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Adhesive properties of some fluoropolymer binders with the insensitive explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)

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ABSTRACT

Adhesion between binders and explosive crystals is of critical importance for the mechanical performance of plastic-bonded explosives (PBXs). The surface properties of several prospective binders have been determined from static advancing contact angle measurements. The surface energies have been used to calculate theoretical work of adhesion to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), a common insensitive high explosive. The fluorinated terpolymer Oxy-461[™], and Kel-F[™] chlorotrifluoroethylene– vinylidene fluoride copolymers show the greatest potential for wetting TATB surfaces, and should promote the best adhesion to TATB in PBX formulations. In general, none of the fluoropolymer binders investigated here exhibit markedly superior adhesion to TATB. Thus, bulk physical properties are likely to be more important when choosing a binder.

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1. Introduction

The use of polymers to "bind" high explosive crystals is paramount to the widespread, safe use of plastic-bonded explosives (PBXs). PBXs are a unique type of composite containing explosive crystals at high loading percentages (typically exceeding 85 wt.%) with the polymeric binder coating the individual explosive grains. The binder serves important roles in reducing the sensitivity of explosive charges to insults such as impact or friction, as well as improving charge mechanical stability. The selection of binders for use in PBX formulations, however, remains largely an iterative, trial-and-error process based on a handful of guiding principles, and limited by constraints dictated by the physical properties of the explosive being formulated (such as solubility, decomposition temperature, etc.).

While the thermomechanical properties of the binder have been shown to be important for manufacturing PBXs [1], binder-explosive adhesive properties have been linked to an ability to fabricate (machine) parts, maintain long-term durability, and inhibit failure. Bower et al. showed that thermomechanical properties such as glass transition temperature (T_g) and extensibility, as well as surface wettability of the binder, are critical for explosive performance and safety [2]. It has been posited that the most common, and limiting, mode of failure in plastic-bonded explosives under thermal or mechanical loads is crack formation and subsequent propaga-

* Corresponding author. *E-mail address:* danadat@lanl.gov (D.M. Dattelbaum). tion along explosive crystal-binder interfaces [3–6]. For example, the mechanical properties of several PBXs were investigated by Palmer et al., revealing that even the most robust material failed by interfacial cracking at tensile stresses as low as 6.8 MPa [6]. Understanding the surface interactions between explosive crystals and polymeric binders is of great interest for potentially improving the production processes and failure limits of PBXs.

Here, the results of an experimental investigation of the adhesive properties of a number of fluoropolymer binders with the insensitive high explosive 1,2,3-triamino-2,4,6-trinitrobenzene (TATB) are reported. The TATB crystal is inherently anisotropic, with molecules adopting a $P_{\bar{1}}$ (triclinic) crystal structure in which the molecules are arranged in sheets in the a-b plane, Fig. 1. The a-b plane is alternatively labeled as the (001) plane in conventional crystallographic notation, while the edge of the a-b plane conventionally labeled (100). The (100) plane is referred to as the edge of the crystal arrangement here because the (0 0 1) planes tend to dominate when the crystal is grown from solution [7]. The edges of the crystal arrangement of TATB are highly oxygen- and amine-rich with strong intra- and intermolecular hydrogen bonding within the a-b plane, whereas in-between plane forces are dominated by π interactions associated with the benzene rings. The packing of planes in the TATB crystal results in an anisotropic crystal structure, leading to highly anisotropic thermal and mechanical properties. Indeed, a phenomenon of irreversible growth and dimensional changes, known as ratchet growth, occurs in temperature-cycled TATB formulations [8]. A review of of TATB properties can be found in Rice and Simpson [9].



Fig. 1. Crystal structure of TATB shown parallel to the *a*-*b* plane (A), and perpendicular to the *a*-*b* plane (reprinted with permission from L. L. Stevens, N. Velisavljevic, D. Hooks, D. M. Dattelbaum, Hydrostatic compression curve for triamino-trinitrobenzene (TATB) determined to 13.0 GPa with powder X-ray diffraction, Propellants, Explosives, and Pyrotechnics 33 (4) (2008) 286–295. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.).

