Shock Waves (1995) 4:325–329

Shock Waves

Influence of glass microballoons size on the detonation of nitromethane based mixtures

H.N. Presles[1], P. Vidal[1], J.C. Gois[1], B.A. Khasainov[2], B.S. Ermolaev[2]

[1]Laboratoire d'Energétique et de Détonique, URA 193 CNRS, ENSMA, F-86034 Poitiers, France
[2]Institute of Chemical Physics, Academy of Sciences of Russia, Kossygin street 4, Moscow 117334, Russia

Received August 1, 1993 / Accepted November 16, 1994

Abstract. Detonation velocities and critical diameters of nitromethane (NM) based explosive mixtures sensitized by glass microballoons (GMBs) were measured. The control parameters of this experimental study were the nature and diameter of the confinement, the GMB size and their mass fraction.

As GMB mass fraction is increased, the diameter effect curves (detonation velocity versus reciprocal charge diameter) become less and less dependent upon the confinement nature and size. Furthermore the shape of these curves, which for low concentration of GMBs is concave downward like that of heterogeneous explosive, tends to be straight like that of homogeneous explosives for larger GMB mass fractions.

The critical diameter is found to be strongly dependent on GMB size and mass fraction. The mechanism of NM sensitization by GMBs is qualitatively analyzed and estimations of the effect of GMB concentration and size on the critical diameter of the mixtures agree with the experimental results.

Key words: Detonation, Critical diameter, Nitromethane, Sensitization, Microballoon

1. Introduction

During last decade glass microballoons (GMBs) were used extensively as sensitizing additives for emulsion explosives (Lee and Persson 1990; Hattory et al. 1982; Yoshida et al. 1985). From fundamental point of view, GMBs provide an interesting possibility to create well controlled spherical inhomogeneities in high explosives (HE) because the GMB mass fraction and diameter can be easily specified. Hence one can obtain quantitative informations on the dependence of detonation performance and sensitivity upon the characteristics of the inhomogeneities and shed light on the mechanism of detonation in heterogeneous explosives and particularly the diameter effect and critical diameter problems.

A few years ago we studied the influence of GMB concentration (with wide GMB size distribution: 5 to 180 μm) on steady detonation performance of NM-PMMA (polymethylmetacrylate)-GMB mixtures (Presles et al. 1989). In a following paper (Gois et al. 1991) experimental results demonstrated how various aspects of the steady state detonation process in this system are influenced by GMBs with diameter in the range 37–50 μm (mean diameter 43.2 μm). For instance the detonation behavior of these mixtures, according to the shape of their diameter-effect-curve (detonation velocity vs reciprocal charge diameter) and their critical diameter, is strongly dependent on the confinement as well as the GMB concentration.

This paper extends our data base with GMB size of 43.2 μm. We also performed similar experiments with two other well-defined GMB sizes (74.4 and 101.9 μm). A complicated relationship between charge diameter effect and confinement strength (steel and plastic) is obtained and the critical detonation diameter is observed to be strongly dependent on GMB size and mass fraction.

These dependencies are explained on the basis of simple considerations of local chemical reaction initiation and growth at the vicinity of GMBs. As a result a "universal" linear dependence of critical diameter ϕ_c versus l_p^3/d_o^2 is predicted which agrees reasonably well with our experimental data (l_p is the distance between the center of two particles considering they are distributed in a cubic set and d_o is the mean GMB size).

2. Experimental conditions

2.1. Mixtures

GMBs supplied by Minnesota Mining and Manufacturing (N. C15-250) were sieved into 12 sizes. We used those of mean size 43.2, 74.4 and 101.9 to prepare our mixtures.These GMBs had a wall thickness of about 1 μm. To obtain stable mixtures with NM it was necessary to increase its viscosity by dilution of 4% (mass fraction) of PMMA.

A particular NM-PMMA-GMB mixture was defined by the mass fraction X of GMBs. Table 1 lists the measured initial density of the mixtures, and the GMB mass and volume fractions. It is important to note that for volume fractions exceeding 40–45% air voids are formed during the preparation of the mixtures.

