Processing Studies of Energetic Materials using Resonant Acoustic Mixing Technology

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ABSTRACT**:**

Resonant Acoustic Mixing (RAM) technology is attracting growing attention as an alternative and improved processing method for energetic materials. This paper describes studies that BAE Systems Land UK has carried out on RAM process parameters and material characterisation, in comparison with conventionally produced compositions.

RAM technology transfers acoustic wave energy to mechanical movement under resonant conditions. The vibration action created can be used to complete various processes, not limited to coating, sieving, and mixing of materials.

Current manufacturing methods within the energetics field can involve large amounts of solvents, long processing times, high waste output, high shear moving parts, and have single large batch limitations. Investigations into the manufacturing of energetic materials (for example, polymer bonded explosives (PBXs), propellants and pyrotechnics) via RAM technology have highlighted many potential advantages. These include shorter time scales, improved mix homogeneity, reduced waste output due to flexibility of load/batch size, and the absence of moving parts (a potential ignition source). In addition, RAM can process higher viscosity products, giving opportunity for the development of new families of energetics.

Land UK has been investigating the ability of RAM to process a range of different energetic materials, including PBXs and Low Vulnerability Ammunition (LOVA) propellant formulations. These studies have involved processing energetic materials using Resodyn's LabRAM and LabRAM II to find suitable manufacturing parameters, then carrying out material analyses to verify material quality. Where possible these data have been compared with those for conventionally produced materials. In addition to physical, chemical, and thermal analysis, in some cases, hazard sensitiveness and performance testing have also been undertaken.

Thus far, trials have indicated that RAM technology produces energetic formulations that are at least equal in quality to materials processed using conventional methods, with RAM presenting the advantages listed above.

Introduction

Various parties, across different industries and research groups, have been investigating the capability of Resodyn's RAM technology [1] to process a wide range of materials, such as pharmaceuticals (e.g. [2]), cement [3], and energetic materials. To date, BAE Systems Land UK have undertaken projects investigating the use of resonant acoustic (RA) technology to process pyrotechnics (including nanothermites), various polymer bonded explosives, and LOVA Propellant. This paper focuses on Land UK's development of a RA-processed PBX; specifically, a programme comparing conventional and RAM processed materials.

The PBX compositions that have been investigated by Land UK are nitramine – RDX (hexogen) or HMX (octogen) – based, with the explosive held within thermally-cured polyurethane (hydroxyl-terminated polybutadiene (HTPB)) binder matrices. This paper discusses a Land UK's proprietary PBX: an aluminised-RDX / HTPB binder based composition – henceforth referred to as Formulation A (Form.A). A LOVA Propellant will also be referenced, in brief. The LOVA here is a nitrocellulose-free composition with an RDX / EVA (ethylene vinyl acetate) binder matrix.

This paper briefly describes the current methods available for manufacturing both PBXs and LOVA, as well as indicating the RAM process parameters that were investigated during the conventional vs. RAM comparison programme. The paper focuses upon analyses that were performed on material samples, stating any differences between the conventional and RAM-prepared materials. Comparisons between physical, chemical, thermal, hazard sensitiveness and performance data, between the two processes has been made. The advantages of the new RAM process have also been highlighted, indicating the key parameters in both processes. Finally, the advantages of RAM-batch vs. RAM-MIC (mix-in-case) methodologies is discussed.

The purpose of the comparison programme reviewed here, was to determine whether there existed any discernible differences between the various material properties of the RAM and conventionally produced energetics. The results will help build a case as to whether it is viable to scale-up RAM manufacture of energetic materials, and thus benefit from the advantages that RAM can introduce.

