doi:10.20944/preprints202209.0017.v1

APPLICATION OF REICHARDT'S SOLVENT POLARITY SCALE [E_T(30)] IN THE SELECTION OF BONDING AGENTS FOR COMPOSITE SOLID ROCKET PROPELLANTS

Franco Cataldo

Actinium Chemical Research, Via Casilina 1626A, 00133 Rome, Italy

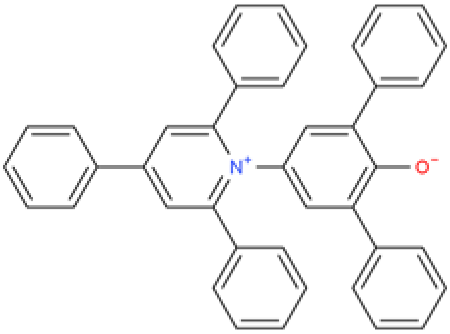
Abstract: Bonding agents (BA) are key compounding ingredients for the correct formulation of composite solid rocket propellants (CSRP). In particular, the addition of BA is essential to achieve suitable mechanical properties of CSRP in terms of adequate tensile strength and elongation at break. It is shown that the polarity of each conventional BA as well as new potential BA can be measured through the Reichardt's E_T(30) polarity scale. Using this criteria it was possible to find a substitute for MAPO (tris-(methylaziridinyl)-phosphine oxide), a conventional BA with the drawback of high toxicity and high reactivity, with TTPT (tris-(pyrrolidine)-phosphine oxide), a completely safe and effective BA. In this work, many other potential BA were evaluated through the Reichardt's E_T(30) polarity scale but only a selection of the potential BA were effectively tested in a standard CSRP. Particular interesting was the evaluation of TTPT vs MAPO showing the ability of the former BA to match the mechanical properties of the latter BA.

Keywords: Bonding agents (BA); composite solid rocket propellants (CSRP); Reichardt's E_T(30) polarity scale; mechanical properties of CSRP.

Introduction

Composite solid rocket propellants (CSRP) are the typical components of solid rocket motors. CSRP are based on highly filled elastomers matrix or binder and are used as energetic materials for military ordnance and rockets propulsion. As lively accounted by Mason and Roland (1), the actual standard formulation of solid composite propellants consists of hydroxyl-terminated polybutadiene (HTPB) (8-10%), an isocyanate crosslinker (1-2%), a crosslinking catalyst (0.1%), a plasticizer (0-10%), the oxidizer (60-90%), metal powder (0-20%), a bonding agent (1%), burn rate modifier (1%), antioxidant (0,1%). The standard oxidizer is currently the ammonium perchlorate while the preferred metal is aluminium (1-3). Of course, many new binders and oxidizers are becoming available (1-5), but the HTPB-based technology remains the current standard CSRP (1).

Among the mentioned compounding ingredients of a CSRP, the bonding agents (BA) are special and critical additives. The BA play a very critical role as compatibilizers between the crystalline and ionic filler or oxidizer represented for instance by ammonium perchlorate from one side and the apolar polymer matrix (e.g. hydroxyl-terminated polybutadiene = HTPB) (2). Although the BA are added into the propellant formulation in relatively small amounts, they lead to significant improvements in the propellant mechanical properties in terms of tensile strength, reducing possible failure risks upon high acceleration and deceleration i.e. the so-called slumping phenomenon (2,3). Other functions of the bonding agents regard the reduction of the accidental ignition risk of the solid propellants by counteracting its delamination (2,3). BA are relatively low molecular weight compounds characterized by the presence of two or more functional groups reactive with the curing agents (3). Perhaps, the most recent, updated and comprehensive review on BA is that of Gan et al. (6). Several classes of BA are presented and discussed in (6), including novel types of bonding agents and evaluation methods regarding the effectiveness of each BA. One key parameter considered in the evaluation of the effectiveness of a bonding agent regards the tensile strength and the elongation at break of the SRP (1,6). Additionally, other methods rely on surface tension evaluation (1,6), differential scanning calorimetry (7) and accelerated ageing of the CSRP (8).



Scheme 1 – Chemical structure of the Reichardt's dye i.e. 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate.