Correspondence to: H.N. Presles

Table 1. Characteristics of the initial state of the NM-PMMA-GMB mixtures and critical diameter

GMB size (μm)	X (%)	Volume fraction (%)	Density (g/cm^3)	l_p (μm)	ϕ_c (mm)
	0.25	1.36	1.129	145.6	24.5 ± 1.5
	0.4	2.11	1.122	135.9	19 ± 1
	1.0	4.20	1.104	100.1	9 ± 1
43.2	2.0	10.83	1.037	73	5.2 ± 0.2
	3.0	14.46	1.004	66.3	3.3 ± 0.2
	4.36	19.16	0.961	60.4	2 ± 0.5
	6.5	23.83	0.921	56.1	1.6 ± 0.1
	10.0	28.22	0.901	53.1	1.4 ± 0.1
	0.35	3.63	1.104	180.9	18.9 ± 0.9
	0.5	4.55	1.095	167.8	13.3 ± 1.3
74.4	2.0	20.00	0.93	102.4	3.1 ± 0.2
	5.0	38.7	0.733	82.3	2.3 ± 0.2
	0.25	3.89	1.1	242	23 ± 2
	0.5	6.90	1.068	200.1	13.5 ± 1.5
101.9	1.44	17.89	0.95	145.7	4 ± 1
	2.7	27.72	0.846	125.9	2.7 ± 0.3
	5.0	44.73	0.661	107.4	2.5 ± 0.4
	8.0	60.06	0.485		3.1 ± 0.2

The right column of Table 1 displays the critical detonation diameter of the mixtures confined in plastic tubes, these data will be discussed below.

2.2. Detonation tubes

We used two kinds of confinement, steel tubes and PMMA tubes. The inner diameter ϕ of the tubes ranged from 1.5 to 30 mm. The wall thickness of the steel tube was always 2 mm and that of PMMA tubes was between 2 and 3 mm.

The tubes were equipped with three ionization coaxial gauges located every 10 cm (accuracy ± 0.05 mm). The distance between the plane of initiation and the first probe was equal to 10 times the charge diameter. Electrical impulses delivered by the gauges were used to trigger an electronic counter (Thomson 632 M 32, accuracy ± 1 ns). A booster made of a plastic explosive was used to initiate the detonation of the mixtures.

3. Experimental results

3.1. Detonation velocity

The amount of the mixture necessary to fill a detonation tube was prepared for each experiment and stirred slowly until it was injected in the tube. The charge was then fired in less than five minutes to keep the GMB distribution in the mixture uniform. The experiments were performed at an initial temperature of 6 ± 2°C.

The experimental results on Figs. 1 and 2 show the relationship between the detonation velocity of the mixtures and the reciprocal charge diameter (one figure per GMB size, respectively 43.2 and 74.4 μm).

Figure 3 shows the same relationship for GMB size of 101.9 μm (X = 1.44%) and also two sets of curves for mixtures of nearly the same density (0.965 g/cm^3) with GMB size of 43.2 μm (X = 4.36%) and 74.4 μm (X = 2%).

Since the nature of the confinement is a very important parameter, we will discuss these results according to the nature of the detonation tube.

3.1.1. Steel confinement

Most of the experimental data have been obtained with GMB size of 43.2 μm (Fig. 1). Their mass fraction X ranges from 1 to 6.5%.

The diameter effect curves are linear on a large range of diameter. Their concave part which is characteristic of heterogeneous explosives is obtained on a narrow diameter range: for instance for X = 2 this range is between 1.6 and 2 mm.

As X increases the slope of the linear part decreases and the velocity deficit corresponding to the concave part of the curves also decreases. Thus, when the distance between GMBs decreases, the detonation velocity becomes less and less sensitive to the charge size. With X = 6.5% the curve is nearly linear so that very heterogeneous explosives seems to behave as homogeneous ones with respect to their diameter effect curve.

Results obtained with the two other GMB sizes (74.4 and 101.9 μm, Figs. 2 and 3 respectively) show the same trends.

Figure 3 shows detonation velocities for mixtures with nearly the same density. Both the detonation velocity D_∞ (detonation velocity for charges with an "infinite diameter" obtained by extrapolating the diameter effect curves backward to the detonation velocity axis where $\phi = \infty$) and the slope of the curves decrease with increasing the number of GMBs per unit volume, i.e. when GMB size decreases. For a given confinement, the curves intersect approximately at the same point, so that the mixtures have the same detonation velocity for a particular charge diameter. For bigger charge diameters an increase of GMB size leads to an increase of the detonation velocity, the opposite is obtained for smaller diameters. These results point out the complexity of the interaction of the detonation wave and the confinement.