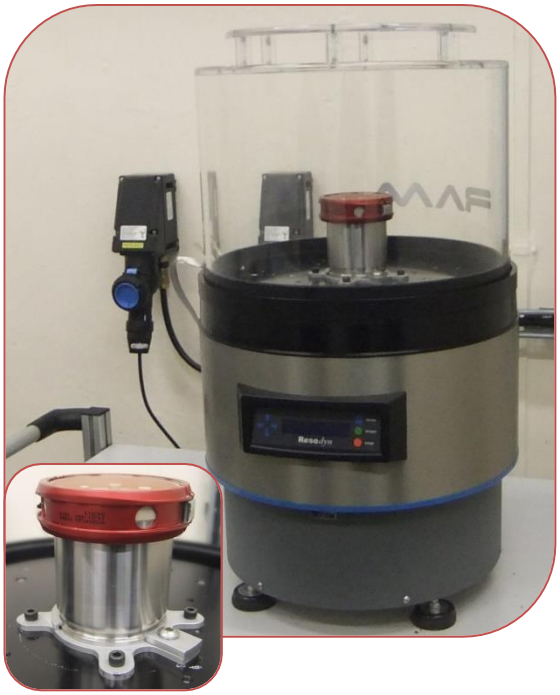


Figure 1: LabRAM at Land UK Glascoed

The Process: Conventional vs. RAM

For both PBXs and LOVA, current manufacturing methods involve bladed mixers, which impart high-shear at localised regions within the mixing vessel. Conversely, RAM processes utilise a low shear action throughout the whole mix vessel.

In terms of processing times, bladed mixers can take 3.5 to 4 hours or few days to complete 5 kg and 1600 kg PBX batches, respectively.

LOVA mixes (6.5 kg or 18 kg) take a minimum of 5 hours to complete, often over two days to allow for extrusion of the propellant at a suitable temperature. These timescales span from the initial loading of material, into the mixing vessel, to mix completion. The filling of vehicles and clean down of equipment have been omitted from mix times. Conventional mixers require materials to be added incrementally, resulting in multiple mix stages, which lengthen the overall time required by the process. In comparison, RA-mixes allow for all materials to be added in a single step, simplifying and shortening the process.

The LabRAM II apparatus has been found to be capable of completing a 1.2 kg batch of PBX in less than 20 minutes, and a sub-kilogram batch of LOVA in 1 hour (approx.). An additional 20 minutes (approx.) was also required to load materials into the mix vessels. On this laboratory scale, the processing times are reduced from conventional methods, however the real benefit of mix duration would be seen on scale-up to the larger RAM 5 (circa 36 kg) and RAM 55 (circa 400 kg) platforms. This is because RA technology is highly scalable, such that the same mix parameters can be applied as the process is scaled-up (i.e. a 20 minute 1 kg batch on LabRAM II, would similarly take circa 20 minutes to mix a 400 kg batch on the RAM 55). This is a significant improvement over the mix times afforded by conventional mixers, which are not scalable in this manner.

The majority of material produced in this comparison trial was processed using a LabRAM apparatus, rather than the LabRAM II. LabRAM II has marked improvements over the LabRAM (e.g. vacuum control and heat control). However, the LabRAM proved more than capable of manufacturing 350 g PBX batches during this work.

The Process: Sample Manufacture

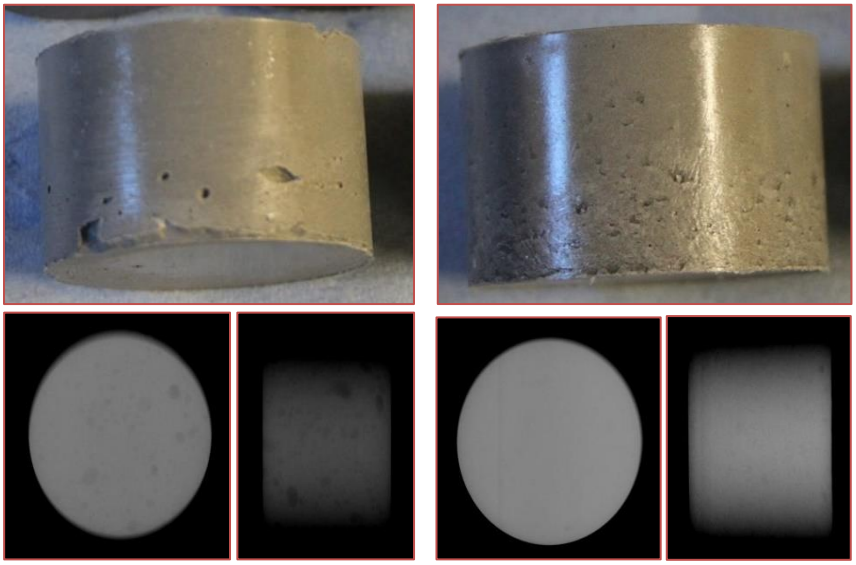
The following sections review the data collected by Land UK during a conventional vs. RAM comparison study conducted on Form.A (an aluminised-RDX/HTPB based composition). The conventional mixer used in the study was a planetary HKV-5 (5 kg batch mixer), capable of processing the PBX in the manner described in the previous section. The RA-mixer used was Resodyn's LabRAM. In both cases, a batch methodology was utilised, meaning that the PBX was processed in a single 'mixing bowl' (vessel), from which the material was then transferred, via vacuum casting or manually filling with suitable utensils, into sample moulds for oven curing.