This work shows an innovative approach in the evaluation and in the selection of the bonding agents based on the application of Reichardt's solvent polarity scale (9-14) and other approaches. In particular, the Reichardt's empirical solvent polarity scale has already shown its effectiveness and usefulness in different fields and applications of chemistry as reported in ref. (9-14), including ionic liquids, solute-solvent interactions and relative solvatochromism (15), micellar systems (16) and so on. The Reichard's solvent polarity scale is based on the use of a dye called $E_T(30)$ which is characterized by a charge-separated zwitterionic structure and consists of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate or 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate (see chemical structure in Scheme 1) (9-14). The $E_T(30)$ dye acts as a molecular probe once dissolved in a solvent medium. More in detail, the Reichardt's dye is a molecule that exhibits a strong and negative solvatochromism, with the largest known hypsochromic shift (blue shift) of its charge-transfer (CT) electronic transition on passing from apolar or less polar liquid medium to high polar liquid. This effect is explained from the fact that the ground state of the $E_T(30)$ dye is characterized by a zwitterionic structure with charge separation and a dipole moment of 15 D while the excited state is instead characterized by a lower dipole moment of only 6 D (12). Thus, the vertical transition to the first excited state results in a significant decrease of the dye polarity since the excited state dipole moment is less than half the value of the ground state. In other words, the solute-solvent interaction which broadly speaking can be visualized by the position of the CT band of the $E_T(30)$, in the excited state interacts better with apolar solvents leading to low energy and long wavelengths electronic transition. In contrast, the $E_T(30)$ interaction with polar solvents requires higher energy and hence the CT band is found at shorter wavelengths. Spange et al. (17) have made a summary of the physical meaning attributed to the Reichardt's solvent polarity scale.

Experimental

The BA MAPO and K54 (Scheme 2) as well as the BA TEPAN and BIFA (Scheme 3) were commercially available chemicals which were used as received. All the other chemicals used in the present work, including the Reichardt's dye (Scheme 1) were purchased from Merck-Aldrich and used without any further purification.

Typical measurement procedure of the liquid polarity with the Reichardt's dye

The Reichardt's dye displays three main electronic transitions in its UV-VIS spectrum. The first two electronic transitions are not sensitive to the liquid polarity and occur at about 304-309 nm ($\varepsilon \approx 37000\text{-}46000\ M^{-1}\ cm^{-1}$) and at 374-389 nm ($\varepsilon \approx 9900\text{-}12000\ M^{-1}\ cm^{-1}$) (12). Only the longest wavelength electronic transition of Reichardt's dye is characterized by a remarkable solvatochromism from about 400 nm to the threshold of the near infrared spectral window, i.e. at about 850 nm with $\varepsilon \approx 5000\text{-}7000\ M^{-1}\ cm^{-1}$ (12). Consequently, in our study on the BA liquids we focused our attention to the latter band, which is due to the intramolecular charge-transfer transition from the HOMO (i.e. from phenolate) to the LUMO (i.e. pyridinium group) (12).

The liquid under study (10 ml) was loaded with the minimum quantity of Reichardt's dye sufficient to reach a reasonably good absorption band in the visible spectral range. The dissolution of the Reichardt's dye was achieved by stirring, seldom by gently heating. Since the Reichardt's dye is also thermochromic, all measurements were made using quartz cuvettes held in a TCC-100 thermoelectrically temperature controlled cell holder maintained at 24°C on a Shimadzu UV2450 spectrophotometer.

The polarity of each liquid BA studied was evaluated according to the following equations:

$E_T(30) = [28591/\lambda_{max}]$ (expressed in kcal/mol) (1)

$E_T(30) = [(28591 \bullet 4.184)/\lambda_{max}]$ (expressed in kJ/mol) (2)

The data are reported in Table 1 together with a series of selected $E_T(30)$ values of other representative liquids/solvents which may be considered pertinent to the present work and taken from other sources (10,11). It is worth reminding here that higher polarity liquids in the Reichardt's scale display the most energetic electronic transitions (corresponding to shorter wavelength position of the electronic transition of the dye), while the opposite reasoning applies to less polar liquids with the dye electronic transition red shifted toward longer wavelengths.