Fluoropolymers are attractive as binders in PBX formulations due to their high densities, high temperature and chemical stabilities, and history of favorable performance [10–12]. Examples of such fluropolymers are Kel-F 800[™], a statistical copolymer of chlorotrifluoroethylene and vinylidene fluoride (75:25 ratio by weight), or FC-2175[™], a hexafluoropropylene and vinylidene fluoride copolymer. Fig. 2 shows a scanning electron micrograph of prills of 95 wt.% TATB/5 wt.% LFC-1[™]/FC-2175[™] obtained by precipitation from acetone solution. The prills are well-coated by the binder, indicating favorable surface interactions between the fluoropolymer and TATB.

Evaluation of the surface properties of polymers may be a useful tool for screening potential binders for TATB in the preparation



Fig. 2. Scanning electron micrograph of TATB-binder "prills" that are commonly pressed to produce plastic-bonded explosive charges (micrograph from E. Hartline, LANL).

of plastic-bonded explosive formulations. Here, we compare the surface properties of Kel-F 800 with related fluoropolymers that differ by their monomer chemistry, using contact angle measurements to measure the surface energies or surface tensions of polymer films.

1.1. Surface energy

Surface properties, including the dispersive and polar components of the surface energy, are relevant for evaluating adhesion between the explosive crystal and polymeric binder. The polar component of the surface energy arises from hydrogen and dipole interactions, while the dispersive component consists of London force interactions [13]. Thermodynamically, the work of adhesion is defined as the increase in free energy from creating two surfaces, and can be defined for liquid–solid interfaces by:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \tag{1}$$

where γ is the surface energy or tension, and the subscripts refer to the solid (*S*), the liquid (*L*), and the vapor or atmosphere (*V*) [14]. This expression was originally derived from Young's equation for equilibrium of a droplet on a surface,

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL} \tag{2}$$

where θ is the angle the droplet makes with the surface [15]. Zisman discovered that a reasonable value for the critical wetting surface energy of a solid could be found by plotting liquids of known surface tensions against the cosine of their contact angle, then linearly extrapolating back to the "perfect wetting" value of $\cos \theta = 0$. However, the critical surface energy was pointed out by subsequent researchers, and Zisman himself, to be different than the thermodynamic quantity of surface energy [16]. Indeed, researchers have found that the Zisman method consistently underestimates the true surface energy [17]. To correctly measure the surface energy, both polar and dispersive contributions are important, and any determination of surface energy must use liquids with a large range of these components [16–20].

Considering both polar and dispersive components, the surface energy of a solid surface can be calculated using the geometric mean method, shown in Eq. (3) [16], where the solid–vapor energy has two components, as noted in Eq. (4):

$$\gamma_{LV}(\cos\theta + 1) = 2(\gamma_{LV}^{d}\gamma_{SV}^{d})^{1/2} + 2(\gamma_{LV}^{p}\gamma_{SV}^{p})^{1/2}$$
(3)

$$\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p \tag{4}$$

where the superscript "*d*" stands for dispersive, and "*p*" stands for polar. In order to find the two unknowns, γ_{SV}^d and γ_{SV}^p , $\cos \theta$ must be measured for at least two liquids with known γ_{LV} , γ_{LV}^d and γ_{LV}^d . Eq. (3) is then solved for the two liquids simultaneously, allowing for γ_{SV} to be calculated with Eq. (4). However, it is common for three or more liquids to be used in order to ensure accuracy [20–22].

It should be noted that contact angles can be measured in a variety of ways, all of which have been shown to produce slightly different results [23]. Generally, contact angles are measured either advancing (wetting) or receding (dewetting), while in motion (dynamic) or while stable (static). Each measurement technique typically yields a different angle, and thus comparison with the literature must be done carefully. In this study, an advancing contact angle is measured to represent the wetting of polymers on TATB during processing. The angle is measured statically as a compromise between ease of measurement and accuracy.

2. Material and methods

2.1. Fluoropolymers

The polymers investigated contain common fluorinated monomers that make up the broad class of industrial fluoroelastomers. These include chlorotrifluoroethylene (CTFE), vinylidene fluoride (VDF), hexafluoropropylene (HFP), and tetrafluoroethylene (TFE). Table 1 details the chemical structures of the fluoropolymers investigated, as well as their as-received form and source. The fluoropolymers in Table 1 are soluble in common organic solvents, such as methyl ethyl ketone (MEK), ethyl acetate (EtOAc), tetrahydrofuran (THF), and toluene.

