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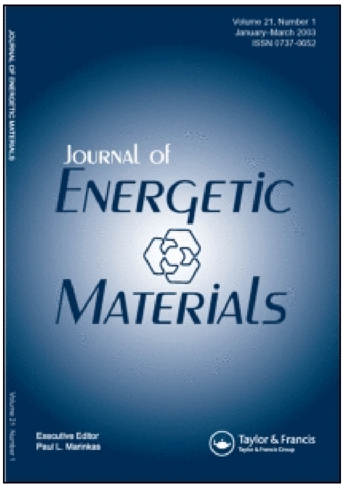

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Mechanical Mocks for Insensitive High Explosives

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Three mechanical mocks were formulated and tested as replacements for the current mock for insensitive explosives LX-17-1 and PBX 9502 because its binder was no longer available. The three polymers evaluated were a butyl/isobutyl acrylate copolymer, ethyl cellulose and a new fluoropolymer, PFR 91. The glass transitions of these polymers were 35, 130, and −10°C, respectively. Two inert fillers, talc and cyanuric acid, were used in the new formulations. Pressing densities and mechanical and thermal properties were used to characterize these mocks. The mock based on the acrylic copolymer most closely emulated these insensitive high explosives.

Keywords: mock, insensitive high explosive, formulation

Introduction

Mock materials for explosives are used when the mechanical, chemical, or thermal properties of an explosive are needed for the fidelity of a test without the hazardous issues associated with the actual explosive. From large-scale flight testing to preliminary evaluation of equipment to be used with explosives, mock materials have served as a means to pinpoint problems prior to processing or fielding live explosives. The requirements for a mock explosive depend on the application. For

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example, when dogs are trained to detect explosives, simulants have been made with sufficiently low concentrations of explosive so that they will not detonate [1]. This allows the dog to become familiar with the actual material without endangering the animal or training personnel. For airport detection, by X-ray, for example, the scattering characteristics of the explosive can be mocked so that training operations can be conducted safely [2,3]. Lawrence Livermore National Laboratory often has applications where emulation of the mechanical properties of an explosive is important.

In the case where the properties of a weapons system are being evaluated, mechanical and thermal characteristics of the mock become very important. Even though the US Department of Energy uses the insensitive high explosives (IHEs), LX-17-1 and PBX 9502, containing 92.5% and 95% triaminotrinitrobenzene (TATB), respectively, in its more modern nuclear weapons, many hi-fidelity, full-system evaluations or field tests require mock explosive materials to minimize assembly or testing hazards. When explosives are pressed into parts, typically a binder is used to reduce sensitivity and provide some strength. Both of these IHEs use Kel-F 800, a copolymer of chlorotrifluoroethylene and vinylidene fluoride, as a binder. The mole ratio of the two monomers is approximately 3 to 1, respectively [4]. Because of cost and environmental concerns, the commercial production of Kel-F 800 has ceased. The limited supply of Kel-F has consequentially impacted the production of the IHE mock RM-03-AC.

Developing a replacement mechanical mock for RX-03-AC that would not use the binder Kel-F 800 became a priority. The mock should behave like LX-17 and PBX 9502 over the stockpile to target sequence temperature range (-54 to 74 °C). Typical compressive strengths of LX-17, PBX-9502, and RM-03-AC at -54, ambient and 74 °C and 0.0001 s^{-1} strain rate are listed in Table 1 [5,6]. The dynamic shear storage (G′) and loss moduli (G″) of LX-17-1, PBX 9502, and RM-03-AC are shown in Figure 1 [7,8]. One of the limitations of RM-03-AC is that its nominal density (1.81 ± 03 g/cc) is somewhat less than the actual explosive so that weights of systems are off. The new mock should have a nominal density similar to LX-17-1 (1.914–1.866 g/cc) and PBX 9502 (1.90–1.89 g/cc) [9].

Typical organic crystals, which have been used in the past as substitutes for explosive crystals, include cyanuric acid, melamine, and pentaerythritol. Because these organic crystals are all lower in density than TATB, talc is used in RM-03-AC to increase the density. Using the same binder in the mock makes emulation of the mechanical

Table 1
Compressive strengths and modulus of PBX-9502, LX-17-1, and RM-03-AC at three temperatures

Temp (°C)	E(comp) GPa	$\sigma(y)$ MPa	$\varepsilon(y)$	$\sigma(b)$ MPa	$\varepsilon(b)$
LX-l7-1					
−50	7.26	40.2	0.02	35.5	0.04
22	6.72	21.5	0.02	19.3	>0.05
50	3.52	11.8	0.02	6.1	>0.05
PBX-9502					
−50	6.54	37.4	0.026	32.4	0.046
24	5.52	22.0	0.022	19.4	0.043
50	3.60	13.7	0.021	10.3	0.045
RM-03-AC					
−50	7.14	—	—	80.4	0.022
24	5.24	34.4	0.026	27.6	0.035
50	2.14	14.8	0.023	10.1	0.037

Note: All measurements were made at 0.0001 s. E(comp) = compressive modulus based on the slope of the stress-strain curve up to 500 microstrain; $\sigma(y)$ = yield stress; $\varepsilon(y)$ = strain at yield; $\sigma(b)$ = stress at break; $\varepsilon(b)$ = strain at break.

properties an easier task since the binder tends to be the continuous phase even at relatively low concentrations, and its transitions are reflected in the mechanical properties of the binder/explosive composite [7,10–12]. Since this is not an option (no Kel-F 800) in the new formulation, the new binder polymer should have a glass transition similar to Kel-F 800 (in the range of 25–35 °C). About 25% of the chlorotrifluoroethylene in Kel-F 800 will crystallize over time, causing plastic bonded explosives (PBXs) made from this binder to stiffen slightly over about a year [4,7,13]. The crystallization behavior cannot be easily simulated with a different binder, but this is a secondary effect.