Due to the relatively new nature of RA technology, RAM process parameters were varied throughout the trial, over a number of mixes, in order to understand which parameters were suitable for manufacturing Form.A. The material properties of the samples manufactured using these different parameters are discussed later and directly compared to the single, conventional method adopted as a baseline in the study. The primary RAM parameters considered during mixing were acceleration level and the duration of the main bulk mix stage. Other factors, such as ingredient layering into the vessel and different mix stages (wetting and de-gassing) were kept constant. To this end, a three stage RA mixing regime was used, incorporating a wetting stage (low G, 2 minutes), a main mix stage (30 to 80 G, 2.5 to 40 minutes) and a degassing stage (low G, 5 minutes). Of these, only the main mix stage was varied.

The sample casting method varied for each method and sample type – see Table 1 for sample types. Samples from the planetary mixer were either manufactured via vacuum

casting directly into the vehicles or manually using utensils. Vacuum casting was used for the larger samples, as the vacuum chamber aids the ability to obtain void-free samples, which were required for some tests (Large Scale Gap Tests (LSGT) and Velocity of Detonation (VoD) trials). Small samples were filled by hand, primarily for simplicity. Small samples consisted of cylinder charges (Metset samples (MS) of 40 mm diameter, 26 mm length) and Dynamic Mechanical Analysis (DMA) casts. Where possible, these samples were subjected to a period of time in a vacuum chamber post-filling, to promote release of any entrained air and improve sample quality.

When manufacturing samples via RAM, all moulds were filled by hand. This was due to the fact that, at the time of the project, no vacuum casting method was available for the RAM vessels. Identical methodologies for small sample manufacture were used for RAM and conventional, planetary samples. However, to aid preparation of the larger LSGT and VoD samples, an incremental piping and vacuum application process was used. Although, not as effective as vacuum casting, this method did enable high-quality samples to be manufactured for use in trials. Figure 2 shows the benefit that post-fill vacuum application has on MS quality, with regards to voids, and the difference in fill quality (sample finish) between vacuum casting and the hand piping method on LSGT tubes. All LSGT and VoD test pieces that were taken to firing trials passed quality control, i.e. no significant internal voids were observed in X-ray images.



Variation in sample quality – not subject to vacuum post fill (L), with vacuum (R)

Figure 2: LSGT Tubes – top of fill for planetary (L) & RAM (R) samples

Comparison of Material Properties

During this material comparison study, chemical, physical, thermal, small scale hazard, and performance tests were carried out on Form.A. Details of the tests are listed in Table 1.

Table 1: Test details – method and sample type

Test	Method	Sample Type
Visual Observations	General visual inspection	All
Chemical Analysis	Multi-stage solvent extraction (BAES In-house method)	Sampling from MSs
Chemical Stability	Vacuum Stability, 40 hours at 120 °C	5g sample (MS)
Thermal Stability	Differential Scanning Calorimetry (DSC), temperature ramp 10 K/min	Sampling from MSs
Glass Transition Temperature (T_g)	Dynamic Mechanical Analysis (DMA)	Sampling from MSs
Density	Liquid displacement	MS
Hardness	Shore A: 30 second dwell	MS
Uniaxial Compression	STANAG 4443	MS
Small Scale Hazard tests (various)	EMTAP Manual [5]	Sampling from MSs
LSGT	EMTAP Test No. 22a [5]	LSGT test pieces [5]
VoD	EMTAP Test No. 47 [5]	1” cylindrical charges

Visual Observations

Visual observations provided a clear indication of whether or not effective mixing action was imparted to the mix sample, when varying RAM parameters. For example, the level of powder (unmixed material) on the RAM vessel walls and lid and/or levels of obvious churning action on the surface of the mix material were seen to correlate with the quality of sample curing, and subsequently the sample hardness.

