The Identification of Bonding Agents for TATB/HTPB Polymer Bonded Explosives [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1992 **339**, 321-333
doi: 10.1098/rsta.1992.0038

The identification of bonding agents for TATB/HTPB polymer bonded explosives

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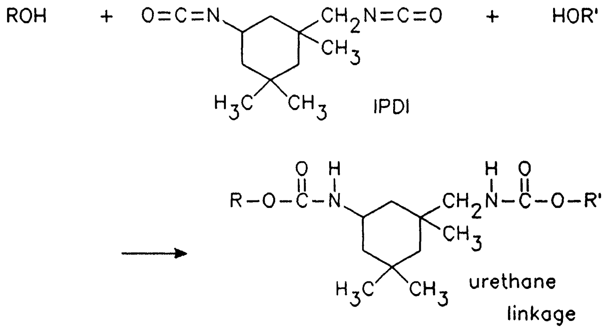
To obtain a polymer bonded explosive (PBX) with acceptable properties it is generally considered necessary to modify the bonding of the filler explosive to the polymer matrix. This is usually achieved by the addition of a 'bonding agent'. This paper describes an investigation of the interaction of some bonding agents with the surface of the insensitive high explosive 1,3,5-triamino-2,4,6-trinitro-benzene. The mechanical properties of the surface modified explosive loaded into a matrix of isocyanate cured hydroxy-terminated polybutadiene have also been studied to elucidate the role of the bonding agent and produce a PBX with high extensibility.

1. Introduction

(*a*) *Background*

There is a requirement for a conventional high explosive with high temperature stability and low sensitivity to initiation by thermal or mechanical shock. International investigation into insensitive high explosives (IHEs) has identified a number of potentially suitable explosive compounds. The exceptional insensitivity of 1,3,5-triamino-2,4,6-trinitro-benzene (TATB) has aroused particular interest.

TATB is a crystalline solid which must be consolidated into a polymeric matrix to provide a useable engineering material. The incorporation of particulate explosives into polymeric matrices to create polymer bonded explosive (PBX) composites is a common method of charge fabrication. The binder of choice in the United Kingdom for the consolidation of TATB is based upon the prepolymer hydroxy-terminated polybutadiene (HTPB). The matrix is cured by the reaction of the HTPB blocks, which have an approximate molecular weight of three thousand, with isophorone diisocyanate (IPDI) to form bridging urethane linkages:



Phil. Trans. R. Soc. Lond. A (1992) **339**, 321–333
Printed in Great Britain

Table 1. *Comparative data for TATB and high performance cyclic nitramine explosive compounds*

explosive	crystal density[a] (g cm^{-3})	detonation velocity[a, b] (m s^{-1})
RDX	1.82	8750
β-HMX[c]	1.96	9100
TATB	1.93	7350

[a] Data from Meyer (1987).
[b] Data for confined material.
[c] β-HMX is the most dense of four HMX crystal habits.

(*b*) *Performance requirements of TATB filled* PBX *composite systems*

(i) *Explosive performance*

Polymer bonded IHE compositions are under development for use in specialized weapon system applications. Within such systems it is the detonation pressure of the explosive charge – the pressure of the emerging detonation shock front – which is used to achieve the desired effect. The dependence of the detonation pressure P_D upon other parameters of an explosive charge is described by the relation

$$P_D \propto \rho V_D^2, \tag{1.1}$$

where ρ is the charge density and V_D is the velocity of detonation. While the crystal density of TATB is comparable to that of other high performance explosives such as the cyclic nitramines RDX and HMX (see table 1), its significantly lower V_D enables the formulation of charges possessing only relatively modest P_D.

The V_D data in table 1 refer to the crystalline explosive materials. The V_Ds of PBX composites are lower than those of the pure explosives and are a function of the explosive loading density in the composite. To obtain equivalent performance, TATB loaded PBX composites must therefore contain a greater explosive loading density than RDX or HMX filled composites. To provide sufficient detonation pressure to guarantee the desired target effect, the TATB volume fraction ($v_{f(TATB)}$) within an IPDI cured HTPB bound composite must be 0.92 or higher.