Table 2 lists binders that were considered based on softening temperatures from [14,15]. Unfortunately, differential scanning calorimetric (DSC) measurements sometimes showed T_gs substantially different than the reported "softening temperature." Since it is well known that cellulosic binders can be plasticized, it might be possible to

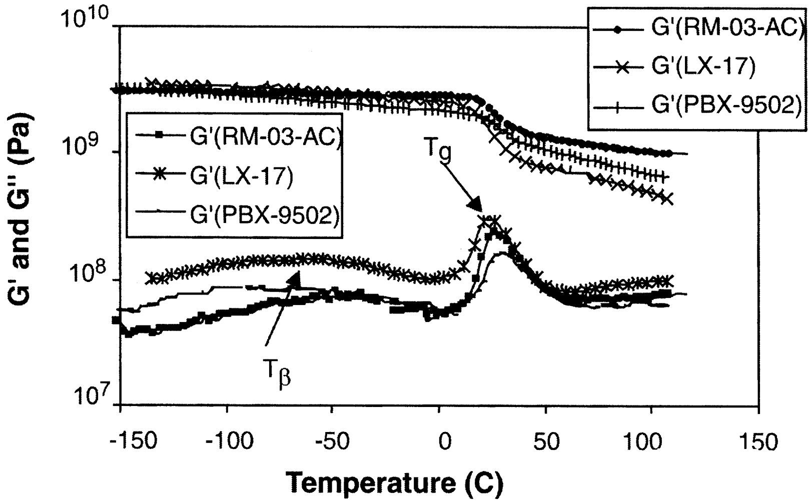

Figure 1. Dynamic mechanical spectra of LX-17-1, PBX-9502, and RM-03-AC show that the shear storage modulus (G′) is quite similar for the explosives and the mock.

formulate a mock with cellulose acetate butyrate and plasticize this material to obtain T_g in the desired range. This binder is plasticized with a eutectic energetic liquid and used by the U.S. Army in their PAX 2A explosive, so it seemed like a reasonable candidate. However, examination of the table showed that ethyl cellulose had the lowest T_g of all the cellulosic polymers, so it was chosen. Ethyl cellulose is commercially available from Dow Chemical Corporation, and Dow kindly supplied us with their Ethocel Standard 10 industrial ethyl cellulose. This polymer is also used as a binder in pharmaceutical and agricultural applications [16], so it looked very promising.

The U.S. Navy uses a polyacrylate binder in PBXN-107, so from Table 2 poly(isobutyl-co-butyl methacrylate) was selected since it has a T_g in the range of interest. This copolymer was purchased from Scientific Polymer Products, Inc. Like most acrylates it is soluble in conventional solvents. Unfortunately it has the lowest density of the polymers considered in this effort. This requires additional talc to compensate for the lower binder densities in mock formulations.

Since eventually there may be a need for replacing the binder in the insensitive explosives, commercially available fluoroelastomers were considered. Commercial suppliers of fluoroelastomers who were

Table 2
Polymers considered as alternate binders for Kel-F 800 in RM-03-AC

Polymer	Density (g/cc)	T_m°C	T_g°C	Mol wt (g/mole)
Kel-F 800	2.02	98	30	60,000
Cellulose acetate butyrate	1.26	235		200,000
Cellulose triacetate	1.31	295		240000
Cellulose tripropionate	1.23		140	
Methyl cellulose			150	86,000
Hydroxypropyl cellulose			130	60,000
Hydroxypropyl methyl cellulose	1.39			86000
Cellulose acetate	1.31	240		
Ethyl cellulose	1.47		43	
Polyethyl methacrylate	1.11		63	350,000
Polyisobutyl MA	1.045		53	260000
Butyl/isobutyl MA copolym	1.09		35	
Hydroxypropyl MA			73	
Lauryl MA	0.929		− 65	250000
Isopropyl MA	1.033		81	3800
N-butyl MA	1.07		15	180,000
Viton GFLT (MVE/HFP/TFE)	1.87		− 24	
Kynar (VF2)	1.82			
Technoflon PFR	2.02			
Dyneon				
Atlas				
Solef	1.78	135	− 30	
Filler				
Talc	2.707			
Cyanuric acid	1.768			129.08

evaluated are listed below with their product line. Dupont Dow Elastomers make the Viton fluoroelastomers, which are copolymers of vinylidene fluoride (VF2) and hexafluoropropene (HFP) and to a lesser extent tetrafluoroethylene (TFE). Atofina makes a wide variety of Kynar resins, which are basically VF2. Solvay also makes a series of VF2 polymers under the trade name Solef. Solvay recently acquired Asimont and the series of Tecnoflon fluoroelastomers Asimont marketed, including copolymers of VF2 and HFP (Technoflon should be similar to Viton) with densities around 1.8 g/cc and terpolymers with similar densities. They also have recently introduced a series of Technoflon perfluorinated polymers with densities of 2.02 g/cc. Daikin makes a series of fluoroelastomers and an interesting thermoplastic elastomer (TPE), but no density or compositional information on these polymers was available. Although 3M has decided to stop marketing Kel-F 800, this company makes a wide variety of fluoroelastomers sold under the trade name Dyneon. Finally Asahi Glass makes Atlas fluoroelastomers based on terpolymers of perfluoroethylene (PFE), propylene, and VF2. These polymers appear to be similar to Viton (FKM) fluoroelastomers marked by Dupont Dow, which are insoluble. The highest density fluoroelastomers in the table were the Technoflons. A preliminary evaluation of Tecnoflon PFR 91 was made in this work.

