCDIPR-PL-Ministry of Defence, Abbey Wood, Bristol, BS348JH, England."

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