Hugoniot-based equations of state for two filled EPDM rubbers

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Abstract. Particle-filled elastomers are commonly used as engineering components due to their ability to provide structural support via their elastic mechanical response. Even small amounts of particle fillers are known to increase the mechanical strength of elastomers due to polymer-filler interactions. In this work, the shock response of two filled (SiO$_2$ or silica and Kevlar™fillers) ethylene-propylene-diene (EPDM) rubbers were studied using single and two-stage gas gun-driven plate impact experiments. Hugoniot states were determined using standard plate impact methods. Both filled-EPDM elastomers exhibit high compressibility under shock loading and have a response similar to adiprene rubber.

1. Introduction

Particle-reinforced ethylene-propylene-diene monomer (EPDM, figure 1) elastomers are used as liner materials in some solid rocket motors, providing structural support and protection of propellant fills. As such, they may be subjected to high strain rate deformation or unintentional impact conditions, requiring that their compressive properties be investigated over a range of conditions (strain rate, temperature, etc.). In the present work, the low-to-intermediate stress shock behaviors of silica-filled and Kevlar-filled EPDM rubbers were investigated using gas gun-driven plate impact experiments. These are the first measurements of Hugoniot states for filled EPDM elastomers used in rocket motor liners.

A total of 8 experiments were performed, 4 on each material, forming the basis of Hugoniot-based equations of state for the two materials. Both rubbers had similar compressibility and were similar in behavior to adiprene rubber [1].

2. Experimental

2.1. Materials

Filled EPDM rubbers were obtained from Kirkhill-TA, Brea, CA, USA. Table 1 summarizes the properties of the Kevlar and silica filled elastomers. The Kevlar-filled EPDM composite used KL70-L6211 EPDM, with a proprietary fill percent. The silica-filled EPDM was designation EPDM KL70-887, and contained approximately 30% silica by weight. Based on the difference in density between silica and Kevlar, the fill percent (by weight) in the Kevlar-filled EPDM
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INTRODUCTION

1. Introduction

EPDM elastomers are commonly used in composite rocket motor liners due to their ability to provide structural support via their elastic mechanical response. These elastomers exhibit high compressibility and are known to increase the mechanical strength of composites when filled with amounts of particle fillers. The glass and melt transition temperatures, $T_g$ and $T_m$, and the heat of fusion, $\Delta H_f$, for silica- and Kevlar-filled EPDM elastomers were determined using differential scanning calorimetry at $2^\circ$C/min heating rates. The difference in initial densities, $\rho_0$, also indicates that the Kevlar-filled material has a greater percentage of filler.

Table 1. Summary of initial and thermal properties of silica and Kevlar-filled EPDM. The glass and melt transition temperatures, $T_g$ and $T_m$, and the heat of fusion, $\Delta H_f$, were obtained by differential scanning calorimetry at $2^\circ$C/min heating rates.

| Property            | Silica-filled | Kevlar-filled |
|---------------------|--------------|---------------|
| filler amount       | $\approx 30\%$ | unknown       |
| $T_g ($^\circ$C)$    | -47          | -47           |
| $T_m ($^\circ$C)$    | -19          | -16           |
| $\Delta H_f$ (J/g$^{-1}$K$^{-1}$) | 2.4          | 6.4           |
| $\rho_0$ (g/cm$^3$) | 1.042        | 0.920         |

Both materials have low temperature glass transitions ($T_g = -47 ^\circ$C) and melt transitions at $T_m = -19$ and $-16 ^\circ$C for the silica- and Kevlar-filled materials, respectively. From integration of the melt endotherm, the heat of fusion, $\Delta H_f$, is obtained. $\Delta H_f$ can be related to the percent crystallinity. From Table 1, the Kevlar-filled material contains $\sim 3$ times the crystallinity of the silica-filled material. The greater crystallinity manifests itself in other ways not reported here. The difference in initial densities, also indicate that the Kevlar-filled material has a greater percentage of filler.