Mechanical properties of HTPB-SRP with different BA

A selection of BA, including the reference MAPO were mixed with HTPB and AP according to standard conditions (1,4) using the typical SRP formulation essentially disclosed in ref. (1). The selected formulation was based on: hydroxyl-terminated polybutadiene (HTPB) (18%), an isocyanate crosslinker (≈2%), a crosslinking catalyst (0.1%), the AP oxidizer (68%), metal powder (14%), a bonding agent (≈1%), burn rate modifier (1%), antioxidant (0,1%). No plasticizers like dioctyl adipate and the like were added to the formulation. The usual casting technique was employed to prepare the propellant samples, starting with the mixing of various ingredients with liquid HTPB for 2 h using a 4 kg stainless steel mixer under vacuum followed by the addition of calculated quantity of the diisocyanate and curing catalyst under vacuum. The test specimens were molded into dumbbell-shaped mold having the JANNAF dimensions (18,19). The samples were cured for 7 days at 60°C. The cured samples were tested at the Zwick dynamometer (using a crosshead speed 50 mm/min at +21°C) to determine the tensile strength and the elongation at break. The data reported are the averaged results of three test specimens for each BA evaluated. A blank, reference sample was prepared without any BA addition, to show the effect of BA on the mechanical properties of the SRP.

Results

Measurement of $E_T(30)$ value of selected current BA and potential BA candidates

Fig. 1 shows that the longest wavelength electronic transition of the Reichardt's dye in the reference BA MAPO occurs at 691.3 nm. Among the phosphoramides that potentially may replace MAPO, tris-(pyrrolidino)-phosphoric acid triamide (TTPT) was selected in this study (see discussion section for further details about this choice). Fig. 1 shows that the Reichardt's dye dissolved in TTPT shows the longest wavelength transition at 543.8 nm with a considerable hypsochromic shift with respect to that recorded to MAPO. The results are summarized in Table 1 also in terms of $E_T(30)$ scale and clearly suggest higher polarity for the TTPT with respect to MAPO. These aspects will be discussed more broadly in the next section. It is also curious that TTPT in addition to the neat peak at 543.8 nm shows also a long tail with a shoulder at 728 nm. The product was pure >97% as analyzed by GC and reported by the vendor. However, it is possible that some impurity present in the product yields the secondary shoulder at 728 nm.

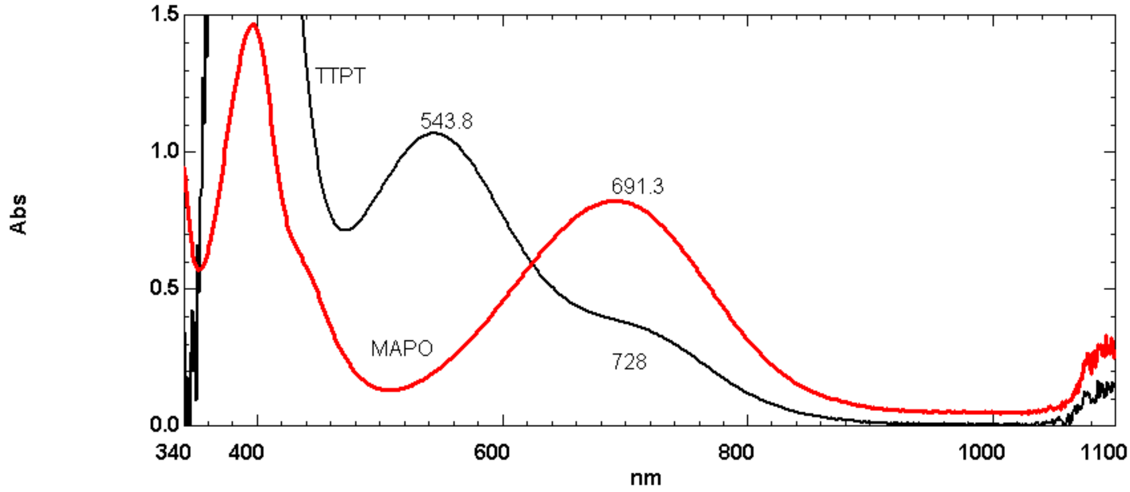


Fig. 1 – Electronic absorption spectra of Reichardt's dye dissolved in MAPO BA liquid and in the trial BA TTPT (for chemical structures see Scheme 2).