(ii) *Mechanical performance*

The pressure exerted by the shock wave emerging from an explosive charge is known to fall rapidly with distance from the charge surface. For the most efficient application of detonation pressure, an explosive component must be in intimate contact with its target when initiated. This requirement demands that the consolidated PBX must be capable of matching the thermal expansion properties of the target component material throughout the military specification temperature range of -54 °C to $+74$ °C. For a TATB/HTPB composite to have sufficient extensibility to meet this requirement, the composite must contain a binder fraction of at least 0.10, thus $v_{f(TATB)}$ cannot be greater than 0.90.

Contradictory demands are therefore placed upon charge formulation by the requirements of mechanical performance ($v_{f(TATB)} \leqslant 0.90$) and explosive performance ($v_{f(TATB)} \geqslant 0.92$). It is clear that the latter limitation – a direct consequence of the relatively low detonation velocity of TATB – must be respected if satisfactory detonation velocity is to be achieved. Recent studies of the composite interphase region suggest possible solutions.

Mechanical performance has been related to composite composition using two general theoretical models. Those models based on the consideration of a filled composite material as a viscous suspension have been reviewed by Nielsen (1974). Alternatively, composite performance has been predicted by the use of 'rules of mixture': these are formulae which relate the behaviour of the formed material to the properties of each of the components and to their mixing proportions (Young 1986). Of the many rules of mixture which have been proposed, the approach of Ishai & Cohen (1967), who modelled the particulate reinforcement as cubic blocks surrounded by the bulk matrix, has produced boundary predictions which have been found to be practically useful for many particulate filled composite systems.

Both approaches show good general agreement in describing the effect of changing filler volume fraction upon composite modulus: the increase of v_f is predicted to cause increased composite modulus. Furthermore, the modulus/v_f curves provided by most of the models are convex to the filler axis, leading to the prediction that the modulus is particularly sensitive to changes in filler volume fraction at high filler loadings. This prediction has been experimentally verified for many composite systems and should apply to TATB/HTPB formulations. Thus an increase of $v_{f(\mathrm{TATB})}$ from 0.90 to 0.92 to satisfy the explosive performance requirement will lead to an increase in composite modulus (i.e. a reduction in composite elasticity) and therefore a decrease in the ability of the composite to match the thermal expansion behaviour of its target.

(*c*) *The interphase*

The models described in §1*b* assume a two-dimensional interface between the filler and binder, with either no particular interaction or perfect interphase adhesion across the interface. In any practical system a three-dimensional volume will exist – the *interphase* region – where the mechanical properties are unlike those of either of the bulk phases (Drzal 1990). The properties of the interphase may be expected to fundamentally affect the mechanical performance of the composite. Yosomiya *et al.* (1989) described a novel rule of mixture – the 'quadratic rule of mixtures' – which included a term intended to account for the existence and quality of the interphase region. The interphase 'quality' must include contributions from many effects but it is likely that *adhesion* between the phases at the interface is most significant. The use of an interphase quality term allows variations in modulus with V_f to be predicted using the quadratic rule of mixtures.

The validity of this conclusion has been experimentally demonstrated by Spanoudakis & Young (1984), who examined the effect of particle–matrix adhesion upon the mechanical properties of a model composite material formed by the consolidation of spherical glass particles in an epoxy matrix. Chemical treatment of the glass particles was used to either increase or decrease filler–matrix adhesion. The investigation demonstrated that the improvement of filler–matrix adhesion provided composites with moduli which were clearly greater than the moduli of the formulations containing particles which had been treated so as to decrease interphase adhesion.

An approach based upon this precedent may therefore make possible the resolution of the TATB/HTPB IHE performance contradiction. By deliberately controlling the quality of the interphase when $v_{f(\mathrm{TATB})}$ is increased to 0.92, it may be possible to restore the composite modulus to an acceptable value.

(d) *Interfacial agents*

The increase or decrease of filler–matrix adhesion in the investigation by Spanoudakis & Young was achieved by the addition of *bonding or releasing agents* to the composite formulation. These are included in a composite formulation in quantities sufficient only to achieve monolayer coverage at the interface between the phases. Most commonly, the agent is applied to the surface of the filler particles by a pre-treatment process.

A bonding agent should ideally be capable of forming formal chemical bonds with both filler and matrix, although hydrogen bonding or dispersion bonding may be sufficient to provide the desired result. For action as a release agent, the interfacial species should ideally bond with one of the phases (usually the filler), where its presence should lower the affinity of the bulk phases for each other. The effective application of bonding or releasing agents to a composite system will therefore require an understanding of the processes by which bonding may be achieved with each of the phases.