A well-established planetary mix method for manufacturing Form.A, that is known to produce good quality material, was utilised during this trial. Thus all mixes and final sample quality did not vary significantly in appearance, and all passed visual quality inspection.

Figure 3: Sample showing uncured regions, indicating mix inhomogeneity.

When inspecting a number of cured RAM samples, there were clear signs of uncured material. t_p was identified as the mix duration required for a given acceleration level to return homogenous, high-quality samples. Uncured material was only present in samples manufactured from mix durations of less than half t_p at 55-80 G, or when processing at ≤50 G. An example of a sample produced from such conditions, indicating a degree of inhomogeneity can be seen in Figure 3. It must be stressed that poor quality samples, such as those shown in Figure 3, did not form part of the comparison dataset discussed in following sections.

Chemical & Thermal Analysis

The basic chemical composition (RDX, Aluminium and binder content) and vacuum stability for RAM samples, processed at various acceleration levels (55-80 G), were found to be highly comparable to the planetary prepared samples. Similar comparability was observed for DSC and DMA/T_g profiles, returning data that would be expected for this material, i.e. endo- and exo-therms corresponding to the RDX melting (ca. 203°C) and decomposition (ca. 224°C) points – that are comparable to literature values [6] and a T_g of -86°C (approx.). The similarity, between RAM and planetary material properties, applied across the range (55-80 G) of different RAM parameters investigated (acceleration and duration variations). This was to be expected, due to the low level of mixing achieved even after 2.5 minutes at these accelerations, the consistency of material loading, and the simplicity of the analysis techniques (including relatively small sample size from bulk). Furthermore, no significant deviation from the material specification of Form.A was observed for any of the samples prepared in this comparison study.

Physical & Mechanical Analysis

As with chemical and thermal tests, the densities of the RAM and planetary samples were comparable, with increased consistency when samples were prepared under vacuum, as would be expected. Figure 4 shows this similarity and the variation reduction resulting from the use of vacuum. The X-rays in Figure 2 also illustrate the decrease in voids, due to vacuum application, which supports the density data.

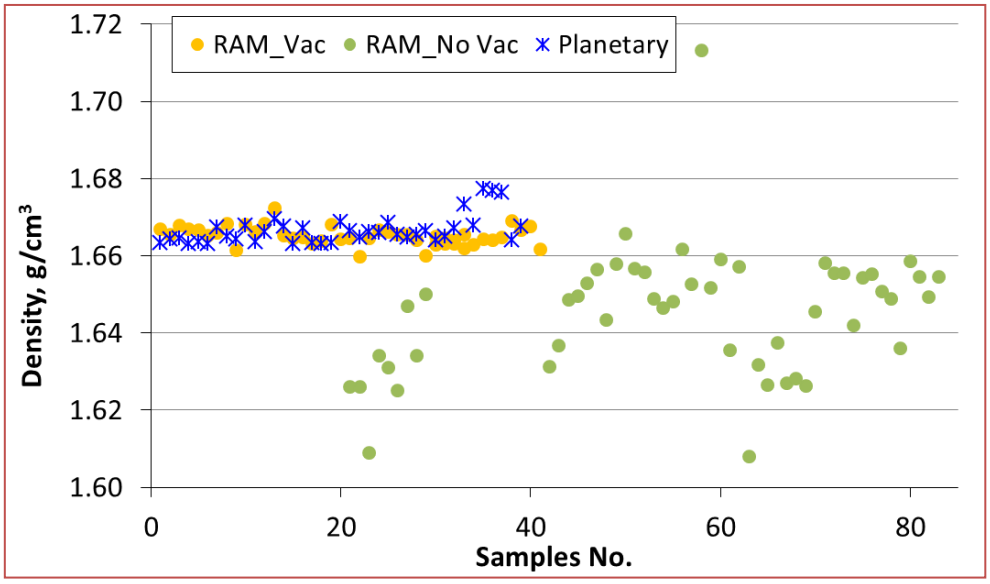


Figure 4: Density comparison – RAM (vacuum & no vacuum application) vs. planetary (vacuum)

Shore A Hardness correlated with the visual observations made during the project. All RAM mixes carried out at ≥ 50 G returned samples that came within the Form.A material specification for hardness. However, the data spread was reduced and values were consistently closer to that of the planetary samples when mixed at ≥ 55 G. Furthermore, hardness generally increased with longer mixing times, up to t_p, but showed signs of overmixing when mixed for 40 minutes, possibly indicating onset of adverse polymerisation due to increased heating experienced in the vessel.