The target density for new formulations was 1.9 g/cc. Requiring 15% binder fixes the weight fractions of fillers cyanuric acid and talc. Estimates of the theoretical maximum density (TMD) for a formulation were made assuming volume additivity. Then the density of the mix (ρ) is given by

$$\frac{1}{\rho_{TMD}} = \sum_i \frac{\omega_i}{\rho_i}, \tag{1}$$

where ρ_i and ω_i are the densities and weight fraction of the ith component, respectively. To use equation (1), the density of the constituents needs to be known. Anhydrous cyanuric acid density is 2.5, but the dihydrate is the common form. The dihydrate loses water to air, so the exact density is not known. Similarly talc is hydrous magnesium sulfate, and the degree of hydration is not known. The talc used in these experiments was NYTAL-99 Industrial talc (R. T. Vanderbilt Co, lot number S581). Estimates of the densities of talc and cyanuric acid were made from equation (1) using a 50 ml volumetric flask with approximately 25 weight percent of the crystal in a mixture of hexanes. The density of the mixed hexanes was 0.6700 g/cc. The densities obtained in this way for cyanuric acid and talc are listed in Table 2.

Experimental

Formulation

Three different mock formulations were prepared at the 50 g scale by hand mixing of a 15–20% solution of binder with the appropriate

Table 3
Mock composites in weight percentage

Component/mock	RM-03-AC	RM-03-AD	RM-03-AE	RM-03-AF
Kel-F 800	15			
PIBBMA[a]		15		
Ethocel S10			15	
PFR 91[b]				15
Cyanuric acid	60.9	32	38	64
Talc	24.1	53	47	21
Acetone		32.75	30.03 (A)	
Toluene/MeOH			39.98/4.42 (T)	
Ethyl acetate			30.0 (EA)	
H-55[c]				34.35
Lacquer concentration		18.87%		18.86%
TMD	1.9695	1.944	2.038	1.944
Measured density	1.810 ± 0.02	1.9028 ± 0.0004	1.9048[d]	1.891 ± 0.011
Percentage TMD	92 ± 1.4	97 ± 1.3	91.2	97.3 ± 0.6

[a] PIBBMA is poly(isobutyl-co-butylmethacrylate).
[b] PFR-91 is a perfluororubber marketed by Asimont.
[c] H-55 is a perfluoronated liquid manufactured by Asimont.
[d] Density when pressed near $T_g = 130\,^\circ\text{C}$.

amount of solids. Table 3 lists the formulation compositions and solvents used. Cyanuric acid from Elf-Atochem was ground for several minutes a mortar and pestle to remove aggregate crystals. NYTAL-99 industrial talc from R. T. Vanderbilt Co., was used as received. Solids to make 50 g were added and mixed by hand in a 250 ml beaker or in a 1 l polypropylene jar for 5 minutes on a paint shaker. This mixture was poured into Teflon dishes and dried at ambient or elevated temperature as needed. Complete drying was estimated when no weight change was observed in the mix after 1 hour. The Teflon dishes were scraped down and the mock was recovered. Larger chunks were ground down to approximately 3 mm in a mortar and pestle. Cylinders were pressed in a Black Hawk press in a single ram die without vacuum at a given temperature at 140 MPa for three 3 minute dwells with 30 s at zero pressure between dwells. DMA samples were cold pressed at 7 MPa initially to increase the length of the sample to 1.5 inches or more.

Table 4
Compressive strengths and modulus of the replacement mocks at three temperatures

Temp (°C)	E(comp) (GPa)	$\sigma(y)$ (MPa)	$\varepsilon(y)$	$\sigma(b)$ (MPa)	$\varepsilon(b)$
RM-03-AD					
−54	8.63	—	—	86.2	0.02
25	6.26	41.3	0.04	40	0.05
74	0.166	2.4	0.05	–	–
RM-03-AE					
− 23 (A)	3.39	23.0	0.015	20.7	0.017
23 (EA)	2.48	20.0	0.015	20.7	0.017
23 (T)	2.89	23.0	0.015	17.2	0.016
23 (T HD)	4.34	40.5	0.017	40.0	0.018
RM-03-AF					
− 54	6.29	51.1	0.028	38.7	0.038
25	0.745	10.1	0.022	2.0	0.027
74	0.45	8.41	0.023	8.33	0.024

Note: All measurements were made at strain rates of 0.0001 s^{-1}. E(comp) = compressive modulus based on the slope of the stress-strain curve up to 500 microstrain; $\sigma(y)$ = yield stress; $\varepsilon(y)$ = strain at yield; $\sigma(b)$ = stress at break; $\varepsilon(b)$ = strain at break.

Thermal Analysis

The glass transition of the polymers used in these mock formulations was measured on a TA 2632 DSC without modulation at 10 °C/min. DSC traces were run on the powdered polymer and then rerun so that any crystallinity or residual stress from processing would be removed and a clear glass transition temperature could be measured. As an estimate of thermal stability of the mock formulations, DSC measurements were run on this instrument without modulation at 10 °C/min from ambient to approximately 500 °C.

Dynamic Mechanical Analysis

Shear storage (G′) and loss (G″) moduli of cylinders of each mock formulation were measured on a Rheometrics Mechanical Spectrometer model 800 (RMS 800) from −150 to 120 °C at five frequencies using collets to secure the samples into the machine. Specimen diameter was approximately $5 \times 38\,\text{mm}$ or more in length. The RMS 800 software also measured the change in length of the specimen during each dynamic mechanical analysis (DMA) temperature increment so that the linear coefficient of thermal expansion could be estimated. Further description of the RMS 800 is given elsewhere [6].

Static Mechanical Properties

The compressive strength and modulus of cylinders of each mock formulation were measured on an Materials Test System (MTS) hydraulic test machine at a strain rate of 0.0001 s^{-1}. Specimen diameter was $1.27 \times 2.54\,\text{cm}$ in length. The compressive modulus, $E(\text{comp})$, was taken from the slope of the stress-strain curve up to 0.05% strain. Yield stresses, $\sigma(y)$, and strains, $\varepsilon(y)$, were based on the maximum in the stress-strain curve. Stress, $\sigma(b)$, and strain, $\varepsilon(b)$, at break were taken on failure of the mock material. Further operation and description of this test machine have been given elsewhere [5]. Results from these tests are given in Table 4.