(i) *HTPB reactivity*

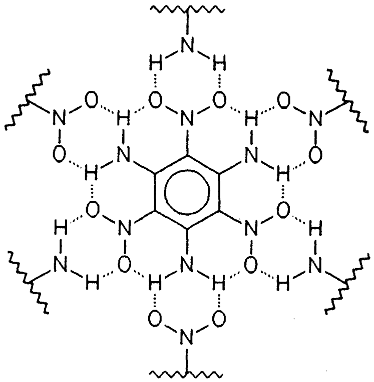
The cure reaction between IPDI and the hydroxyl functionality of the HTPB was shown previously. A bonding agent with a hydroxyl or isocyanate functionality may similarly be expected to react with the HTPB. Alternatively a condensation reaction between a bonding agent with an alkoxyl function and the HTPB could take place:

$$\underset{\text{alkoxy coupling agent}}{\mathrm{R{-}OC}_n\mathrm{H}_{2n+1}} + \underset{\text{binder}}{\mathrm{HO{-}R'}} \longrightarrow \mathrm{R{-}OR'} + \mathrm{HOC}_n\mathrm{H}_{2n+1}.$$

A less formal interaction between a bonding agent and the binder phase can be encouraged if long alkyl chains are present on the interfacial agent. Enhanced bonding can result from entanglement of the long chains with the bulk matrix material, a process which relies upon dispersion forces.

(ii) *TATB reactivity*

The TATB crystal structure is composed of graphite-like infinite planes. Each molecule in the plane is held in position by six intra- and twelve inter-molecular hydrogen bonds, as shown below.



The extensive hydrogen bonding provides a highly stable and unreactive material with a melting point above 400 °C. It is almost completely insoluble in common organic solvents. In strong acids, ionic species are formed, prejudicing the stability of the crystalline material. The establishment of formal chemical bonds between the bonding agent and the TATB crystal therefore appears unlikely.

The possibilities for less formal bonding are not well understood but the following may be noted.

(*a*) An adsorbate may achieve less formal interaction with the explosive by acid–base or hydrogen bonding processes at the dislocated edges of the crystal layer planes.

(*b*) The possible existence of a firmly retained water layer on the TATB crystal surface has been reported by R. R. McGuire. If its presence is confirmed, it may be possible to use the bound water as a bonding agent by reaction directly with the matrix isocyanate.

It was therefore decided to conduct an investigation aimed at the further characterization of the TATB crystal surface.

2. Experimental

(*a*) *Gas adsorption*

Gas adsorption isotherms were obtained using a C.I. microbalance accurate to 0.01 mg in a glass vacuum system. Samples (approximately 120 mg) were degassed at 10^{-2} to 10^{-4} torr at 120 °C for at least 1 h before the commencement of adsorption measurements. Weight loss during degassing was recorded. Nitrogen isotherms were obtained at 77 K. Water isotherms were obtained at room temperature. Experimental pressures were measured using a Baratron 170 Series pressure sensor.

(*b*) *Inverse gas chromatography*

Inverse gas chromatography was conducted in accordance with the general procedures described by Conder & Young (1979). The carrier gas used was helium, delivered at a head pressure of 322 kPa. Flow rates were measured with a bubble flow meter. The following probes, injected in 0.1 µl aliquots, were used: (*a*) *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and benzene as probes of dispersion interactions; (*b*) butan-1-ol and chloroform as acidic probes; and (*c*) heptylamine, triethylamine and *N*-methyl pyrrolidine as basic probes.

The column adsorbent was 1.76 g TATB. Determinations were made at 170 °C, 185 °C, and 200 °C.

(*c*) *Dye adsorption*

Dye adsorption from aqueous solution was carried out using the method of Giles & Trivedi (1969). TATB samples of 40 mg were agitated in 1.5 ml dye solutions and the supernatant liquor examined in a 10 mm path length sample cell in a UV–visible spectrophotometer. Beer–Lambert behaviour was observed at concentrations up to 0.04 mmol dm^{-3}.

(*d*) PBX *composite formulation*

PBX composites were prepared for both Brazilian and uniaxial tensile testing as follows.