Figure 5(top) shows the improved material hardness characteristics observed when higher accelerations were utilised (greater hardness and increased consistency). Figure 5(bottom) compares the results from a single RAM mix regime (carried out nine times) and two planetary mixes. It demonstrates the repeatability of RAM mixing between batches (with regards to Shore A hardness properties), as well as the variation seen within a batch. The variation shown within a batch was similar to conventional samples, and most likely due to the fact that the Shore A durometer point could be measuring either the binder matrix material (which is relatively soft) or the RDX crystals held within the cross-linked polymer.

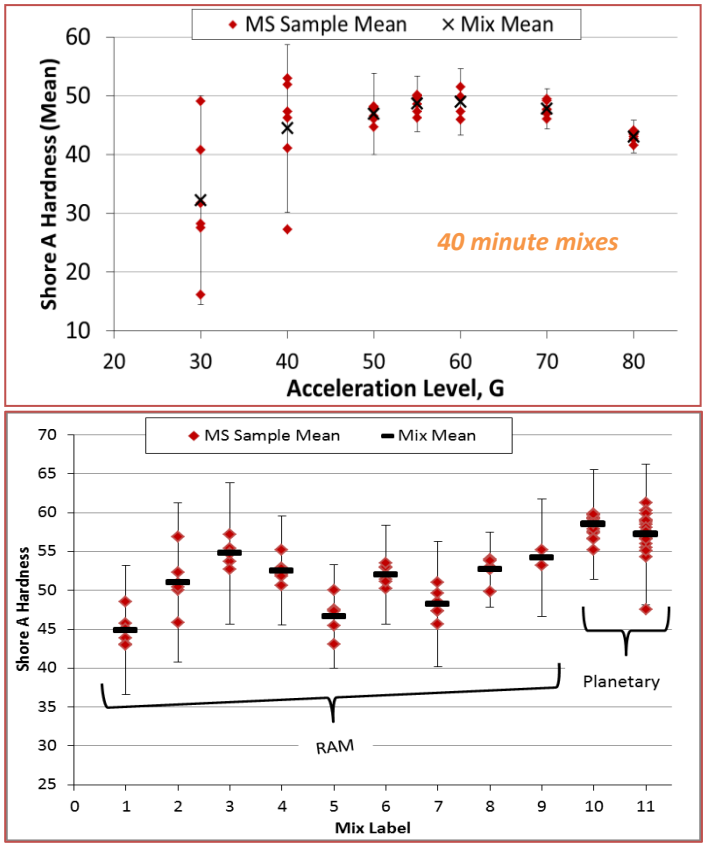


Figure 5: Shore A Hardness data – RAM comparison at different accelerations levels (top), and RAM (60 G) vs. planetary comparison (bottom)

Although not significantly higher, the two planetary batches did return harder samples, which could indicate a difference in how the PBX components are dispersed in the mix, and thus how the polymer matrix is forming. Given the RAM sample harnesses are higher than the minimum requirement for Form.A, this was not considered a detrimental observation, although a point of interest for future investigations.