The other three commercially available BA, namely K54 (chemical structure shown in Scheme 2) as well as TEPAN and BIFA (see Scheme 3 for chemical structures) were also studied with the Reichardt's dye and the resulting electronic absorption spectra are reported in Fig. 2. Among these BA, the most energetic electronic transition is shown by BIFA at 607.1 nm, followed by the polyamine TEPAN at 642.2 nm and then K54 with the maximum at 682.4 nm. Also in this case, the electronic transitions of these BA are translated into the ET(30) scale in Table 1 using eq. (1) and (2).

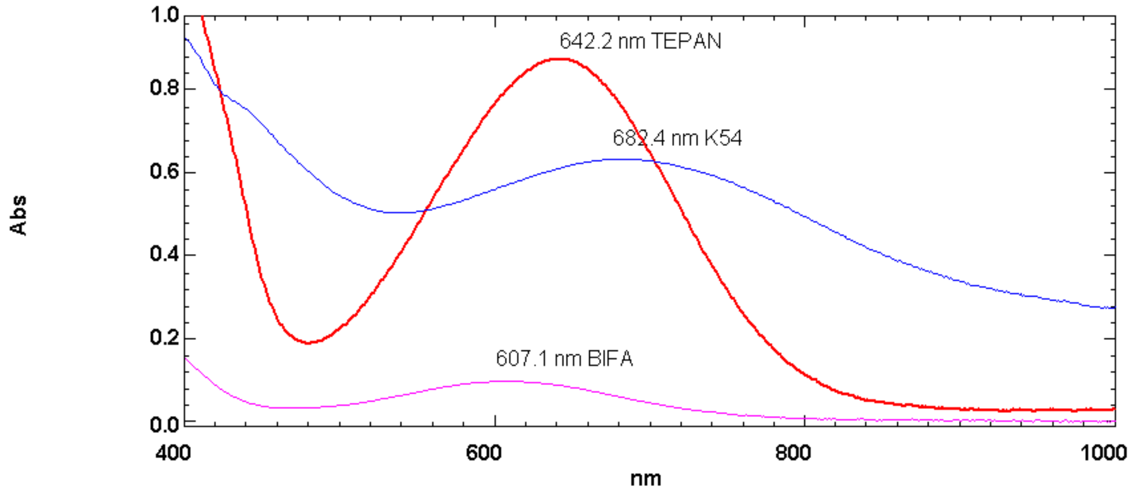


Fig. 2 – Electronic absorption spectra of Reichardt's dye dissolved in the following BA: TEPAN (red curve), K54 (blue curve) and BIFA or HX752 (pink curve) (for chemical structures see Scheme 2 and 3).

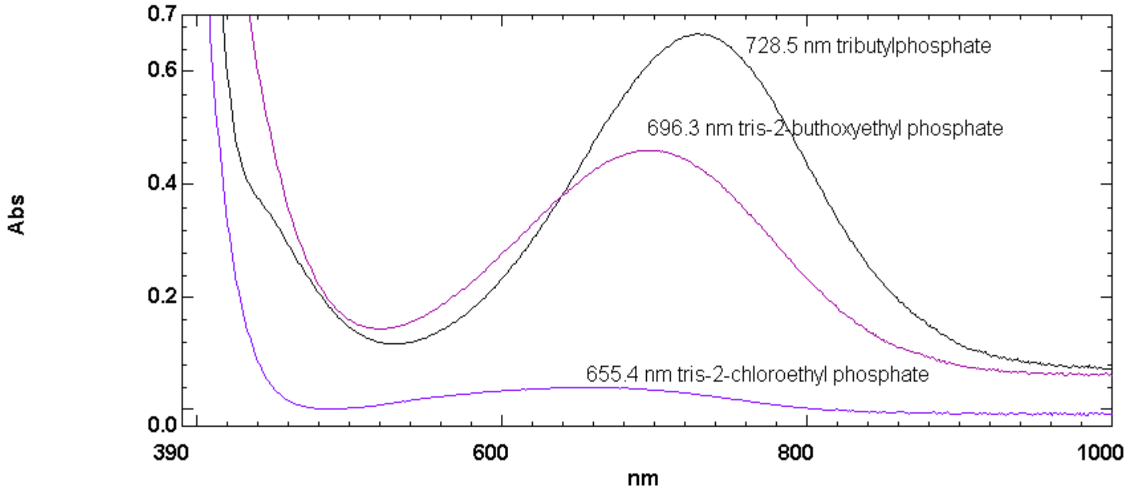


Fig. 3 – Electronic absorption spectra of Reichardt's dye dissolved in the following liquids: tributylphosphate (black curve), tris-(2-buthoxyethyl)-phosphate (dark pink curve) and tris-(2-chloroethyl)-phosphate (violet curve) (for chemical structures see Scheme 5).