A few comments are pertinent regarding the materials listed in Table 1. Oxy (or Exon) 461 is not commercially available but has been previously used in PBX 9407, which consists of 94% cyclotrimethylenetrinitramine (RDX) and 6% binder. Of historical note is that production of Kel-F 800 was paused from 2002–2007 and resumed using a different process that avoided the use of perfluorinated surfactant. Consequently, the new production material studied here has fewer impurities (undetectable vs. 2% in old production material) and a smaller granule size than the original material often reported in the literature [24]. In addition, new production Kel-F 800 has only a single melt endotherm at 110 °C, compared with two endotherms (~84, 110 °C) observed in many of the older production lots, which may be indicative of more ordered crystalline structures.

Differential scanning calorimetry (DSC) was used to measure the thermal properties of all fluoropolymers used in this study. These results provide an initial assessment of the thermal transitions, which bound the processing and use temperatures for the binder candidates. DSC measurements were performed on a TA Instruments Q2000 Modulated Differential Scanning Calorimeter. The temperature was controlled using a refrigerated cooling accessory (RCA90). The samples were encapsulated in aluminum Tzero™ pans. The instrument was calibrated with indium and sapphire standards. Unless otherwise noted, the DSC scans were run at 10 °C/min heating rate from -90 to 250 °C. The glass transition temperature (T_{σ}) was defined as temperature at the midpoint in the endothermic heat flow step transition. The melting temperature (T_m) was defined as the maximum temperature of the melting endotherm and the heat of fusion (ΔH_f) was defined as the area under the melting endotherm.

2.2. Contact angle measurements

A half-angle contact angle meter (ChemInstruments, Mentor, OH) was used to measure the static advancing contact angle of several liquids on the polymer films. A representative schematic is shown in Fig. 3, depicting a droplet of water on a polymer surface.



Fig. 3. A typical deionized water droplet on Kel-F 3700[™] film, illustrating the surface energies and work of adhesion from Eq. (1).

Solutions of 3 wt.% polymer were prepared by placing as-received bulk specimens in either EtOAc or MEK, followed by ultrasonic-induced vibration for at least 15 min to ensure dissolution. Glass microscope slides (Fisher Scientific, Pittsburgh, PA) were used as film substrates, and were cleaned prior to coating by sequential acetone, ethanol and water washes, and atmospheric plasma etching for 5 min. The films were formed by dip coating the slides at a rate of 25 mm/min in a humidity-controlled glove box (% humidity = 25–30%).

The films were dried in air for at least 2 d prior to making contact angle measurements using water (18 M Ω /cm), glycerol (Invitrogen, ultrapure), and diethylene glycol. A fourth liquid, either hexadecane (Acros, 99+%) or dimethyl sulfoxide, was also measured in order to give a larger range of polar and dispersive liquids, as shown in Table 2. Hexadecane was used in situations where the dimethyl sulfoxide showed evidence of dissolving the film. Contact angles were measured again after one week to ensure the repeatability of the original measurements.

A summary of the surface energies for the test liquids, and reference solids, including TATB, is given in Table 2.

There is some discrepancy in the values of γ_{SV} for TATB. Rivera and Matuszak used an advancing dynamic contact angle method to measure the energies of several polymers and TATB [21]. However, Rivera and Matuszak did not specify any particular crystallographic face for the TATB measurement. Gee et al. reported substantially dissimilar values, Table 2, for the two crystallographic surfaces of (0 0 1) and (1 0 0), in addition to calculations of amorphous fluoropolymer surface energies [10]. By comparison, the (1 1 0) and (1 0 1) faces of PETN (pentaerythritol tetranitrate) differ by only ~5 dyn/cm [16]. It is beyond the scope of this paper to reconcile the differences in the two studies, though it should be noted that Gee et al. used simulations on isolated planes while