2.2. Plate impact experiments

Gas gun-driven plate impact experiments were performed using a 72 mm diameter single stage light gas gun, and a two-stage, 50 mm bore (launch tube) light gas gun at Los Alamos National Laboratory described previously [2]. Two types of experiments were performed. The first, two (0.94 cm in length) electromagnetic gauge elements contained in a single electromagnetic gauge membrane were sandwiched between layers of the elastomer samples, providing direct measurement of particle velocity wave profiles at the impact face, and 2 additional Lagrangian positions in the material. The principles of electromagnetic gauge operation have been described previously [3, 4]. Figure 2 shows a photograph of a gauge membrane glued to a Kevlar-filled EPDM sample. The gauges are the vertical elements in the center of the sample, and consist of $5 \mu$m Al sandwiched between two $10 \mu$m-thick FEP-Teflon membranes forming a package $\approx 25 \mu$m thick. The gauges were glued to the EPDM samples using Epon 815 epoxy with glue bonds generally $< 10 \mu$m thick. The EPDM samples were $\sim 0.125$ inch thick. The embedded gauge targets were impacted by either z-sapphire or Kel-F 81 (polychlorotrifluoroethylene, $\rho_0 = 2.14$ g/cm$^3$) impactors launched by the light gas guns. Example particle velocity wave profiles from all 6 gauges (2 each at 3 Lagrangian positions) from shot 2s-433 on Kevlar-filled EPDM are
shown in figure 3. Projectile velocities were measured to < 0.1% using an optical method.

Figure 2. Photograph of a Kevlar-filled EPDM rubber sample cut to size and shape for plate impact experiments. An electromagnetic gauge package is glued to the surface of the sample, and contains two “stirrup” gauge elements. “Active,” net voltage producing, gauge elements are the vertical Al segments which are ≈ 0.94 cm long.

In the second type of experiment, polymer samples were affixed in the front of polycarbonate (Lexan™) projectiles, and impacted into oriented [100] Lithium Fluoride (LiF) windows with an Al reflector coated on the impact face. Dual velocity-per-fringe (vpf) VISARs [5] were used to measure the interface particle velocity. From the measured projectile velocity and interface particle velocity, the Hugoniot state was determined by impedance matching to the LiF Hugoniot; \( \rho_0 = 2.638 \, \text{g/cm}^3 \), \( C_0 = 5.15 \, \text{km/s} \), \( S = 1.35 \) [1]. Figure 4 shows a schematic of the front surface impact experiments. Figure 5 shows example interface velocity wave profiles from shot 2s-432, in which the Kevlar-filled EPDM was impacted into LiF at 2.878 km/s. The ripples in the wave profiles are due to heterogeneities in the sample from the Kevlar filler.

Figure 4. Schematic diagram of front surface impact experiments. The sample is affixed to the front of a Lexan™ projectile and impacted into a single-crystal LiF window. Interface velocity is measured using dual VISARs. The reflector is 8 kÅ of vacuum plated Al.

Figure 5. Example interface velocity wave profiles from shot 2s-432.
3. Results and discussion
A series of gas gun-driven plate impact experiments were performed on silica- and Kevlar-filled EPDM rubbers, imparting several microsecond duration supported shocks into the materials with shock input stresses ranging from < 1 to nearly 15 GPa. The Hugoniot states determined in the experiments are summarized in table 2, and are the first experimental shock data on particle reinforced-EPDM elastomers that we are aware of.

The measured Hugoniot states for silica and Kevlar-filled EPDM are shown in the \(U_S - u_p\) and \(P - V\) planes in figures 6 and 7. In the \(U_S - u_p\) plane, the data have been fit to a linear Rankine-Hugoniot relationship. Many polymers, liquids, and “porous” or free volume-containing materials, have Hugoniots with downward curvature in the \(U_S - u_p\) plane, and \(C_0\) from a linear fit often exceeds the ambient condition bulk sound velocity by 300-700 m/s [6]. Linear \(U_S - u_p\) fits shown in figure 6 appear to extrapolate well to \(u_p = 0\).