(i) *Interfacial agent application*

Interfacial agents were applied by the agitation for at least two hours of the TATB sample with a solution of the agent in dichloromethane. After agitation the solvent

Table 2. *PBX composite sample formulation*

component			mass fraction
TATB	—	—	0.96
HTPB	0.0364[a]	0.0396[b]	0.04
IPDI	0.0032[a]		
anti-oxidant		0.0004[b]	

[a] These mass fractions provide a 1.1:1 NCO:OH ratio.

[b] These mass fractions provide a binder phase containing 1% anti-oxidant by mass.

was removed to provide the surface treated TATB as a dry powder. An agent concentration of 10 mmol kg^{-1} was arbitrarily chosen.

(ii) *Binder application*

The PBX composite samples were prepared with the mass fractions shown in table 2, providing an approximate TATB v_{f} of 0.92. The TATB weight fraction shown in the table does not include added interfacial species. Where an interfacial agent which contained hydroxyl functionality was used, sufficient excess IPDI was added to provide a 1:1 NCO:OH ratio, thereby maintaining the HTPB/IPDI ratio shown in table 2.

Moulding powders were formulated by adding (treated or untreated) TATB, HTPB, IPDI and anti-oxidant to a quantity of dichloromethane, followed by the slow evaporative removal of the solvent in a suitable mixer. This provided a powder which was then pressed into either disc (Brazilian) or dog-bone (uniaxial) pellets. The pressed pellets were cured at 70 °C for at least four days.

(*e*) *PBX mechanical testing*

(i) *Brazilian testing*

Brazilian testing was conducted by the general method described by Hondros (1959), modified to include curved anvils to reduce the possibility of edge failure (Awaji & Sato 1979). Applied loads were measured by a load cell and the stresses recorded as the function of time at intervals of approximately 200 ms. Strain measurements were conducted by the analysis of double-exposure laser speckle photographs so as to extract the in-plane displacement field at the sample surface, using the techniques described by Huntley *et al.* (1987).

(ii) *Uniaxial testing*

Uniaxial testing was conducted on an Instron universal test machine. A 20 N load cell was used with a cross-head speed of 0.1 cm min^{-1}. Fracture surface micrographs were obtained using a JEOL JSM 840A Scanning Electron Microscope.

3. Results and discussion

(*a*) *Gas adsorption*

Little weight loss was recorded during TATB degassing, even when the conditions were pushed to the point of onset of sublimation. The adsorption of H_2O was found to be normal and reversible, and gave similar results to N_2 adsorption. These results

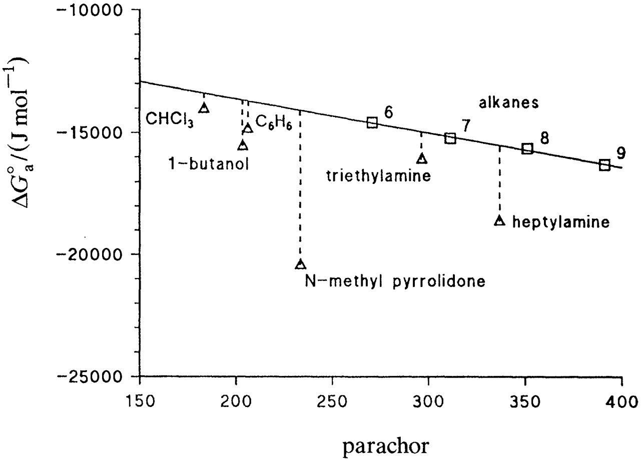


Figure 1. Evaluation of dispersive and specific interactions by inverse gas chromatography (IGC) analysis. Determination at 170 °C.

lend no support to the existence of a firmly bound water layer on the TATB surface. The exploitation (§1*d*(ii) above) of surface-bound water was therefore pursued no further. The H_2O and N_2 adsorption isotherms for TATB were characteristic of macroporous solids. BET analysis indicated surface areas of 1.38 to 3.26 $\mathrm{m^2\ g^{-1}}$ (N_2) and 1.52 to 2.38 $\mathrm{m^2\ g^{-1}}$ (H_2O).

(*b*) *Inverse gas chromatography*

The *retention volume* – the volume of carrier gas required to elute an injected probe – is a thermodynamic quantity. The free energies of adsorption of injected probe species, calculated from their retention volumes, can be compared using a novel graphical technique to provide information concerning dispersive and specific contributions to the adsorption process (Papirer & Balard 1991). The free energies of adsorption determined in this investigation at 200 °C are shown in figure 1.