Table 1

Chemical structures and as-received form of flue	oropolymers investigated.
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Polymer name	Chemical structure	As-received form
THV 220™	Poly(tetrafluoroethylene-co-hexafluoropropylene-co-vinylidene fluoride) (40:40:20 TFE:HFP:VDF by weight)	Off-white granules from 3 M, Inc.
FC-2175™/LFC-1™ (mixed in both 50:50 and 75:25 ratios by weight)	Poly(hexafluoropropylene-co-vinylidene fluoride) in high (FC-2175)/low (LFC-1) MW forms (40:60 HFP:VDF)	White gum/Amber viscous liquid from 3 M, Inc.
Kel-F 800™	Poly(chlorotrifluoroethylene-co-vinylidene fluoride) (75:25 CTFE:VDF by weight)	White granules from 3 M, Inc.
Oxy 461™ (Exon 461™)	Poly(chlorotrifluoroethylene-co-tetrafluoroethylene-co-vinylidene fluoride) (monomer ratios unknown)	White granules from DOE storage (not commercially available)
Kel-F 3700™	Poly(chlorotrifluoroethylene-co-vinylidene fluoride) (31:69 CTFE:VDF) by weight)	White granules from 3 M, Inc.
Viton A™	Poly(hexafluoropropylene-co-vinylidene fluoride) (20-23 mol HFP:77- 80 mol VDF)	White pellets from DuPont

Table 2

Summary of test liquids and reference solids, energies in dyn/cm.

Test liquid	γ_{LV}	γ^{p}	γ^d	Refs.
Water	72.8	51	21.8	[25]
Glycerol	63.1	26.1	37	[17]
Diethylene glycol (DEG)	44.4	12.7	31.7	[25]
Dimethyl sulfoxide (DMSO)	44	8	36	[25]
Hexadecane	27.6	0	27.6	[21]
Reference solid	γsv	γ^{p}	γ^d	Refs.
Poly(tetrafluoroethylene) (PTFE)	19.1	0.5	18.6	[16]
Triaminotrinitrobenzene (TATB)	36.5	24.7	11.8	[21]
Calculated TATB (001)	66			[10]
Calculated TATB (100)	208			[10]

Rivera and Matuszak measured grown TATB crystals. In addition to the surface energies reported here, work of adhesion calculations using Rivera and Matuzak's TATB values are compared to simulations from Gee et al.

3. Results and discussion

3.1. Differential scanning calorimetry

The mechanical properties of polymeric binders are dominated by their thermal transitions. Below the glass transition temperature (T_g) , the polymer is glassy and has a modulus on the order of 10¹⁰ dyn/cm². For an amorphous polymer, the elastic modulus can decrease by three orders of magnitude as the polymer is heated above T_g and the polymer begins to flow above T_g . For semicrystalline polymers, the crystalline structure acts as intermolecular cross-links that increase the modulus between T_g and T_m . Above T_{σ} , the modulus is proportional to the level of crystallinity and small levels of crystallinity can increase the elastic moduli by more than an order of magnitude [25,26]. Above T_m , the polymer flows and can be easily processed. Table 3 summarizes the thermodynamic properties associated with constituent homopolymers. With exception of HFP, all monomeric constituents can crystallize upon polymerization. In addition to T_g , Table 3 shows the equilibrium melting temperature (T_m^0) and the heat of fusion for a 100% crystalline polymer (ΔH_f^0).

A fundamental understanding of thermodynamic transitions of the homopolymer components is necessary for understanding the effects of copolymerization of various monomers. This understanding is particularly important if future work requires tailoring a specific property (e.g. T_g or T_m) for the HE binder. Changes in the copolymer composition can dramatically affect the thermal and associated mechanical properties of the copolymer. For example, the T_g of copolymers can often be predicted using the generalized Fox equation:

$$\frac{1}{T_g} = \sum_i \frac{W_i}{T_{g_i}} \tag{5}$$

where T_{g_i} (in K) is the glass transition temperature and w_i is the weight fraction of component *i* [27]. Generally, copolymerization

 Table 3

 Thermodynamic properties of fluorinated homopolymers [28].

Polymer	T_g (°C)	T_m^o (°C)	ΔH_f^o (J/g)
PTFE	-73	332	82
PHFP	162	N/A ^a	N/A ^a
PVDF	-61	210	104
PCTFE	52	220	43

^a No melting endotherm or crystallinity was observed.

also reduces the melting point and level of crystallinity in semicrystalline copolymers [18].