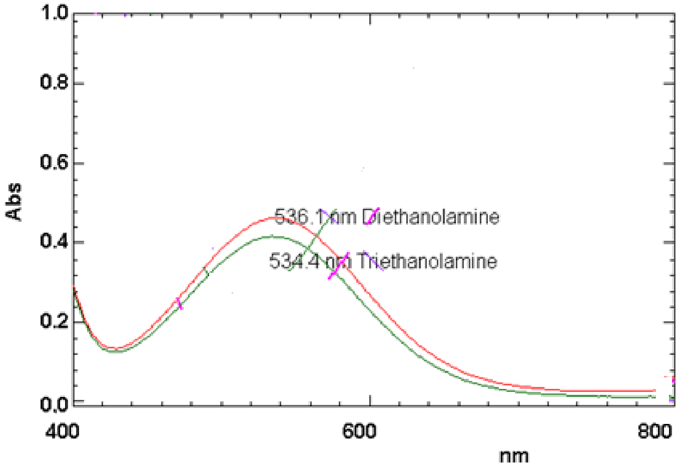


Fig. 4 – Electronic absorption spectra of Reichardt's dye dissolved in the following liquids: diethanolamine (red curve); triethanolamine (green curve).

As new potential BA, in addition to TTPT, a series of alkylphosphates were taken into consideration. The chemical structures of the selected alkylphosphates considered here are shown in Scheme 5. Since the $E_T(30)$ of simple alkylphosphates like trimethyl-, triethyl- and tri-n-propylphosphate was already measured and tabulated (10,11), we focused on the measurement of the $E_T(30)$ of tributhylphosphate, tris-(2-buthoxyethyl)-phosphate and tris-(2-chloroethyl)-phosphate. Fig. 3 shows the Reichardt's dye longest wavelength transition in the latter three liquids and the results are also reported in Table 1 in terms of $E_T(30)$ values. As heuristically expected, the polarity increases on passing from tributylphosphate to tris-(2-buthoxyethyl)-phosphate and reaches the maximum negative solvatochromism on the chlorinated derivative and tris-(2-chloroethyl)-phosphate.

In addition to the phosphates, we have also considered in this study the $E_T(30)$ value of diethanolamine and triethanolamine, molecules which have the double functionality alcoholic and amine and belong to the BA