Results and Discussion

Formulation

RM-03-AD was prepared by dissolving the poly(isobutyl-co-butyl methacrylate) in acetone to make an 18.87% solution. The solution was not particularly viscous. After drying, approximately 6.255 g of mock was used to press mechanical compression test samples based on a TMD of 1.944 g/cc. The average nominal density of these pressings is given in Table 3. The DMA pressed part gave a density of 1.9206 g/cc. These part densities are excellent considering the pressing pressure and low temperature. Formulation with this acrylic polymer was straightforward and should not present any scale up problems.

RM-03-AE was prepared from three different lacquers based on manufacturer's recommendations [16]. Approximately 20% solutions of ethyl cellulose in acetone, ethyl acetate, and toluene were prepared and stirred overnight in 1 l polyethylene jars. The ratios of cyanuric acid and talc given in Table 3 were added to the viscous solutions of ethyl acetate and acetone, but the toluene solution was too viscous to accept the fillers. Toluene was chosen because it was reported to give good coating characteristics to ethyl cellulose, and so approximately 10 g more of toluene were added. This was allowed to mix overnight, but the solution was still too viscous to accept filler. Dow recommends thinning toluene solutions of ethyl cellulose with

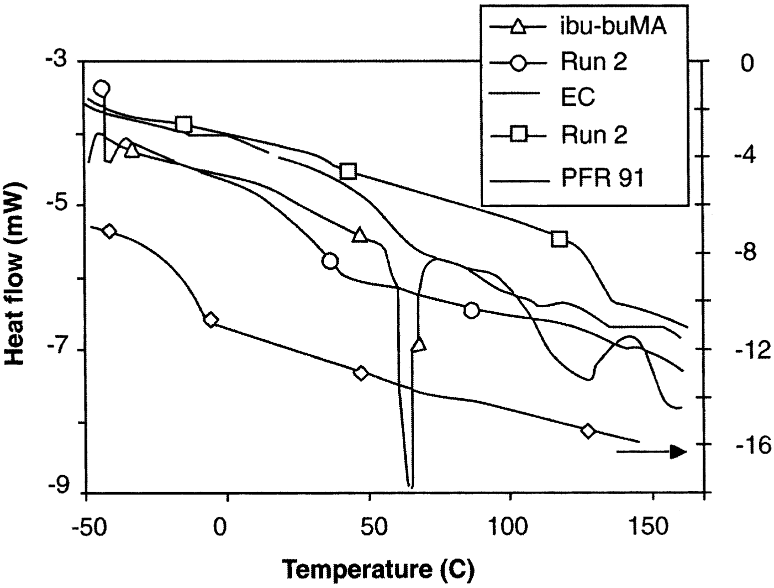

Figure 2. DSC traces of polymer binders used in formulation of RM-03-AD and -AE show glass transitions more clearly in the second run. The T_g of PFR-91 was obtained on the first run.

methanol. When 4.42 g of methanol were added, the solution thinned out nicely, and the solids were added. The jars were sealed and shaken on a paint shaker, poured into Teflon dishes, and dried at 70 °C. Within 5 hr the acetone and ethyl acetate mixes had dried to within 0.1 g of constant weight over 2 hr. The toluene sample, however, was still losing weight and was allowed to dry for another 2 days. The resulting samples were all tough and difficult to grind down to 3 mm pellets. The letters -A, -EA, or -T indicate RM-03-AE samples prepared from different solvents (acetone, ethyl acetate, or toluene, respectively).

None of the RM-03-AE samples pressed well at 55 °C. Compression cylinders made from RM-03-AE-EA had an average density of 1.774 ± 0.009 g/cc. Those made from RM-03-AE-A had average densities of 1.787 ± 0.004 g/cc. TMD for this formulation was 2.038 g/cc, which implies a void volume of about 12.5%. The DSC results on ethyl cellulose are shown in Figure 2. While the first run in the figure shows what appears to be a glass transition at about 60 °C, in the second run the glass transition of ethyl cellulose appears at about 130 °C. When RM-03-AE-T samples were pressed at increasing temperature between 84 and 130 °C, higher densities were obtained as shown in Figure 3. Clearly, as the glass transition is approached from

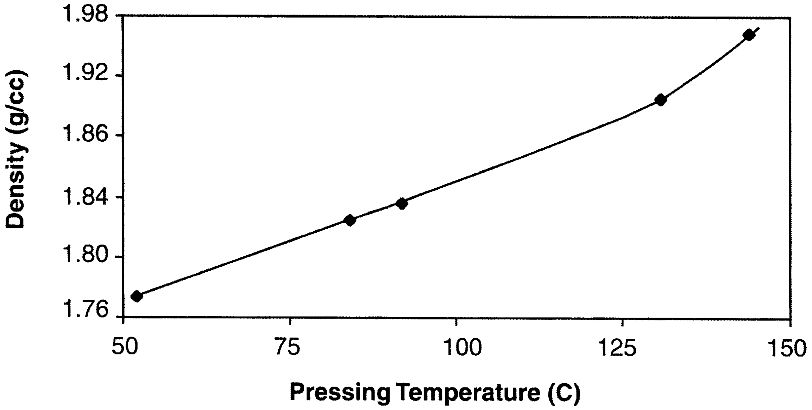

Figure 3. The effect of temperature on the pressing density of RX-03-AE-T shows that as the glass transition is approached the density increases.

below, the pressed density improves. The best density obtained was 1.9048 g/cc or 91.2% TMD when the sample was pressed at ~130 °C.