DSC endotherms for the "as-received" fluoropolymers binders are shown in Fig. 4.

Comparison of the copolymer DSC data with the homopolymer transitions in Table 3 reveals how variation of the monomer content in the polymer allows the glass transition to be tuned between that of the homopolymers. For example, for Kel-F 800, the homopolymers of PCTFE and PVDF have glass transition temperatures (T_g) of +52 and -61 °C respectively [28]. The T_g of Kel-F 800 is closer to that of PCTFE, due to its 75 wt.% content in the copolymer. Likewise, the T_g of Kel-F 3700 is significantly lower than Kel-F 800, -16 °C, due to the greater VDF content [29,30]. With exception of Kel-F 800 and Oxy 461, all the polymers tested in this study have T_g 's below ambient temperatures. The DSC results from Fig. 4 are summarized in Table 4 and compared to predicted T_g 's from the Fox equation.

The measured T_g 's of Kel-F 800 and Kel-F 3700 agree reasonably well with the T_g 's predicted by the Fox equation. The T_g 's of the remaining copolymers show substantial deviations from those modeled by the Fox equation. Similar observations have been observed for other fluoropolymers systems, such as VDF/HFP copolymers [31]. More advanced models have been developed for prediction of T_g of fluoropolymers, however, information on the sequence distribution of the monomers units is required [32]. The sequence information can be determined using nuclear magnetic resonance (NMR) but is beyond the scope of this work.

Copolymerization generally disrupts the symmetry of the polymer backbone thus reducing the ability of the crystallizable monomers from organizing into unit cells. For this investigation, all of the copolymers contain at least one crystallizable monomer component. Reduction in T_m and% crystallinity by copolymerization improves the solubilities of the fluoropolymers in organic solvents and enables the possibility of tuning thermal and mechanical properties while maintaining high densities and other advantageous properties such as low coefficients of friction and chemical stabilities. From DSC, the level of crystallinity is typically determined by:

$$\% \text{ crystallinity} = \frac{\Delta H_f}{\Delta H_f^o} \times 100 \tag{6}$$

where ΔH_f is the measured heat of fusion under the melting endotherm and ΔH_f^0 is the heat of fusion of the 100% crystalline polymer shown in Table 1.

Kel-F 3700 and Kel-F 800 are both copolymers of VDF and CTFE, with a potential for two different crystalline structures to be formed upon copolymerization [33]. Fig. 4 shows an absence of an endothermic peak associated with melting for Kel-F 3700, indicating that there is no crystallinity in the "as-received" sample. The lack of crystallinity in the Kel-F 3700 suggests the monomer ratio is such that neither the VDF nor CTFE monomer sequences possess the symmetry or the kinetics to form unit cell structures. For Kel-F 800, the CTFE sequences slowly crystallize if annealed above ambient temperatures (T_g). However, even at the optimum crystallization temperatures, the level of crystallinity in Kel-F 800 rarely exceeds 10–15% [16,30].

Viton A, LFC-1, and FC-2175 are copolymers containing various ratios of VDF/HFP. The Viton A studied here contains approximately 20 mol.% HFP monomer. Both FC-2175 and LFC-1 contain 40 mol.% HFP and differ only by molecular weight, with FC-2175 having a molecular weight of 85 KDa and LFC-1 and having a molecular weight ca. 10 KDa. From a structural perspective, only the VDF sequences can crystallize in the VDF/HFP copolymers. The incorporation of HFP units along the polymer chain disrupts the symmetry of the VDF units, reducing their ability to organize into unit cell structures. The addition of HFP significantly increases



Fig. 4. DSC data of "as-received" binder samples. The "+" indicates T_{p} .

Table 4Summary of DSC results for the fluoropolymers.

Sample	T_g obs (°C)	T_g Fox (°C)	T_m Max (°C)	$\sim \Delta H_f(J/g)$
Kel-F 800	27	27	110	6
Kel-F 3700	-17	-22	N/A ^a	N/A ^a
Viton A	-19	-11	83	1.8
FC-2175	-21	35	65	0.8
LFC-1	-27	35	91	3.4
THV220	4	-27	140	14
Oxy-461	${\sim}50$	N/A ^b	N/A ^a	N/A ^a

^a No melting endotherm or crystallinity was observed.