3.1.2. PMMA confinement

Five diameter effect curves are shown in Fig. 1 for mixtures confined in PMMA tubes with GMB size of 43.2 μm and values of X varying from 1 to 6.5%. Up to X = 4.36% the curves are concave downward and thus characteristic of heterogeneous explosives. This trend disappears as X increases and the diameter effect curve for X = 6.5% is linear up to its critical diameter ($1.5 < \phi_{cX=6.5} < 1.7$ mm).

The increase of GMB concentration leads to a decrease of the interparticle distance. A larger number of hot-spots increases the energy release rate, so that the diameter effect curves become less and less sensitive to the charge diameter.

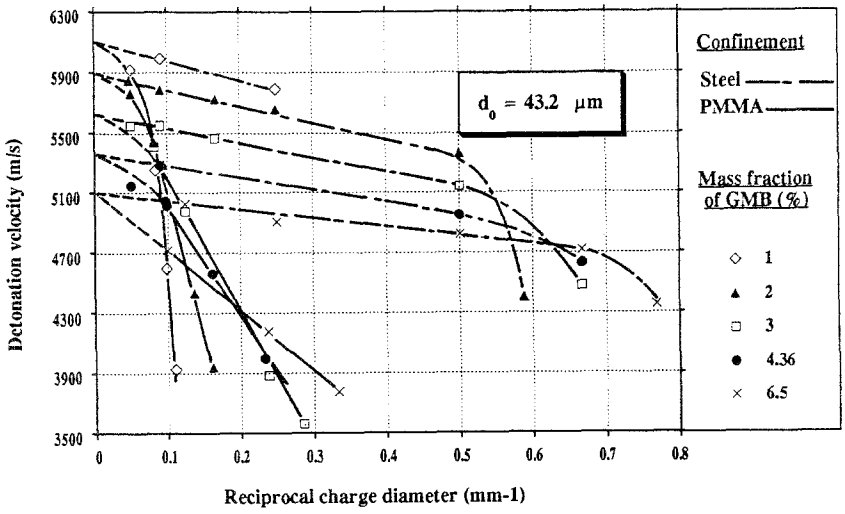

Fig. 1. Detonation velocity vs reciprocal charge diameter for GMB size of 43.2 μm

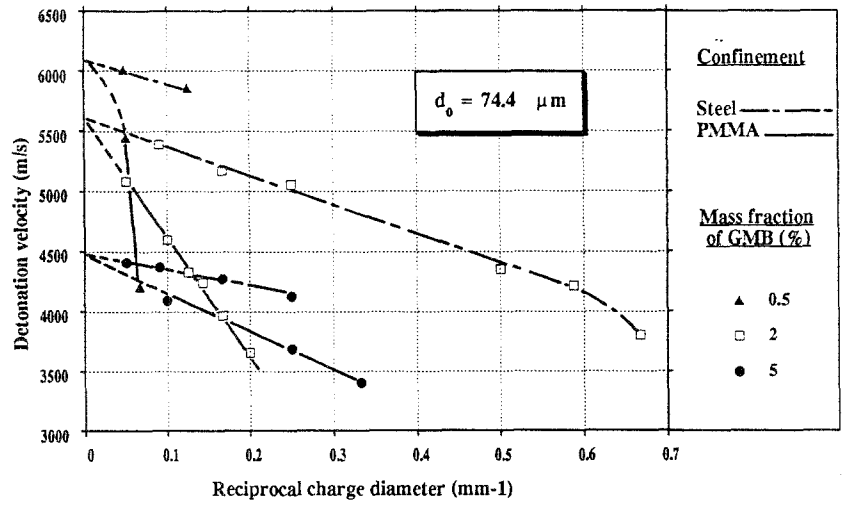

Fig. 2. Detonation velocity vs reciprocal charge diameter for GMB size of 74.4 μm

Similar curves on Fig. 2 obtained with GMB size of 74.4 μm show the same trends.

Another interesting property can be deduced from this figure. When X increases the slope of the curves obtained with mixtures confined in PMMA tube decreases faster than those obtained with steel tube; this demonstrates that the velocity curves becomes less and less sensitive to the nature of the confinement.