RM-03-AF was prepared from Technoflon PFR 91. Five fluoropolymers [17] from Asimont (PFR 91, 94, 95HT, 5910 M, and P 459) were tested for solubility in ethyl acetate and acetone (common formulating solvents). All except P 459 were insoluble at both ambient and 50 °C. The perfluorinated tributyl amine produced by 3 M, FC-43, would only swell PFR 91 at 50 °C. Since binder density above 2 g/cc is desirable in IHE formulations [9], a perfluorinated solvent (Galden HT-55 lot # 040600) was used to dissolve Tecnoflon PFR 91[18]. An 18.86% solution of PFR-91 was dissolved overnight at 50 °C in Galden HT-55. The viscosity of this solution was quite high, but talc and cyanuric acid could be added to make a mock of doughy consistency. A lower concentration solution might be needed to enhance mixing and coating at larger scale. The Galden HT-55 was evaporated at ambient overnight and then at 50 °C for 3 hr, with negligible weight change. Samples were pressed at a temperature of 68 ± 3 °C. Densities of these parts averaged 1.891 ± 0.011 g/cc or 97.3% TMD. This density range is excellent. Formulation and pressing processes have not been optimized, but this binder shows promise for IHE formulation.

Characterization

Polymer Binders

During the time when the formulations were made, DSC was used to measure the glass transition temperatures of the binders. The DSC traces for first and second runs of the neat polymers are shown in Figure 2. The copolymer of isobutyl and butyl methacrylate glass transition was, as expected, 32 °C, slightly higher than Kel-F 800 (25 °C). The glass transition of ethyl cellulose was 130 °C on the second run. The first-run discontinuity in heat flow occurred at 62 °C, which would have been promising. This difference may be due to absorption of about 2% water by this polymer. Technoflon PFR 91 had a glass transition of −10 °C.

Mechanical Properties

Figure 4 shows the stress-strain curves of RM-03-AD at −54, 25, and 74 °C. The compressive moduli of this mock were 7.66×10^9, 5.36×10^9 and 8.96×10^8 Pa at −54, 25 and 74 °C, respectively. These values

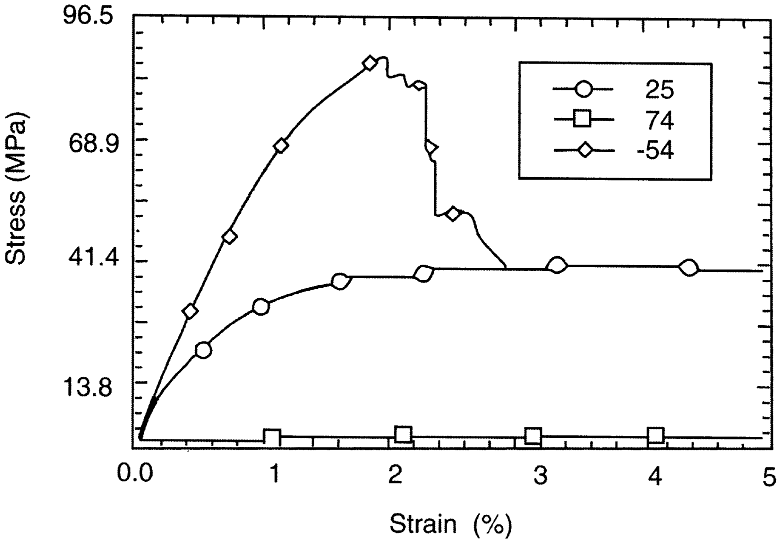

Figure 4. Stress-strain measurements at 0.0001 s^{-1} strain rate for RM-03-AD show brittle-to-ductile behavior with increasing test temperature.

compare well with LX-17 (7.13×10^9, 4.60×10^9 and 3.47×10^8 Pa) at approximately the same temperatures and strain rate) and PBX 9502 except at high temperature, where the acrylic mock is substantially weaker. The RM-03-AD formulation yields at only 2.41 MPa, whereas LX-17-1 yields at almost 3 times this value. Since the RM-03-AE glass transition was higher than expected, resulting in very low densities, only ambient compressive strengths were tested. Formulations made from acetone (RM-03-AE-A), ethyl acetate (RM-03-AE-E), and toluene/methanol (RM-03-AE-T) lacquers but pressed below the T_g of ethyl cellulose all had relatively low densities. The three samples pressed at 50 °C were brittle with poor ultimate properties, as shown in Figure 5. Increasing the pressing temperature to 130 °C with only a single pressing cycle improved the modulus and stress at break at ambient from 2.3 to 3.7 GPa and 20.7 to 40 MPa, respectively. This is consistent with improved density and better binder flow as the pressing temperature approaches the binder glass transition. The stress-strain curves of RM-03-AF at these temperatures are shown in Figure 6. Since the T_g of Tecnoflon PFR 91 is below ambient,

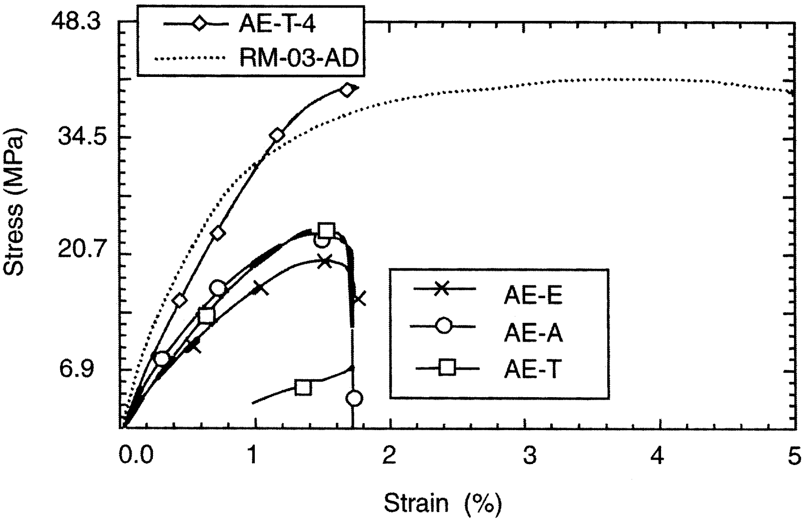

Figure 5. The effect of solvents (E = ethyl acetate, A = acetone, and T = toluene/methanol) on the stress-strain curve for RM-03-AE pressed at 50 °C was small. Pressing above the glass transition for ethyl cellulose increased RM-03-AE compressive strength. See Table 3 for more information.

this mock is much softer than RM-03-AC at ambient. It is interesting to note that there is a slight upswing in the ambient and 74 °C curves, probably indicative of stress crystallization of this polymer. Similar "stress hardening" behavior has been observed in some RM-03-AC samples.