^b The equation was not used because the composition was not known.

the T_{m} and reduces T_{m} and the level of crystallinity. It has been found that VDF/HFP copolymers with HFP contents >20 mol.% produce an amorphous rubber [28]. For Viton A the observed T_g is -19 °C, which is somewhat less than the T_g of -11 °C predicted by the Fox equation. FC-2175 and LFC-1 contain 40 mol.% of HFP; however, the observed T_g 's for both copolymer compositions are slightly less than that of Viton A. This is surprising, since the greater concentration of HFP is expected to raise T_g , and the Fox equation predicts the T_g of this composition to be 35 °C (Table 4). Similar discrepancies between observed and calculated T_g 's have been observed for other VDF/HFP copolymers and fluorinated copolymers [20]. Low molecular weight polymers have a greater fraction of chain ends relative to the polymer backbone, creating larger free volumes, which act to depress the glass transition temperature as predicted by the Flory-Fox equation [29]. Furthermore, the slight crystallinity in the LFC-1 may also be due to crystallization of the short polymer chains. The lack of entanglements of the short chains facilitates better packing of the VDF units. Quenching and rescanning LFC-1 from the melt reveals a crystallization endotherm followed by melting. Upon reheating the quenched FC-2175, only the T_g is observed. The greater molecular mobility of the short chains in LFC-1 promotes faster crystallization, while chain entanglements and steric constraints associated with long chains reduce the rate and mobility to chain segments to organize into crystallite structures.

Lastly, THV 220 is a terpolymer of TFE, HFP and VDF. The crystallinity observed in THV 220 may be more complex since two of the three comonomers have the potential to crystallize. Analogous to the VDF/HFP copolymers, the HFP disrupts the crystallinity of the TFE segments, thereby reducing the melting temperature while enhancing processibility and solubility. There have been many investigations that have determined the influence of small amounts of HFP in on the crystal structure of PTFE backbones. It has been shown the less than 1 mol.% HFP prohibits the polymorphic transitions at 19 and 30 °C [21,28].

3.2. Surface energy and adhesion

At least 10 contact angle measurements were taken of each polymer film with each liquid, and the results are summarized in Table 5. The error on each measurement is $\sim 2^{\circ}$.

The static advancing contact angle of water on polytetrafluoroethylene (PTFE) was used to verify the method, agreeing well with literature values of between 108° and 119° [16,34,35]. All of the binders showed low water wettability; an unsurprising consequence of the inclusion of fluorine in the polymer backbone. Despite a few occasions of relatively high standard deviation (e.g. DMSO on PTFE), the error introduced in surface energy calculations is small because the energy is a function of the cosine of the angle. Thus, the overall accuracy of the energy calculation method is high.

Polar and dispersive contributions to the binder surface energy were calculated using the geometric mean approach described above. Dalal found that judicious choice of dissimilar liquids for calculating the solid surface energy resulted in smaller standard deviations than averaging results from a large number of liquids [20]. Table 6 shows the results of geometric mean calculations for all liquids and for selected dissimilar pairs, as well as the thermodynamic work of adhesion to TATB. In this case, the dissimilar pairs were H₂O/DEG and H₂O/DMSO or hexadecane.

Calculation of surface energies using the $H_2O/glycerol$ comparison consistently resulted in large outliers, as seen in the higher standard deviation for "all test liquids" reported. The only exceptions were PTFE, Viton A and 75% FC-2175/25% LFC-1, which had approximately the same uncertainty using all solvent pairs. As a verification of the geometric mean calculations, the PTFE surface energy of 22.2 dyn/cm is in the range of 18–23.9 dyn/cm reported by Wu for various energy determination methods [19]. Table 7 compares the results for PTFE, Kel-F 800, and Viton A from this work with those in the literature.