The linear Rankine-Hugoniot fit coefficients, \(U_S = C_0 + Su_p\), are, for the silica-filled EPDM, \(C_0 = 1.823 \pm 0.031\) km/s, \(S = 1.855 \pm 0.023\), and for the Kevlar-filled EPDM, \(C_0 = 1.657 \pm 0.048\) km/s, \(S = 2.027 \pm 0.038\). Figure 7 shows that both elastomers are quite compressible under

| Shot No. | EPDM fill | \(u_{proj}\) (km/s) | \(\rho_0\) (g/cm\(^3\)) | Expt. type | Impctr. mat. | \(P\) (GPa) | \(u_p\) (km/s) | \(U_S\) (km/s) | \(V\) (cm\(^3\)/g) |
|----------|-----------|---------------------|------------------------|------------|--------------|-------------|--------------|--------------|------------------|
| 1s-1522  | Kevlar    | 0.186               | 0.923                  | Gauge      | Al\(_2\)O\(_3\) | 0.33        | 0.180        | 2.00         | 0.9764           |
| 1s-1466  | Kevlar    | 0.385               | 0.923                  | Gauge      | Al\(_2\)O\(_3\) | 0.83        | 0.372        | 2.40         | 0.9159           |
| 2s-433   | Kevlar    | 1.990               | 0.913                  | Gauge      | Kel-F81      | 4.86        | 1.250        | 4.26         | 0.7067           |
| 2s-432   | Kevlar    | 2.878               | 0.921                  | FS         | EPDM         | 11.82       | 2.148        | 5.98         | 0.6957           |
| 1s-1521  | Silica    | 0.186               | 1.041                  | Gauge      | Al\(_2\)O\(_3\) | 0.40        | 0.179        | 2.13         | 0.8796           |
| 1s-1472  | Silica    | 0.377               | 1.031                  | Gauge      | Al\(_2\)O\(_3\) | 0.94        | 0.359        | 2.53         | 0.8327           |
| 2s-434   | Silica    | 2.524               | 1.061                  | Gauge      | Kel-F81      | 7.53        | 1.530        | 4.64         | 0.6315           |
| 2s-443   | Silica    | 3.066               | 1.033                  | FS         | EPDM         | 13.78       | 2.233        | 5.98         | 0.6065           |

Figure 6. New Hugoniot data and linear fits for silica and Kevlar-filled EPDM rubbers in the \(U_S - u_p\) plane. Also shown for comparison is the Hugoniot locus for adiprene rubber, \(\rho_0 = 1.094\) g/cm\(^3\).

Figure 7. New Hugoniot data for silica- and Kevlar-filled EPDM rubbers in the \(P - V/V_0\) plane.
dynamic compression with volumetric compressions of $\sim 10 - 15\%$ below 1 GPa and nearly 35\% at 12 - 14 GPa. Because adiprene rubber, $\rho_0 = 1.094$ g/cm$^3$, has similar $U_S - u_p$ characteristics (figure 6) its compressibility should also be similar.

The measured particle velocity wave profiles in the Kevlar-filled EPDM also showed structure, ripples. We presume that these are due to the shocks propagating over the Kevlar filler particles. Also, at low shock input stresses, transmitted shock waves in both materials had rounding on the front of the wave. This low-pressure wave front rounding behavior is consistent with a viscoelastic response observed in other polymers [7]. The rounding in particle velocity at the top of the shock front is due to shocking first to an “instantaneous” state on a “stiffer” Hugoniot, followed by viscoelastic relaxation to an “equilibrium” condition.

4. Conclusions
New Hugoniot data for two different filled EPDM rubbers are presented up to nearly 15 GPa. Similar to adiprene rubber, the two materials were found to be quite compressible under modest shock pressures. For example, compression ratios, $V/V_0$ of 0.85 - 0.9 (or compressions, $1 - V/V_0$, of 10 - 15\%) are observed at shock pressures below 1 GPa. At 12 - 14 GPa, the rubbers are compressed $\sim 35\%$. The compressions of the two rubbers are not appreciably different in the $P - V/V_0$ plane.

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