When GMB size decreases the smallest mass fraction X leading to a linear curve increases. For instance with GMB size of 101.9, 74.4 and 43.2 μm, X is respectively 1.44, 2 and 6.5% and the interparticle distance 145.7, 102.4 and 60.4 μm. Note that these mixtures have about the same volume fraction of GMBs: 17.9, 20 and 19.16%. Consequently, the shape of the curve depends both on the interparticle distance and the GMB size. These features clearly indicate that these parameters have to be taken into account in a model intending to explain the influence of GMBs on the detonation characteristics of these explosive mixtures.

3.2. Critical diameter

We extended our previous results on critical diameter of NM-PMMA-GMB mixtures confined in PMMA tubes in two ways:

- we studied a larger range of X ($0.25 \leq X \leq 10\%$) with GMB size of 43.2 μm.
- we studied the influence of GMB size using GMBs of 74.4 and 101.9 μm.

Figure 4 shows the critical diameter of the mixtures (confined in plastic tubes) with respect to their density for the different GMB diameters. One can see that there are two different branches of the ϕ_c dependence versus density: (i) at moderate densities the minimum critical detonation diameter seems nearly the same (2 to 3 mm) whatever the GMB size and (ii) ϕ_c increases rapidly when density approaches the theoretical maximum density of the base explosive mixture, i.e. when GMB volume fraction decreases to zero.

At first glance, Fig. 4 shows that GMB parameters affect only slightly the critical diameter. However this impression is due to a very strong dependence of ϕ_c on the initial density for relatively large values of this parameter. The same data are replotted on Fig. 5 versus GMB spacing l_p. One can see that the higher the GMB spacing the higher the critical diameter, these dependencies being very strong. Moreover, for a given l_p, increase in the GMB size results in a strong decrease of critical diameter. However we can see from Figs. 1–3 that with plastic confinement the critical velocity is about 3500 m/s, thus

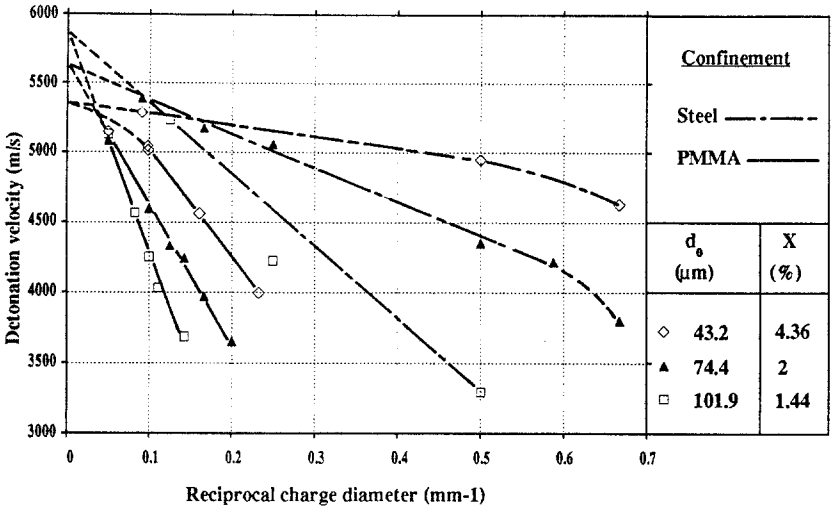

Fig. 3. Detonation velocity vs reciprocal charge diameter for mixtures with density around 0.95 g/cm^3

practically independent of charge density, GMB mass fraction and size. In the case of steel tubes this critical velocity can hardly be measured due to extremely small critical diameters ($\phi_c < 1.5$ mm for GMB size of 43.2 μm and $X > 3\%$).

3.3. *Comments on critical Diameter*

Strong dependence of critical diameters on GMB spacing shown on Fig. 5 is the main feature of our experiments and we believe it is related to the mechanism of detonation chemical reaction. Here we attempt to explain this very strong effect using results of modeling of hot spot formation during GMB collapse behind a shock front (Khasainov et al. 1993). Results of this analysis elucidate the details of a mechanism of hot spot formation during GMB collapse. Namely a local chemical reaction behind the detonation front would be initiated in a thin layer of high explosive surrounding the GMB while main part of the HE is still cold.