Table 5

CONTACT ANALES OF LEST HOURDS OF THE DITION THINS () TSTAINATO DEVIATION	Contact angles	s of test liquid	s on the binder	films (°)	±standard deviation
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Polymer	Water	Glycerol	DEG	DMSO	Hexadecane
50 FC-2175/50 LFC-1	101 ± 4.1	98 ± 3.0	79 ± 3.0	-	45 ± 0.5
75 FC-2175/25 LFC-1	102 ± 3.6	93 ± 3.5	75 ± 2.5	24 ± 3.5	_
Kel-F 800	97 ± 1.1	88 ± 1.5	62 ± 1.7	59 ± 2.4	-
Kel-F 3700	98 ± 1.2	91 ± 2.3	61 ± 1.6	-	13 ± 1.0
Oxy-461	87 ± 2.1	77 ± 3.7	51 ± 3.3	45 ± 3.7	-
PTFE	111 ± 2.8	91 ± 3.8	79 ± 3.6	67 ± 9.1	-
THV	101 ± 1.0	94 ± 1.1	72 ± 1.6	69 ± 3.8	-
Viton A	97 ± 2.3	101 ± 1.8	77 ± 1.7	49 ± 2.1	-

"-" Indicates the measured angle was not used due to observed dissolution of the film.

Table 6

Surface energy of the polymer binders and work of adhesion to TATB (dyn/cm, ±standard deviation).

Polymer	Dissimilar liquids			All	Dissimilar
	γ^d	γ^p	γs	γs	W_a to TATB
50 FC-2175/50 LFC-1	16.5 ± 5.1	2.2 ± 1.2	18.8 ± 3.9	16.7 ± 4.5	40.2 ± 4.3
75 FC-2175/25 LFC-1	15.1 ± 6.0	5.6 ± 2.4	20.7 ± 3.6	19.4 ± 3.4	48.1 ± 4.1
Kel-F 800	26.4 ± 0.5	1.2 ± 0.1	27.6 ± 0.4	24.5 ± 5.4	42.7 ± 0.4
Kel-F 3700	27.1 ± 0.4	0.9 ± 0.0	28.0 ± 0.4	25.0 ± 5.3	41.7 ± 0.4
Oxy-461	29.1 ± 3.2	3.3 ± 0.7	32.4 ± 2.5	29.7 ± 5.0	51.6 ± 2.7
PTFE	22.2 ± 2.9	0.0 ± 0.1	22.2 ± 2.9	22.9 ± 2.3	30.8 ± 3.1
THV 220	19.9 ± 0.9	1.4 ± 0.2	21.3 ± 0.7	19.1 ± 4.0	39.5 ± 0.6
Viton A	15.2 ± 5.3	4.0 ± 1.8	19.0 ± 3.6	18.3 ± 3.0	44.4 ± 4.0

Table 7

Comparison of experimentally determined surface energies from this study with literature values for polymers and individual copolymer components (dyn/cm). Also cited is the method used previously for determining the surface energy.

Polymer	γ_s (this study)	γ_s Refs.	Method
PTFE	22.2	18 [19] 18.8 [19] 22.6 [19] 23.9 [19]	Critical surface tension Geometric mean Harmonic mean Liquid homolog
Kel-F 800 Viton A	27.6 26.3	32 [21] 27 [10] 28 [10] 29.7 [21]	Geometric mean Molar parachors Molecular dynamics sim. Geometric mean
PCTFE		26.9 [18] 31 [19]	Geometric mean Critical surface tension
PVDF		32.3 [18]	Geometric mean
PHFP		18.5 [36]	Geometric mean

Kel-F 800 and Viton A are the only investigated materials for which the surface free energies have been previously reported. Small differences were observed between our calculated values for γ_s and those of Rivera and Matuszak for Kel-F 800 [21]. However, the surface energy of Kel-F 800 determined from the contact angle measurements is in remarkable agreement with recently calculated values using a molar parachors group additive method (27 dyn/cm) and molecular dynamics simulations (28 dyn/cm) [10]. In general, the agreement of the values in this study with the literature lends confidence to the methods and solvent combinations chosen here.