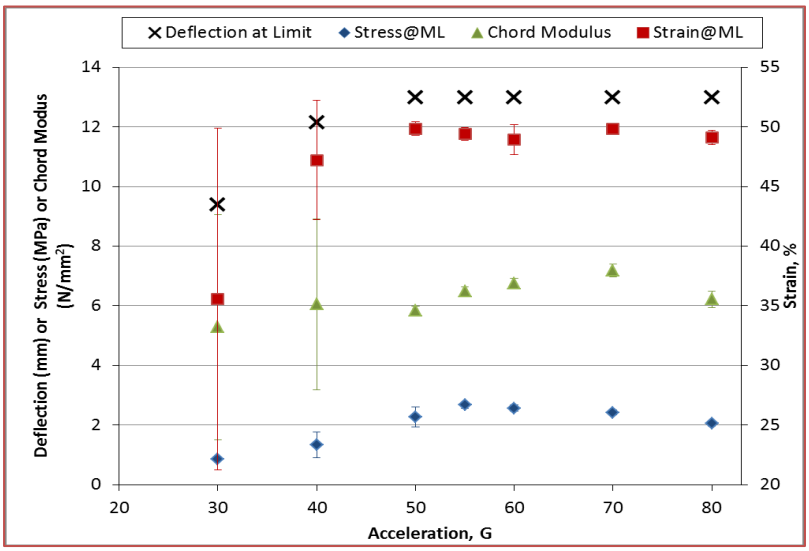


Figure 6: Compressive strength mean mix data; one standard deviation from means is shown

Compressive properties (compressibility and strength) were significantly improved and more consistent when Form.A was processed at > 50 G, for times nearer t_p. This is shown by the mean data points and their associated standard deviations in Figure 6. These data support the Shore A hardness results, and the suspected inability for the RAM action to disperse the mix components (particularly isocyanate) sufficiently at < 50 G. As with Shore A Hardness, the compressive properties appeared to change slightly when mixed for 40 minutes (compared to times up to t_p). The

samples appeared to become less compressible, but slightly stronger, further suggesting a change in how the polymer matrix was formed when submitted to longer periods of agitation and heat.

The graph in Figure 7 shows the variation between the compressive properties of RAM samples (at a single acceleration level and mix duration $t_{p,}$ and for 40 minutes) and planetary samples. The two planetary mixes showed a significant reduction in compressive strain, i.e. the samples failed (fracture) before the 50% compression limit of the test was reached (13 mm deflection limit shown in Figure 7). In comparison, the RAM samples generally reached the compression limit of 13 mm without fracturing. The lower elasticity of the planetary samples is shown by the higher chord modulus (stiffer samples), and resulting failure at lower stresses. These data also support the higher Shore A Hardness measurements of the planetary samples compared to RAM.

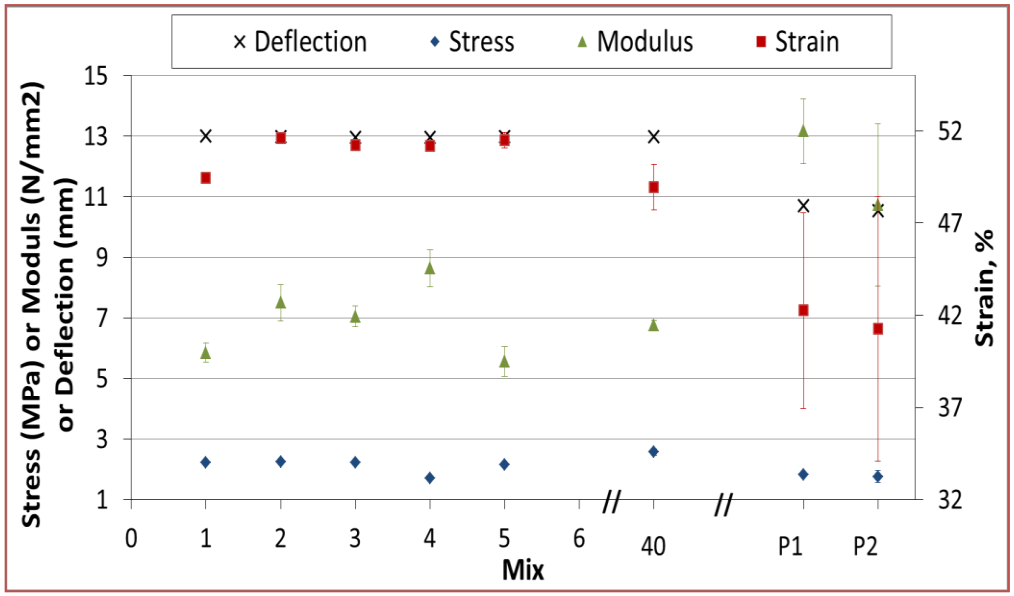


Figure 7: Compressive strength comparison – RAM (60G, t_p and 40 minutes) vs. Planetary

At this stage there is no clear explanation for the observed reduction in the compressibility of planetary samples compared to RAM. However, it could be due to the different methods of mixing; localised high shear verses low shear throughout the mixture, causing the dispersion of the components to differ, including the arrangement of the polymer system. This in turn is likely to alter the way the cross-linking occurs between the polymer chains (spatially as well as the degree of crosslinking), which would be directly related to the material stiffness and compressibility.