The shear storage (G′) and loss (G″) moduli for the new mocks compared to RX-03-AC are shown in Figure 7. The results are consistent with thermal analysis (DSC) and static stress-strain measurements. Poly(isobutyl-co-butyl methacrylate) in RM-03-AD has a glass transition temperature near that of Kel-F 800 in RM-03-AC, and as a result the shear storage modulus starts to drops off at 38 °C, compared to 26 °C for RM-03-AC. This emulates the dynamic mechanical properties reasonably well when the binders are not identical. However, the drop in modulus when passing through the transition is much more dramatic in RM-03-AD than in RM-03-AC. In linear polymers on passing through the glass transition the modulus reduction is about three orders of magnitude. When no chemical cross-links are

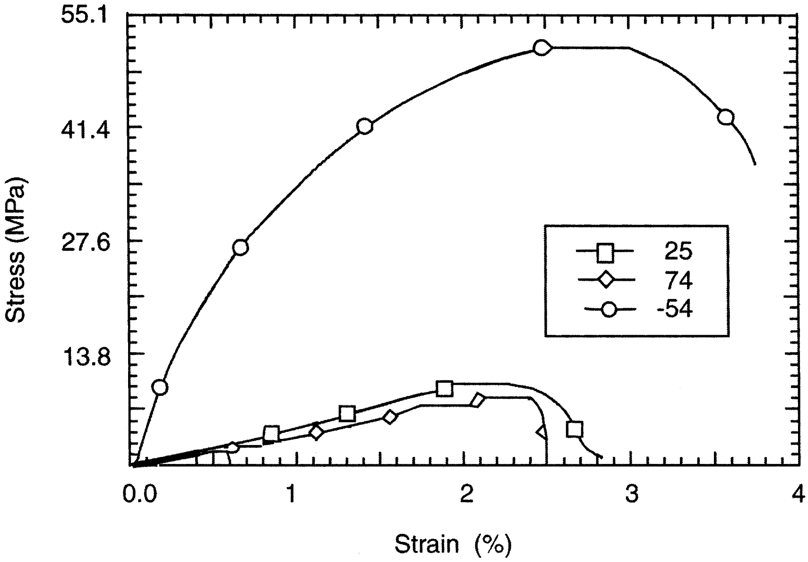

Figure 6. Stress-strain measurements at 0.0001 s^{-1} strain rate for RM-03-AF show the effect of the glass transition at −10 °C.

present and the polymer has sufficiently high molecular weight for entanglements to occur, the modulus of the rubber plateau is on the order of 10^6 Pa. In filled systems the modulus above T_g normally correlates with the concentration of the filler. While these formulations all contain approximately 15% by weight binder, the volume fraction of filler varies between 14.6% for -AF up to 26.8% for -AD, but no consistent trend is observed on this basis either. The reason for the absence of a larger drop-off in shear storage modulus for RM-03-AC at the glass transition is not known. This may be related to interactions between the binder and fillers, or since the density of RM-03-AC was much lower than expected, it may be due to poor dispersion of this binder on the filler particles. It could also correlate with the crystallinity in Kel-F. Additional work is needed to understand the variation in relaxation strengths observed between different binders and mock fillers.

When long time or low-frequency behavior is inconvenient to measure, in some instances modulus measurements can be made over short frequency spans at incremental temperatures and shifted about a reference temperature to cover a much larger time or frequency

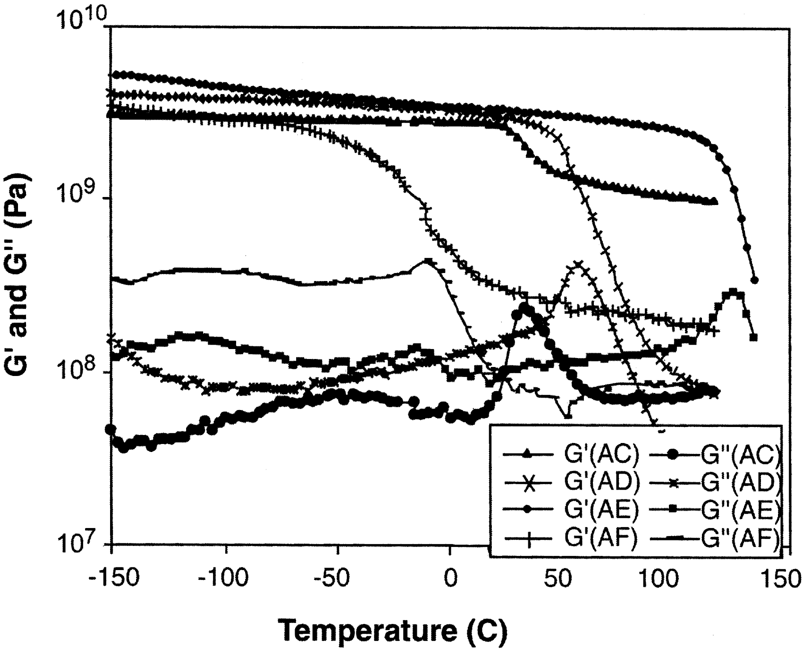

Figure 7. Dynamic mechanical spectra of new mocks compared with RM-03-AC (90024) show many differences.