TABLE 1 - SUMMARY OF THE ET(30) VALUES OF BONDING AGENTS AND OTHER LIQUIDS

	λ_{max}	$\tilde{\nu}$	$E_T(30)$	$E_T(30)$	ε_r	μ	Notes	Reference
	nm	*cm^{-1}*	**kcal/mol**	**kJ/mol**	Dielectric constant	Debye		
Triethanolamine (TEA)	*534.4*	*18713*	**53.5**	**223.8**	29.4	3.57	ref. (10) reports ET(30) = 49.6 kcal/mol	**This work**
Diethanolamine	*536.1*	*18653*	**53.3**	**223.1**	24.0	2.8		**This work**
tris-(tripyrrolidino)-phosphoric acid triamide (TTPT)	***543.8***	***18389***	**52.6**	**219.9**	**45.1**	**7.3**	ε and μ fm J. Chem. Soc. Chem. Comm. (1974) 295; μ =5.52 D in Bz 7.3 D in bulk	**This work**
1,1-isophthaloyl-bis-(2-methylaziridine) (HX752 or BIFA)	***607.1***	***16472***	**47.1**	**197.0**				**This work**
Propylene carbonate	*618.5*	*16168*	**46.2**	**193.4**	66.1	4.9	ref. (10) reports ET(30) = 46.0 kcal/mol	**This work**
Dimethyl sulfoxide	*625.0*	*16000*	**45.7**	**191.4**	47.2	4.0	ref. (10) reports ET(30) = 45.1 kcal/mol	**This work**
Acetonitrile	*627.0*	*15949*	**45.6**	**190.7**	36.6	3.9		9-11
TEPAN (*)	***642.2***	***15571***	**44.5**	**186.2**				**This work**
Sulfolane	*649.8*	*15389*	**44.0**	**184.1**	43.3	4.8		9-11
Trimethylphosphate (TMP)	*655.7*	*15251*	**43.6**	**182.4**	20.6	3.2		9-11
Tris-(2-chloroethyl)phosphate (TCEP)	*655.4*	*15258*	**43.6**	**182.5**				**This work**
N,N-Dimethylformamide (DMF)	*661.8*	*15110*	**43.2**	**180.7**	38.2	3.8		9-11
N,N-Dimethylacetamide (DMAC)	*666.4*	*15006*	**42.9**	**179.5**	38.8	3.8		9-11
N-metil-pirrolidone (NMP)	*677.5*	*14760*	**42.2**	**176.5**	32.2	4.1		9-11
Tris-(2,4,6-dimethylaminomethyl) phenol (K54)	***682.4***	***14654***	**41.9**	**175.3**				**This work**
Triethylphosphate (TEP)	*685.6*	*14586*	**41.7**	**174.4**	13.2	3.08		9-11
Benzonitrile	*688.9*	*14516*	**41.5**	**173.6**	25.2	4.2		9-11
tris-(2-methyl-1-aziridinyl)-phosphine oxide (MAPO)	***691.3***	***14465***	**41.4**	**173.0**	**14.6**	**3.5**	ε and μ fm J Mol Struct 69 (1980) 273 data on APO	**This work**
Tris-(2-buthoxyethyl)phosphate (TBUOP)	*696.3*	*14362*	**41.1**	**171.8**				**This work**
Tri-n-propylphosphate (TPP)	*706.0*	*14165*	**40.5**	**169.4**	10.0	3.75		9-11
Hexamethylphosphoramide (HMPA) or Hexamethylphosphoric acid triamide (HMPT)	*699.0*	*14306*	**40.9**	**171.1**	31.3	5.5	fm ref. 10,11 μ = 4.37 in bz and 5.5 in bulk	9-11
Hexamethyl phosphorothioic acid triamide (HMPTS)	*723.8*	*13816*	**39.5**	**165.2**	39.5	4.8	ε and μ fm J Phys Chem 78 (1974) 1018-1020	9-11
Tributyl phosphate (TBP)	*728.5*	*13727*	**39.2**	**164.2**	8.3	3.07		9-11
Aziridine or ethylenimine					18.3	1.9		
Diethylamine	*807.6*	*12382*	**35.4**	**148.1**	3.68	0.92		9-11
Trietylamine	*890.7*	*11227*	**32.1**	**134.3**	2.4	0.66		9-11

(*) reaction product between tetraethylenepentamine and acrylonitrile

All data on dielectric constants and electric dipole moment are from Lange's Handbook of Chemistry 15th edition, unless otherwise stated.

class of alcohol-amine (6). Fig. 4 shows the electronic absorption spectra of the Reichardt's dye dissolved in these two liquids. Table 1 reports also the corresponding $E_T(30)$ values. As shown in Table 1, our measurement shows a slightly higher $E_T(30)$ value of 53.5 kcal/mol for triethenolamine with respect to the tabulated value of 49.6 kcal/mol reported in ref. (10,11). Such value was also measured on diethanolamine with $E_T(30)$ = 53.3 kcal/mol as shown in Table 1.