Hazard & Performance Testing

A select number of small scale hazard tests were performed on Form.A samples, in accordance with the EMTAP Manual of Tests [5], including Rotter impact (EMTAP 1A) to ascertain the Figure of Insensitiveness (F of I), Temperature of Ignition (T of I) (EMTAP 3), Electric Spark Discharge (EMTAP 6), Ease of Ignition (EMTAP 4) and Train Test (EMTAP 5). The results for these tests are stated in Table 2 along with the LSGT and VoD test results. All performance and hazard data suggested RAM and Planetary mixing produced

material with very similar hazard and performance characteristics. Given there was no difference in formulation, this was an expected outcome.

Table 2: Hazard and performance data

Test	RAM	Planetary
F of I	111	112
T of I	210	214
Electric Spark	Ignitions at 0.45J, No ignitions at 0.045J	
Ease of Ignition	Fails to ignite	
Train Test	Ignites and supports the train steadily throughout	
LSGT, 50% point & Pressure	32.0 mm, 4.4 GPa	29.3 mm, 4.8 GPa
VoD, m/s	7503 ±228	7563 ±145

Advantages & Key process parameters

The data reviewed above indicates that manufacturing PBXs, specifically Form.A, via the conventional planetary bladed mixer or a RAM, does not significantly affect the fundamental properties of the PBX material. However, when assessing the key parameters of the different processes, there are several advantages to the RAM method, which would offer significant benefits when manufacturing at increased scales with large RAM platforms (compared to the LabRAM utilised for this programme of work).

The main difference is mix time. The RAM mix durations that returned a satisfactory Form.A mix, at various accelerations, were 17-32 minutes (including the wetting and degassing stages). In comparison, the required planetary mix duration is 100 minutes, excluding the time required for multiple increment additions compared to the single initial addition step needed for RAM. Although beneficial at this scale, the direct scalability of RAM parameters across the various RAM platforms, means this advantage would be accentuated with the larger quantity batches (e.g. RAM 55 should also be capable of processing 400 kg within circa 30 minutes, compared to the 3 days it can take to process a 1600 kg PBX planetary mix).

To further illustrate the reduced time required to process via RAM, Land UK completed a LOVA propellant mix in approximately one fifth of the time required for the conventional mixing method. Furthermore, due to the excessive duration required, the conventional method is usually carried out over 2 days to allow time to extrude the propellant when the material is still at the ideal temperature. Whereas the shorter RA mix time, allows for extrusion to be completed the same day as mixing. Another potential advantage that was observed during the LOVA trials was the reduced level of solvent that was required for the RAM processing method – this will be assessed further by Land UK in future work.

Flexibility is another limitation for planetary mixers. Currently, mixing in batches (a single bowl vessel) is the only option. Therefore, if significant variation in mix size is required, then different size mixers are generally needed. For example, it would not be advisable to mix <2.5 kg in the 5 kg mixer, as the same level of mixing is not achieved if the mixture level is reduced considerably. Furthermore, the vacuum cast method is not so efficient with a low

vessel fill. Conversely, RAM has the capability to be flexible. Although the size of the RA platform does limit the payload that can be processed, adjustments can be made to vary the payload (up to a maximum). More prudently, a mixing 'bowl' can be replaced by various vehicles (singular, or multiple) to enable mixing-in-case (MIC). MIC, thus results in improved throughput and / or process efficiency when operating at the larger scale.

For PBXs, post-mix processing generally involves vacuum casting the uncured 'slurry' into the required vehicles. For a 1600 kg mixer, this can result in a minimum of 200 kg waste material (if utilising the whole batch), due to pipework and material that cannot be utilised at the vessel base. Although this potentially could be the same for a RAM-batch approach with a similarly large payload, RAM-MIC gives the opportunity for significantly reduced or zero waste.