Computed dependencies of ignition delays on pressure may be approximated as $t_{\text{ign}} \approx 1/(P - P_{\text{crit}})^n$ with n about 2–3 and P_{crit} about 10–30 kbar depending on governing parameters. At $P > 50$ kbar t_{ign} would be essentially less than 1 μs. The subsequent evolution of the chemical reaction might proceed as a burning wave. Therefore, the distance l_p between neighboring GMBs is an important parameter for the detonation propagation limits.

Let us introduce a few assumptions. First, we neglect the ignition delay in comparison with the characteristic time of reaction heat liberation, though it is worth noting that at shock pressure of about 40–45 kbar, which corresponds to the critical detonation velocity ≈ 3500 m/s, t_{ign} can be of the order of 1 μsec (Khasainov et al. 1993). Second, it was shown by computation results (Leiper and Cooper 1989) that "the critical diameter of heterogeneous explosives scales with the chemical reaction rate", in particular, fast reactions give small diameters and vice versa. Third, the dependence of this reaction rate on shock pressure may be discarded, because critical detonation velocity (and, hence, shock pressure) is practically independent of GMB spacing, l_p, and size, d_o, as is mentioned above. Consequently, the chemical reaction rate is proportional to the

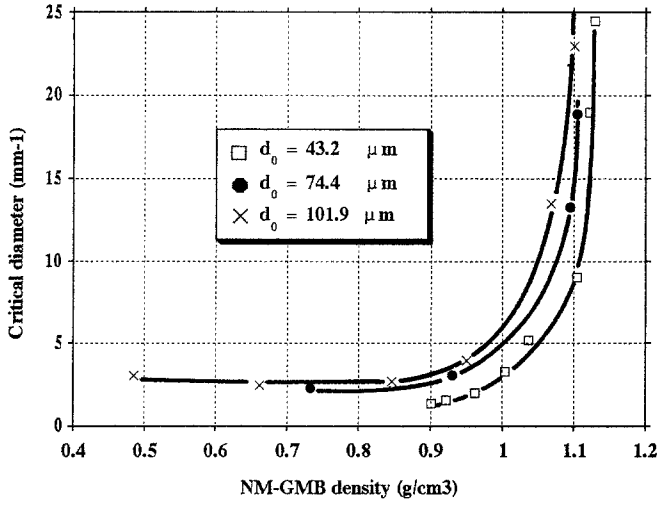

Fig. 4. Critical diameter vs charge density

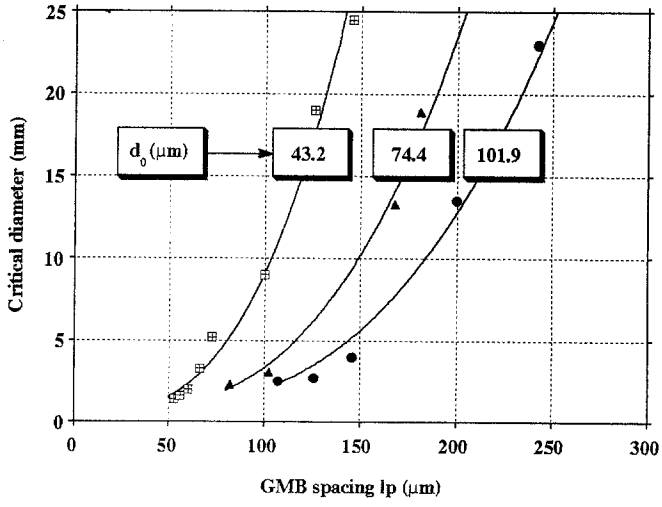

Fig. 5. Critical diameter vs GMB spacing for different GMB sizes

total surface of ignited hot spots per unit volume, so that the critical diameter ϕ_c is inversely proportional to the product of the number N of GMBs per unit volume and GMB surface.