The abscissa of figure 1 is the Sugden's parachor of the probe species, although any relevant physical parameter could have been used. The linear regression of the four alkane data points shown in the figure is assumed to represent the occurrence of purely dispersive adsorption processes. The distance of each data point from the line therefore provides a measure of the specific interactions in the adsorption process. The figure shows that the specific interactions of the primary amine and *N*-methyl pyrrolidone with the TATB surface are significantly greater than those of acidic probes and the tertiary amine. Acid–base interactions between adsorbates and the crystal dislocations seem to provide the most significant form of interaction, indicating that the crystal is acidic in character.

The determination of retention volumes over a range of temperatures allows the plotting of adsorption isosteres, from which the isosteric heats of adsorption can be determined. The isosteric heats of adsorption of the four alkane probes were 32.2 ± 2.5 kJ $\mathrm{mol^{-1}}$. These heats are approximately one third of those determined by Carrot & Sing (1986) for the adsorption of *n*-pentane onto microporous carbon adsorbents, and are typical of adsorption on non-porous solids.

Table 3. *Results of dye adsorption investigation*

probe dye	dye adsorbed[a] (mmol kg^{-1})
acid blue 45	0
m-cresol purple	0
p-nitro phenol	0
acid red 88	0.30
methylene blue	0.58
orange II	0.06
crystal violet	0.69

[a] At equilibrium concentration of 0.01 mmol dm^{-3}.

(*c*) *Dye adsorption*

It was decided to further examine acid–base interactions on TATB surfaces by studying the adsorption of a number of structurally similar dye molecules. The adsorption process followed Henry's Law up to an equilibrium dye solution concentration of 0.01 mmol dm^{-3}. Adsorption at this concentration has therefore been used for comparison purposes. The results are shown in table 3.

Table 3 shows that significant adsorption of methylene blue and crystal violet was observed, whereas none was observed for their close structural analogues, acid blue 45 and *m*-cresol purple. As crystal violet, methylene blue and acid blue 45 are salts which would be fully dissociated in water, it is unlikely that ionic effects are responsible for the observed differences in adsorption behaviour. Significantly, only crystal violet and methylene blue contain the strongly basic dimethylamino functionality. The observed adsorption can therefore be explained in terms of the interaction of basic sites on the adsorbate with acidic functionality on the TATB. The most likely form for this interaction would involve the donation of electron density from the lone electron pair on the dimethylamino-nitrogen to the electron deficient amine protons at dislocations in the TATB crystal.

The comparative behaviour of the azo dyes orange II and acid red 88 is more difficult to explain and any further speculation is not profitable. Structurally, the dyes differ only by the presence of an extra fused-aromatic ring in the conjugation system of the latter material.

(*d*) *PBX formulation*

On the basis of the above results the following candidate interfacial agents were selected for inclusion in test *PBX* samples.

(*a*) 4-(Dimethylamino)phenethyl alcohol (figure 2*a*), was selected as a candidate bonding agent. This molecule contains both a strongly basic substituent providing the opportunity for bonding with the TATB surface, and hydroxyl functionality providing a mechanism for bonding with HTPB. Application was conducted in dichloromethane solution.

(*b*) FC-805 (figure 2*b*), a perfluoroalkyl-substituted chromium complex used for the grease-proofing of paper products was selected as a candidate releasing agent (3M U.S.A.). The molecule has previously been used as a bonding agent in TATB filled composites with fluorinated binder systems (Pruneda *et al.* 1990). The complex was found to be insoluble in dichloromethane and was applied in isopropanol solution. It

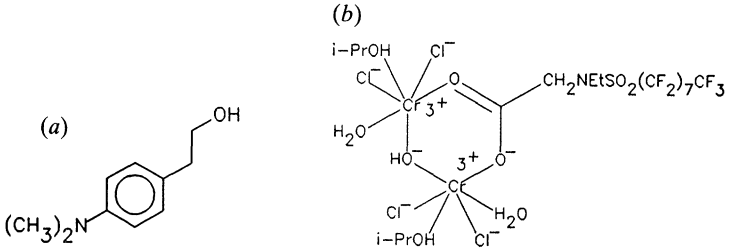


Figure 2. Candidate interfacial agents: (*a*) 4-(dimethylamino)phenethyl alcohol; (*b*) FC-805.