A conventional (vacuum cast) vs. RAM-batch (vacuum cast) vs. RAM-MIC programme of work was carried out to manufacture small (<500 g) shaped charge warheads (SCs). Table 3 summarises the differences between the main processing parameters required when six-off SCs were manufactured. Where relevant the requirements for one batch or a single MIC SC are also stated. This emphasises the flexibility of RAM, due to the fact there is only one option with the planetary mixer. For example, unless a much smaller planetary mixer was available, a minimum of a 3 kg batch would have been required for a single 320 g SC, with the other parameters remaining constant. Significant waste material would result in such an instance.

Table 3: SC Manufacturing - comparison of methods; 6-off and 1-off (in brackets)

Parameter	**Conventional** (5kg planetary mixer)	**LabRAM II – Batch** (1.1 kg batch was equivalent to 3-off SCs)	**LabRAM II – MIC** (one at a time)
Mix Preparation; ingredient addition	100 mins	40 mins (~20mins per batch)	120 mins (~20mins each)
Total Mix Duration	100 mins	36 mins (18 mins)	102 mins (17mins)
Mix mass for 6-off SC	5 kg	2.2 kg (1.1 kg)	2.1 kg (350 g)
Waste	3.08 kg	280 g (140g)	180g (30 g)
Filling Time	~40 mins	60-80 mins (40 mins)	N/A
Total time	240 mins	156 mins (78 mins)	222 mins (37 mins)
Cleaning	Cleaning of follower plate and vacuum cast vessel attachment, mixing bowl and lid. And general cleaning of room and weighing utensils	Cleaning of follower plate and vacuum cast vessel attachment, mixing bowl and lid. And general cleaning of room and weighing utensils	Cleaning of header and lid. General cleaning of room and weighing utensils

Conclusion

Land UK have carried out a comparison study for manufacturing a proprietary aluminised-RDX / HTPB binder based PBX with both an RA-mixer and a conventional planetary mixer. This programme of work was undertaken primarily to ascertain whether, the materials processed via the two methods produced comparable material with similar material properties. These results could then be used to support a case for the scale-up of RAM manufacture, in which the benefits that the RAM process can provide would be emphasised.

Initially, work was carried out to ascertain which combinations of RAM parameters enabled production of samples of satisfactory quality for material analyses. It was judged that acceleration levels between 55-80 G returned good quality samples. Mix duration, t_p, was identified as the time required for a given acceleration level to return homogenous, high-quality samples, although times >½ t_p were found to be sufficient. Samples produced from these mixes were carried forward for comparison with the planetary samples. Conversely, a single methodology was used for the planetary mixer: a well-established method for this composition, known to produce good quality material.

The sample manufacturing method (filling of vehicles) was found to be reasonably influential on sample quality, in terms of voids. The vacuum cast method currently used with planetary mixers was not available for the RAM method at the time of this programme, so a less effective method of hand filling was utilised. However, it is believed that the quality of the sample preparation method did not significantly alter subsequent material data.

Overall, the material properties, including chemical composition and stability, thermal and physical characterisation, as well as hazard and performance test results, did not show significant variation between the samples manufactured via RAM and planetary methods. The compressive properties of the samples were the characteristic that showed clear differences, namely that RAM samples were more compressible than the planetary samples, with the planetary samples fracturing before the maximum load was applied. The number of planetary mixes carried out was minimal when compared to RA mixes, so it is a recommendation of this work to repeat these tests over a broader range of planetary mixes to verify results. It is not known at the moment why this difference occurred. It is possible that the RAM causes more intimate mixing throughout the mix, which causes the polymer matrix to cross-link differently.

Given the material produced by both methods exhibited no significant differences in their properties, the advantages of RAM would appear to lie in the process parameters. For the comparison trial, the advantages found were (a) mix duration (< 30 mins compared to 100 minutes) and, (b) a single addition step (~20 mins) vs. multiple timely increments (~100 mins total). In addition to these, through the completion of other programmes, Land UK have also found that RAM can potentially reduce solvent requirements in processing (LOVA), as well as providing increased flexibility and significant waste reduction. These advantages, are particularly observed when RAM-MIC is utilised. Furthermore, all advantages would be accentuated if larger RAM platforms were employed, due to the transferability of the RAM parameters across the different scales.

Acknowledgements

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