Inspection of Table 6 shows that overall the surface energies for the fluoropolymers studied do not differ by more than 15 dyn/cm across the series. The values for the range of fluoropolymers reported here are in line with the values reported for the related fluoropolymers PTFE, PVDF, PCTFE, and polytrifluoroethylene by other researchers [16,18]. These groups have both reported correlations between the polar and dispersive components of the surface energy and degree of substitution of the backbone –H atoms with –Cl or –Fl. All of the binders in this study contain over 50% F-for-H substitutions, and the complexity of the monomer compositions makes correlations of the subtleties of the backbone structures with surface energies difficult. For evaluation purposes, most of the binders had total surface energies similar to Kel-F 800. The exceptions are the FC-2175/LFC-1 mixtures. Unlike the other binders that can be cast to form "high quality" films, the FC-2175 is a high viscosity gum, while the LFC-1 is a liquid [37]. The starting forms may influence thin film formation and surface morphology that subsequently affect surface energies. Interestingly, the surface energies of the two CTFE/VDF copolymers, Kel-F 800 and Kel-F 3700, are quite similar, despite known differences in molecular weight and monomer composition. Kel-F 3700 has a molecular weight that is an order of magnitude greater than Kel-F 800, and more than twice the VDF content.

Gee et al. calculated the surface energies and work of adhesion between TATB and four binders including Kel-F 800 and three high- T_g , amorphous fluoropolymers using molecular dynamics (MD) simulations [10]. The MD simulations were validated by computation of the polymers' glass transition temperatures. The works of adhesion of Kel-F 800 were 76 dyn/cm for the (001) surface and 271 dyn/cm for the (100) surface of TATB, again illustrating the anisotropy of TATB crystals. Here, the calculated work of adhesion using Rivera and Matuszak's TATB surface energies in Table 6 was 43 dyn/cm, a significantly lower value than either surface simulated by Gee et al. It is possible that the difference between the simulations of Gee et al. and Rivera and Matuszak's measurements is derived from surface defects, or other experimental variables (such as the crystallographic direction tested in the experiments which was not specified). In Gee's study, the fluoropolymer binders showed a greater Wa, or more favorable interaction, with the (100) surface compared to the (001) surface. The (100) interface was found computationally to be a "rough" surface, with exposed nitro- and amino-groups, and increased surface area, promoting binder-crystal adhesion and dipole-dipole interactions between the polar moieties and -Fl in the polymers' backbones. Similarly the spreading coefficients were also found to be greater for (100) vs. (001), indicating that the binders better wet the (100) surface as well.

Of the binders studied here, Oxy 461, the CTFE-TFE-VDF copolymer, may exhibit slightly improved adhesion to TATB over the other binders. Kel-F 800 is in the middle of the range of values. Overall, the difference in the work of adhesion across the series, shown in Table 6, is not large (\sim 12 dyn/cm), as may be expected due to the similarities in copolymer compositions. There appears to be little interpretable correlation between -F substitution or side group (HFP) content on the copolymers' surface properties, due to the complexity of the copolymer compositions across the series. Since the adhesion to TATB is similar across the series, it is expected that the polymers' physical properties (thermal expansion coefficient, crystallization/melting, elastic modulus) would dominate any observed differences in the mechanical properties of TATB-fluoropolymer PBX formulations. For example, Rizzo et al. have previously reported that TATB formulated with high- T_{σ} binders can reduce the bulk linear coefficient of thermal expansion (by up to 25%), and ratchet growth phenomena (by up to fivefold), particularly between 40-70 °C [38].

4. Conclusions

A series of fluoroelastomer binder candidates have been evaluated for their adhesive interactions with the high explosive crystal TATB by measuring their respective surface energies using contact angle methods. The surface properties, and work of adhesion to TATB, were found to be similar across the series. The copolymer compositions of the binders are varied, and no strong correlations of the surface energies with backbone structure were found to exist across the series. By using the calculated values of the surface energies for TATB from Rivera and Matuszak, the work of adhesion of the binders to the different interfaces was determined. While the adhesion of the binder to the crystal is not the only factor for determining the best possible binder in a plastic-bonded explosive, the common failure mode of a crack propagating along crystal-binder boundaries indicates that adhesion is critical for composite durability. Based on these results, Oxy 461 might be expected to show slightly improved adhesive strength to TATB. The remaining binders in the series are expected to have similar adhesion to TATB compared with Kel-F 800, and may be sensible choices for substitution in PBX formulations. Due to the similar adhesive properties of the binders, the thermal and mechanical properties of the binders are expected to be a more dominant factor in overall PBX mechanical performance.

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