Table 4. *Brazilian test results*

(In unaxial tensile tests, using dumbbell-shaped specimens it has been observed that the failure tensile stress is higher than those in a Brazilian test by a consistent factor of two times (Burt & Lewis, personal communication).)

code	agent	tensile strength / MPa	failure strain/millistrain
BD41/1	none	0.95 ± 0.07	6.0
BD44/1	4-DMAPhEtOH	0.46 ± 0.02	1.7
BD45/1	FC-805	0.49 ± 0.09	4.6 ± 1.3

was hoped that application to the TATB surface would result in bonding between the polar substituents on the ring system and the explosive crystal. As the candidate is insoluble in dichloromethane, it should not be removed from the TATB during the preparation of the moulding powder. It was hoped that the perfluoroalkyl chain would be presented away from the surface and so act as a releasing agent.

PBX samples containing untreated TATB were also prepared.

(*e*) *PBX mechanical testing*

(i) *Brazilian testing*

Data collection methods for the Brazilian test procedure were briefly described in (§2*f*) above. Stress/time data are digitally recorded approximately every 200 ms. Strain/time data are collected independently using the double-exposure laser speckle technique. Typically an interval of 40 s between exposures, with an exposure time of 4 s were used to record the laser specklegrams. The duration of a test (i.e. *ca*. 300 s), means that five to six speckle patterns are recorded before failure of the specimen. Consequently, to obtain a continuous strain/time curve, the intermediate strain values are interpolated by fitting either a second or third degree polynomial to the data from the specklegrams. A continuous stress/strain curve was then obtained by calculating the strain for each recorded stress/time data point, thereby eliminating the time parameter.

Table 4 contains the results from the Brazilian tests. The tensile strength values quoted, correspond to the calculated tensile stress at the centre of the disc shaped sample at the onset of failure. The failure strain quoted is the corresponding estimated tensile strain at the centre of the sample. Values for the elastic moduli have not been given. This is because it is not possible with the existing sample size (i.e. 10 mm diameter by 3.4 mm thick), to measure small strains with sufficient accuracy. In addition the elastic régime of the sample needs to be identified by means

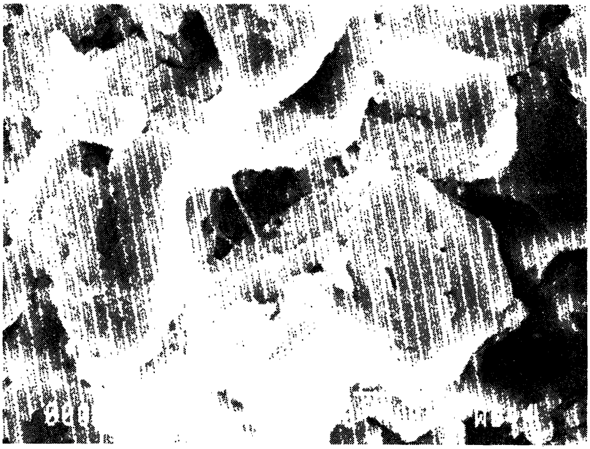


Figure 3. Fractograph of Brazilian test fracture region of sample containing untreated TATB.

of loading/unloading experiments, which is not possible with the existing experimental arrangement.

Several conclusions can be drawn from the results shown in table 4.

(*a*) Most significantly, the results demonstrate that the addition of 10 mmol kg^{-1} of each of the two interfacial agents has a marked effect upon the mechanical behaviour of the composite.

(*b*) The Brazilian test results show that the tensile strain in the formulation containing the proposed release agent (i.e. FC-805), at its failure stress of *ca.* 0.5 MPa is significantly higher than the corresponding strain in the control formulation at the same stress. This implies that the effective modulus has been reduced in accordance with the work of Spanoudakis & Young.

(*c*) The Stereoscan 250 Mk 2 scanning electron microscope was used to look down into narrow cracks of *ca.* 2–5 μm width in samples from both the control formulation and that containing the release agent, after a Brazilian test. In the case of the control filaments of pulled out polymer, bridging the cracks, were easily observed (see figure 3). However, in the case of the sample containing the release agent, even after extensive searching no evidence of filaments could be observed. This suggests that the adhesion between the binder and filler had been reduced, which is consistent with the proposed role of the agent FC-805. The formation of pulled out polymer strands as seen in the control material may have resulted from a cavitation failure in the binder.