range [19,20]. For a wide variety of amorphous polymers, the WLF equation has been used for time-temperature superposition of the modulus about the glass transition temperature:

$$\log[a(T)] = \frac{-C_1(T - T_r)}{C_2 + T - T_r}, \qquad (2)$$

where $a(T)$ is the amount a modulus value measurement made at frequency ω and temperature T must be shifted with respect to the reference temperature T_r (usually the glass transition) to produce a continuous modulus curve as a function of frequency. C_1 and C_2 are constants. The Rheometrics Orchestrator time-temperature superposition program was used to calculate the shift factor, $a(T)$, for a set of data. Since shifting data below 35 °C produced discontinuities in the shift factor, data in the temperature range from 36 °C to 100 °C were shifted for RM-03-AD. Similarly for RM-03-AC data were shifted

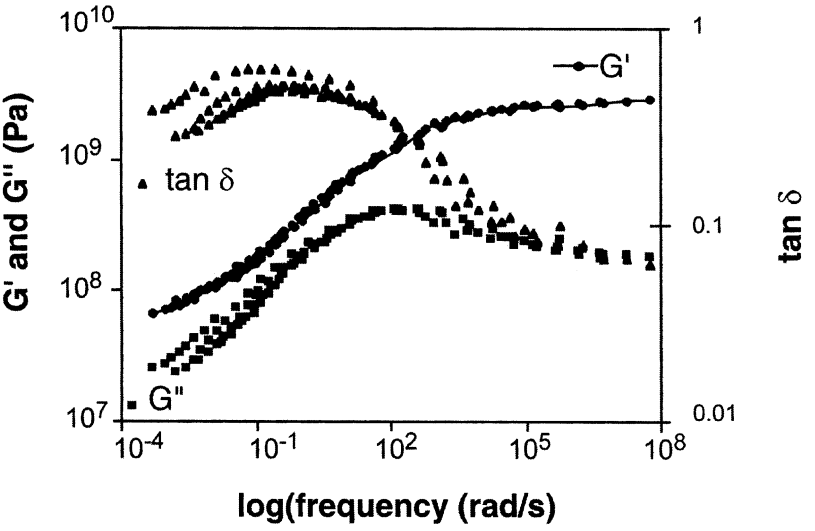

Figure 8. The master curve of RM-03-AD showed a larger relaxation strength in G′(ω) compared to RM-03-AC. The curve is generated by shifting data measured at constant temperatures along the frequency axis with respect to a reference temperature of 65.7 °C.

over the temperature range from 17 to 80 °C. Within the range investigated, the fits were reasonable. Master curves were generated by applying the shift factor to G′, G″, and tan delta data generated different temperatures to give Figures 8 and 9. Although the shear storage modulus (G′) data shifted reasonably well, discrepancies were seen at the low-frequency (high-temperature) end in all master curves for G″ and tangent delta. Comparison of the two curves shows that the relaxation strength of the RM-03-AD mock is much stronger than the RM-03-AC mock. This implies that creep may be more of a problem with this new mock.

Thermal Expansion

The thermal expansion coefficient of RM-03-AC and RM-03-AD are compared in Figure 10. As the temperature is increased in the RMS 800, the sample expands and the length of the fixture is adjusted to restore constant load. The change in length is plotted on the right-hand axis of the figure, and a linear expansion coefficient (LCTE or α_l)

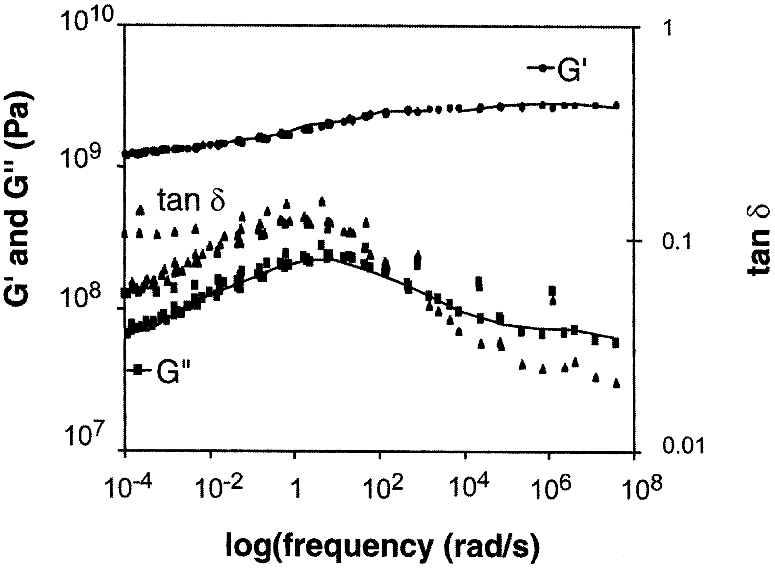

Figure 9. Shifting data about the reference temperature of 32.8 °C generated this master curve of RM-03-AC.

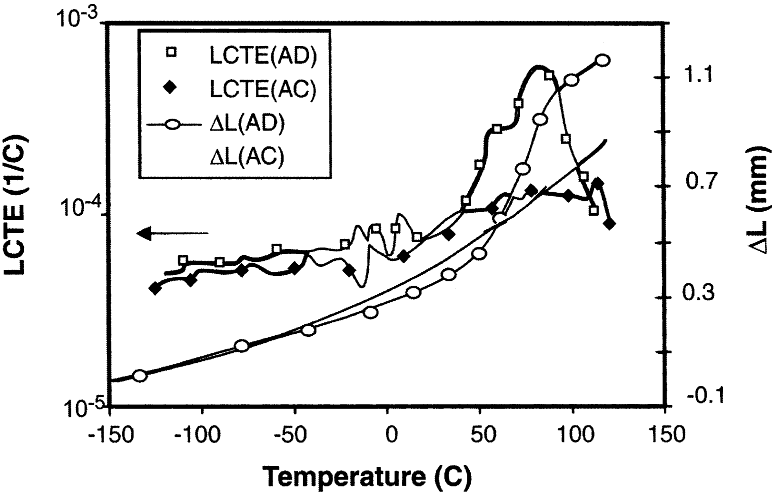

Figure 10. Linear thermal expansion coefficients of RM-03-AC and RM-03-AD are quite similar over the STS range. The major problem area is above T_g (near 50 °C or higher).