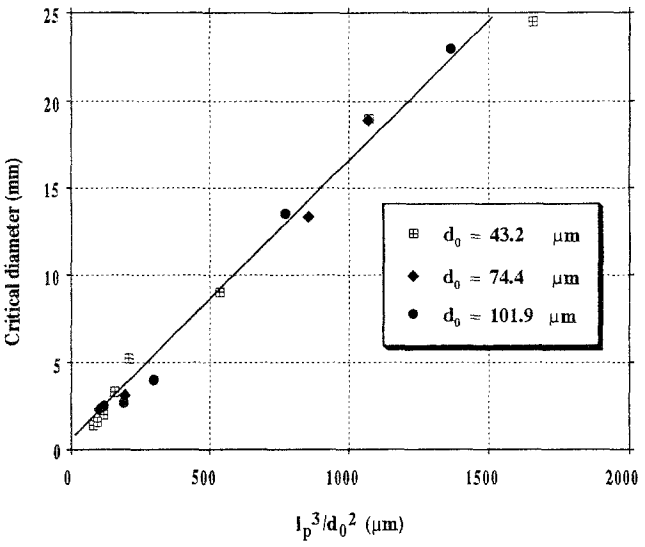

Fig. 6. Universal correlation between critical diameter and GMB parameters

Taking into account that N is inversely proportional to l_p^3, we arrive at

$$\phi_c \sim (Nd_o^2)^{-1} \sim (d_o^2/l_p^3)^{-1} \sim l_p^3/d_o^2 \,. \tag{1}$$

Experimental critical diameters shown on Fig. 5 (note that l_p is indicated in Table 1) are replotted against l_p^3/d_o^2 on Fig. 6 (points with GMB volume fraction $>$ 44% were not taken into account). One can see that experimental points for all three GMB sizes agree reasonably well according to this "universal" plot. Experimental points can be approximated by the linear dependence

$$\phi_c = 0.464 + 0.0159 l_p^3/d_o^2 \tag{2}$$

where l_p and d_o are measured in μm and ϕ_c in mm with correlation coefficient 0.992. This correlation is quite close to the theoretically predicted dependence (1).

4. Conclusions

The detonation velocity and the failure diameter of nitromethane based explosives sensitized by glass microballoons (GMBs) were studied for two kinds of charge confinement (plastic and steel) and three well defined GMB sizes (43.3, 74.4 and 101.9 μm). GMB mass fraction was varied from 1% to about 10%.

Complicated relationships between the detonation velocity and the charge diameter were obtained whatever the confinement nature. The shape of the diameter effect curves which for low concentration of GMB is characteristic of heterogeneous explosives tends to that of homogeneous explosives when glass microballoons concentration increases. At the same time these curves become less and less dependent on the confinement nature and the charge diameter. Once an initial density and a confinement are specified, the influence of GMB size on the detonation velocity depends on the charge diameter: for large charge diameters an increase of GMB size leads to an increase of the detonation velocity, and for small ones the opposite trend is observed.

Critical detonation diameters strongly depend on GMB size and mass fraction. These dependencies are explained on the basis of simple physical considerations of local chemical reaction initiation and growth at the vicinity of GMBs. A universal linear dependence of critical diameter ϕ_c versus l_p^3/d_o^2 is predicted which agrees reasonably well with all our experimental results. This correlation indicates that critical diameter is inversely proportional to the specific surface of GMB per unit volume of the heterogeneous mixture.

References

Gois JC, Presles HN, Vidal P (1993) Effect of hollow heterogeneities on nitromethane detonation. Progr Astronautics Aeronautics 153:462–470

Hattory K, Fukatsu J, Sakai HJ (1982) Effect of the size of glass microballoons on the detonation velocity of emulsion explosives. Ind Explos Soc Japan 43:295–309

Khasainov BA, Ermolaev BS, Presles HN (1993) Shock wave initiation of chemical reaction in liquid high explosives sensitized by glass microballoons. Presented at the Tenth Symposium (International) on Detonation

Lee J, Persson PA (1990) Detonation behavior of emulsion explosives. Propellants Explosives Pyrotechnics 15:208–216

Leiper GA, Cooper J (1989) Reaction rates and the charge diameter effect in heterogeneous explosives. Proc. Ninth Symposium (International) on Detonation OCNR 11 3291–7:197-207

Presles HN, Campos J, Heuzé O, Bauer P (1989) Effects of microballoons concentration on the detonation characteristics of nitromethane - PMMA mixture. Proc Ninth Symposium (International) on Detonation OCNR 11 3291-7:925–929

Yoshida M, Iida M, Tanaka K, Fujiwara S, Kusakabe M, Shino K (1985) Detonation behavior of emulsion explosives containing glass microballoons. Proc. Eighth Symposium (International) on Detonation NSWC MP 86-194:993–1000