(*d*) The effect of the proposed bonding agent (i.e. 4-DMAPhEtOH), however, is more difficult to explain. The Brazilian test results show that this agent also reduces the tensile strength by a factor of approximately two. However, in this case the extensibility of the composition at its failure stress of *ca.* 0.5 MPa is approximately twice that of the control formulation at the same stress.

4. Conclusions

The TATB crystal surface has been examined using gas adsorption, dye adsorption and IGC techniques. It has been determined that TATB is a low surface area macroporous solid. No evidence of surface resident moisture has been found. The surface has been found to have acidic characteristics. Acid–base interactions appear to offer the best strategy for achieving strong adsorption onto the surface. It is likely that this mode of bonding will occur at dislocations such as plane boundaries and macropores.

Brazilian testing was conducted at the Physics and Chemistry of Solids Section, Cavendish Laboratory, Cambridge University, to whom the authors extend their thanks.

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Discussion

J. SHARMA (*Naval Surface Warfare Center, U.S.A.*). TATB has a layered structure and hydrogen bonding. Does it show any evidence of intercalation? The first property is likely to promote, the other to oppose intercalation.

A. BAILEY. Yes, there is evidence of intercalation. While probing the characteristics of the TATB surface using IGC it was necessary to determine the residence time of an unadsorbed molecule in the TATB column. This is conventionally done with methane when studying the interactions of higher hydrocarbons with the surface. Methane was found to have an abnormally long retention time (similar to that for octane). This unexpected interaction was attributed to intercalation of methane in the TATB layered structure.

E. C. BAUGHAN (*London, U.K.*). It has been shown that solvents behave in two ways towards the explosive TATB: (i) by generalized van der Waals interactions; (ii) by *specific* interactions between groups and groups on the explosive and applied this to their choice of 'bonding agents'. Such behaviour was also observed for the polymer explosive nitrocellulose with specific interactions between its nitrate groups and the C=O groups of ketones and esters. Specific interactions may be recognized by *negative* deviations from Raoult's Law and should be of general importance in polymer technology. (See E. C. Baughan, A. L. Jones and K. Stewart, *Proc. R. Soc. Lond.* A **255**, 478 (1954).)

A. BAILEY. The two techniques yield similar information though IGC is easier and quicker to use. We do not find any evidence of specific interactions between carbonyl groups and the nitro groups in TATB.