Evaluation of selected BA in a standard CSRP

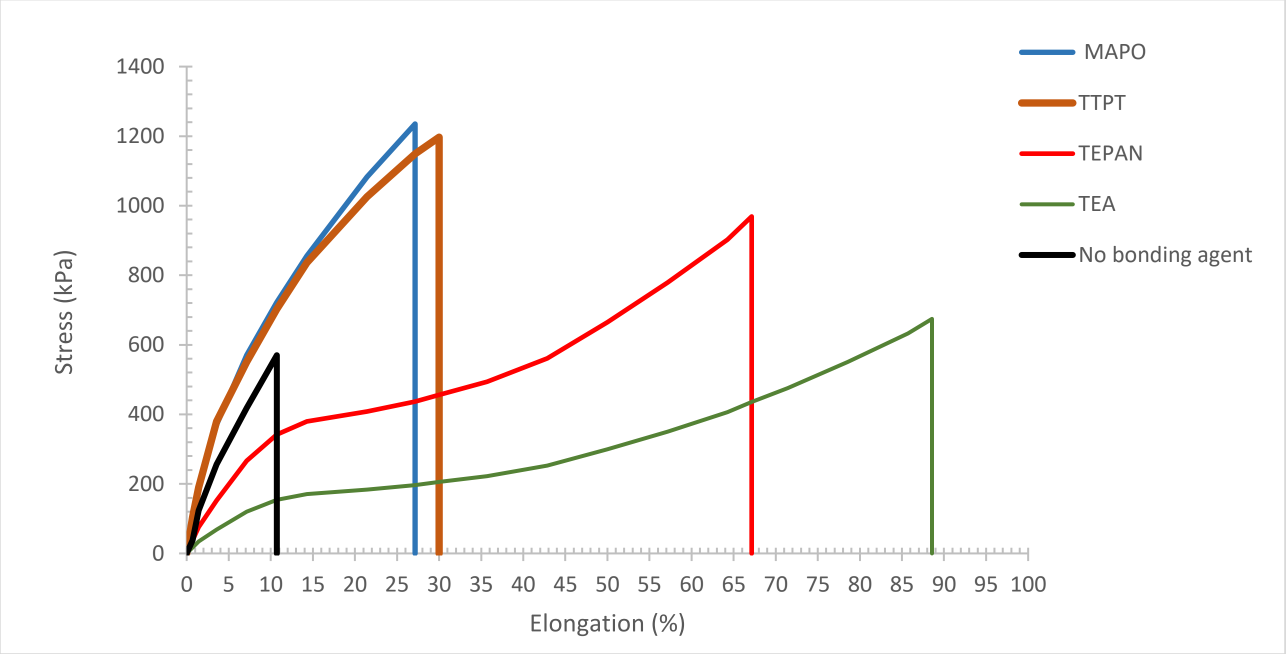


Fig.5 – Stress-strain properties of CSRP standard formulation compounded with 1% of different types of BA. MAPO represents the standard BA (blue trace), also TEPAN can be considered another standard (red trace). It is evident that TTPT (brown trace), proposed as new BA is matching the performances of MAPO while TEA (green trace) is not at the same level of TEPAN in terms of tensile strength (see discussion section form more details). The black trace is an example of SRP standard formulation compounded without BA.

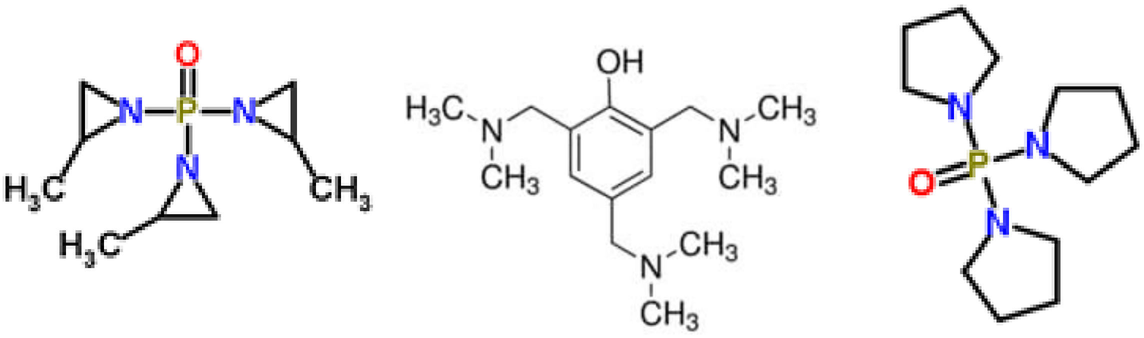
The evaluation of current and potential BA through the Reichardt's dye has revealed that the higher $E_T(30)$ value is offered by triethanolamine (TEA) followed by the phosphoramide TTPT (see Table 1). Thus, it was expected an excellent compatibilization effect between the AP filler and the HTPB binder or matrix exerted by these two potential BA. On the other hand, the current BA like BIFA (or HX752), TEPAN and K54 are characterized by lower $E_T(30)$ values (respectively 47.1, 44.5 and 41.9 kcal/mol) in comparison to TEA and TTPT (53.5 and 52.6 kcal/mol). It was then decided to evaluate both TEA and TTPT against TEPAN, excluding BIFA since its mechanism of action as BA is different than that of TEPAN and more similar to MAPO. The BA K57 was excluded from the evaluation in CSRP because its considerably lower polarity in the $E_T(30)$ Reichardt's scale and mechanism of action similar to that of TEA and TEPAN. Conversely, TEPAN can be seen somewhat similar in its mechanism of action to that exerted by TEA and TTPT. Finally, MAPO was evaluated in CSRP because it is the absolute reference BA, being a standard BA since long time in CSRP. The evaluation with the Reichardt's dye has revealed that MAPO is not characterized at all by a specially high polarity, since its $E_T(30)$ = 41.4 kcal/mol even closer to normal alkylphosphates which indeed were evaluated as well with the Reichardt's dye in Table 1. Previously, it was shown that either MAPO and APO are not characterized at by specially high donor number (DN) values (20), a circumstance more firmly confirmed later by other authors (21). The special or even unique properties of MAPO in terms of mechanism of action with AP was already discussed elsewhere (6) involving also the ring-opening polymerization of the aziridinyl rings (see also the discussion section).