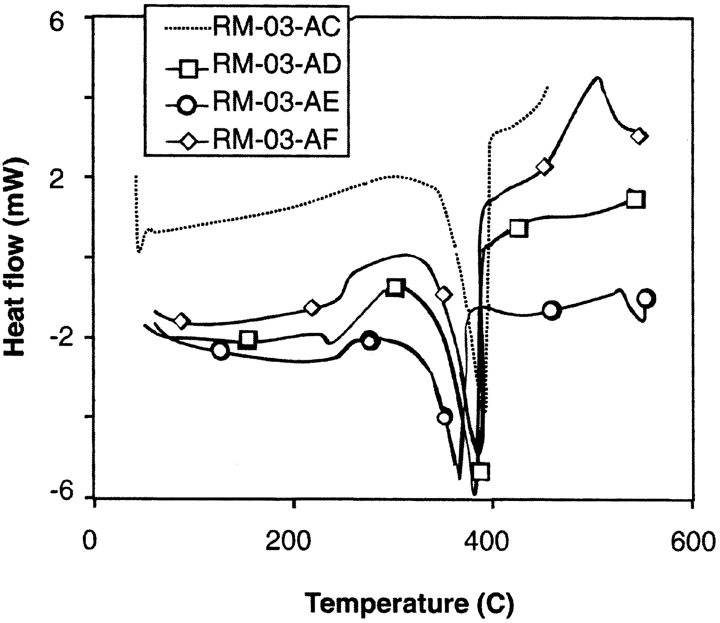

Figure 11. DSC traces of new mocks do not show any exothermic behavior over the temperature range from ambient to 550 °C. Their behavior is quite similar to RM-03-AC.

is calculated from ΔL according to

$$L_0 = L_0(1 + \alpha_l \Delta T) \qquad \text{or} \qquad \alpha_l = \frac{1}{L_0}\left[\frac{\Delta L}{\Delta T}\right], \tag{3}$$

where L_0 is the original length and L is the length after the change in temperature (ΔT). Above and below the glass transition the sample volume should increase with temperature at a different rate. Therefore the coefficient of thermal expansion should pass through a discontinuity at the glass transition. Unfortunately when the RM-03-AD sample became soft, creep caused anomalous results (as can be seen in the figure above 60 °C).

Exothermic Behavior

Normally mock formulations considered for use in a system receive an extensive evaluation to determine whether or not they will decompose rapidly in the environment where they will be used. The first step in this evaluation is typically a small-scale thermal test. At LLNL the DSC is used for this evaluation. The exothermic transitions in the mock are evaluated from ambient up to several hundred degrees Celsius. In cases where large exothermic reactions are observed (as in the case of real explosives) more work is required to demonstrate that no hazards will result when the mock is used. Figure 11 shows the DSC results of RM-03-AC, -AD, -AE, and -AF from ambient to 550 °C. As can be seen in the figure all of the mocks showed an endotherm at about $335 \pm 6\,^{\circ}$C. Since cyanuric acid decomposes rather than melts, this endotherm is probably associated with its decomposition.

Conclusions and Suggestions for Future Work

This effort has shown that it is possible to formulate mock explosives that have mechanical and density characteristics that are similar to the real explosive without using the same binder system. The RM-03-AD mock has reasonable fidelity to LX-17 and PBX-9502 except at elevated temperatures. Its density and low-temperature modulus are very similar. The glass transition temperature of the binder is close to that of Kel-F 800. At temperatures above the binder T_g, the modulus of RM-03-AD was much lower than the actual explosives. This could be improved by the addition of a cross-linking agent to the binder lacquer prior to formulation. Cross-linking the acrylic copolymer would reduce the creep of the mock at elevated temperature. The limitations of this approach include (1) shelf life reduction from indefinite to perhaps 1 year and (2) incorporation of a small amount of residual decomposition products from the cross-linking agent in the mock. The yield characteristics of RM-03-AD at low temperatures tend to be more brittle than LX-17 or PBX 9502. This might be mitigated by addition of a plasticizer that would also help in reducing the glass transition temperature slightly so that improved emulation of mechanical properties would occur. The complications that occur due to plasticization of the binder include migration of the plasticizer into other components during thermal or mechanical evaluation of a device, which might produce spurious results. Evaluation of peroxide cross-linking agents in RM-03-AD could prove useful. Plasticization, however, is not currently recommended.

Clearly the mixing procedure used to formulate 50 g quantities is unsuitable for scale up. Because the solubility of cyanuric acid is quite small in cold water, the inverse slurry coating method might be applicable to scaling RM-03-AD [21]. Preparation of a mock from the ethyl cellulose is not recommended. Preparation of the RM-03-AF, based on the PFR 91 polymer, will also be difficult with conventional methods, since the perfluorinated solvent is immiscible with water making slurry coating difficult. The "drum drying" procedure used at the DOE Pantex plant for RM-03-AC formulation might be applicable. Pressing has also not been optimized. Pressure and temperature cycles should be determined for optimum density. Additional work on the formulation to obtain densities that more closely match either LX-17 or PBX 9502 could be done, if the need arose. RM-03-AD densities of 1.903 fall well within the LX-17 density range and are only slightly higher than PBX 9502 nominal densities. Finally, some quality control analysis for the final product should be generated. Simple compositional analysis, density, and perhaps a mechanical measurement should suffice. This would ensure the compositional accuracy of each mix and give some indication of consistency of the binder coating and mechanical properties.

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