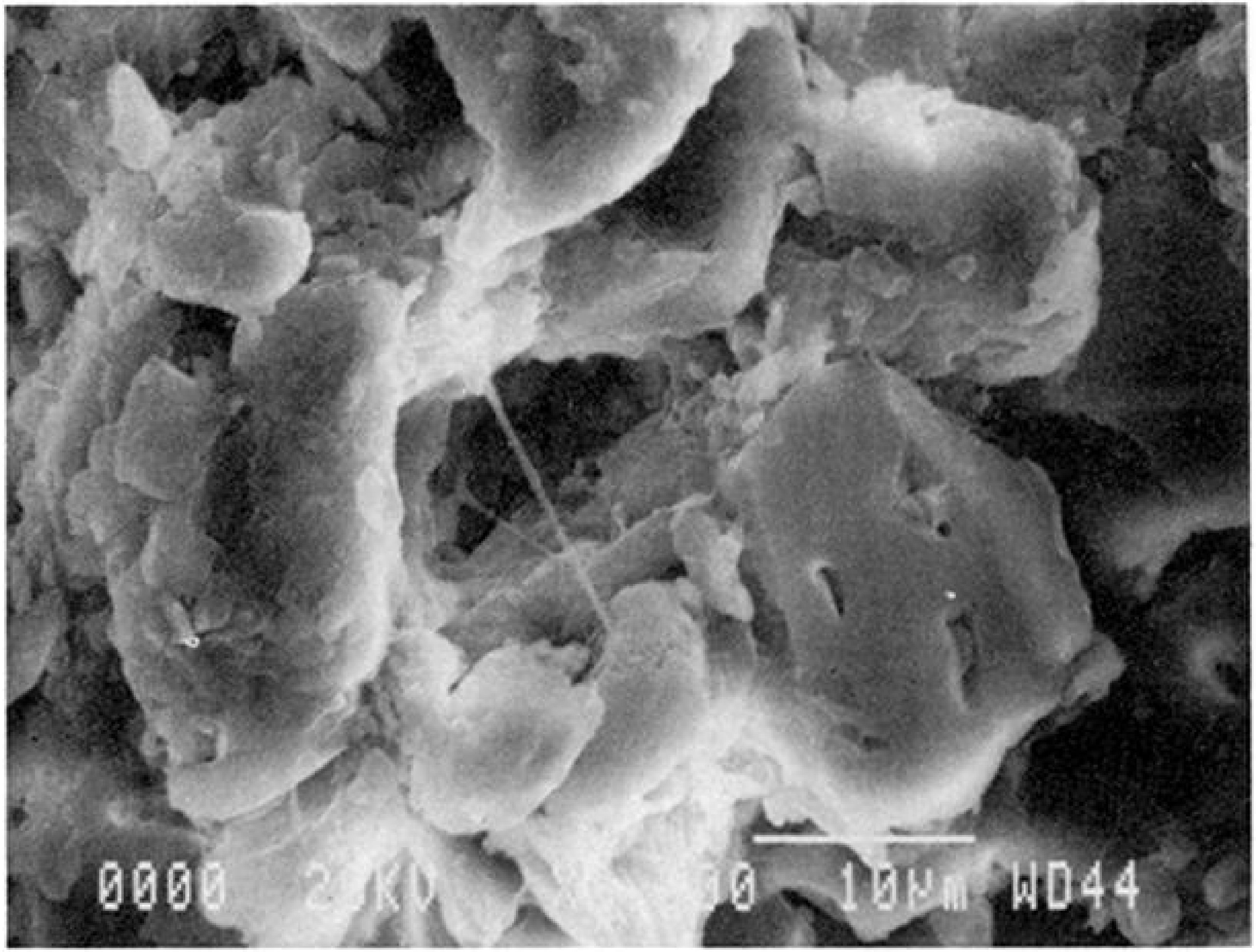
Comments

M. M. CHAUDHRI (*Cambridge University, U.K.*). As TATB is a layered material, having only the van der Waals type of bonding between the layers, it must be very weak. Has anyone tried to measure the fracture surface energy of these crystals? One possible method is the indentation technique (see, for example, J. T. Hagan, and M. M. Chaudhri, *J. Mater. Sci.* **12**, 1055 (1977); S. J. P. Palmer and J. E. Field, *Proc. R. Soc. Lond.* A **383**, 399 (1982)). However, for this method crystals of at least a few hundred micrometres are needed. Also, since the crystals are likely to be much weaker than the matrix, I wonder whether the bonding between the crystals and the matrix is important at all.

J. N. SHERWOOD (*Strathclyde University, U.K.*). The principal problem in carrying out such an assessment is to obtain crystals of a similar volume and dimension. Being relatively insoluble it is not easy to grow such specimens. Thus experimentation would be limited to microscopic experiments which might be carried out via fracture tests with a microhardness tester.

Regarding crystal growth, I was most interested to learn that the dyes examined adsorbed so strongly at the TATB crystal surfaces. This property might make them efficient habit modifiers during crystal growth. Use of them during the growth process could yield crystals of improved shape and quality for fracture energy and other experiments.

B. C. BEARD (*Naval Surface Weapons Center, U.S.A.*). Dr Chaudhri raised the question concerning the difficulty of determining the role of slip planes in impact initiation in laminar materials such as TATB particularly in light of the absence of any determination of the forces required to cause interlaminar slippage. I offer a well-documented method for the determination of laminar slip forces as determined by Atomic Force Microscopy. Forces in the range of 10^{-8} N can be reproducibly measured by this approach. The application of this technique requires a sample size of no more than a few micrometres. Therefore materials such as TATB that are available in only very small particles present no impediment to this approach. References offered in support are C. M. Mate, R. Erlandsson, G. M. McClelland and S. Chiang, *J. Vacuum Sci. Technol.* A **6**, 575 (1988); R. Erlandsson, G. Hadziioannou, C. M. Mate, G. M. McClelland and S. Chiang, *J. Chem. Phys.* **89**, 5190 (1988).



igure 3. Fractograph of Brazilian test fracture region of sample containing untreated TATB.