Fig. 5 shows the mechanical properties of a standard CSRP in terms of stress strain properties. The CSRP compounded without any BA, it is immediately evident the low tensile strength (570 kPa) and the extremely low elongation at break (about 11%), which is due to the complete absence of the interaction between the HTPB binder (crosslinked with isocyanate) and the AP filler containing also Al particles. On the other hand, Fig. 5 shows the excellent performances of MAPO, which instead is able to rise considerably the key parameters represented by the tensile strength and the elongation at break respectively at 1235 kPa and 27% of elongation at break. Definitely, MAPO works well and it is an effective BA. Fig. 5 shows that also the new candidate BA phosphoramide derivative TTPT works as well as MAPO although its mechanism of action does not involve at all the ring-opening polymerization of the pyrrolidine. TTPT gives a tensile strength of about 1200 kPa with an elongation at 30%. These data suggest that TTPT is matching in full the performances of MAPO as BA in CSRP with a different mechanism of action and overcoming the great concerns linked to the high toxicity of MAPO.

Fig. 5 show also the performance of TEPAN and TEA in the standard CSRP. These two BA are able to supply higher elongation at break to the CSRP with the drawback of a reduction in tensile strength, which is more severe with the use of TEA. Of course, TEPAN and TEA are confirmed suitable BA in the hands of the CSRP compounder as a tool to produce especially high elasticity to the CSRP.

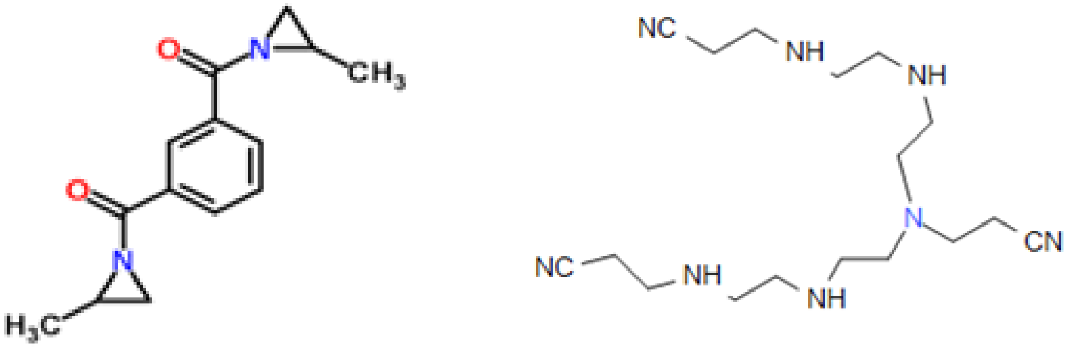
Discussion

As already stated in the introduction, the present study is focusing on a series of common bonding agents (BA) used in standard HTPB-based SRP. More in detail, the conventional bonding agents considered here are MAPO tris-(2-methyl-1-aziridinyl)-phosphine oxide shown in Scheme 2 together with K54 bonding agent which is tris-(2,4,6-dimethylaminomethyl) phenol. The other two conventional bonding agents considered here are respectively the BA BIFA or HX752 which is 1,1-isophthaloyl-bis-(2-methylaziridine) and TEPAN i.e. the reaction product between tetraethylenepentamine and acrylonitrile whose chemical structures are shown in Scheme 3.



MAPO K54 TTPT or TPPT

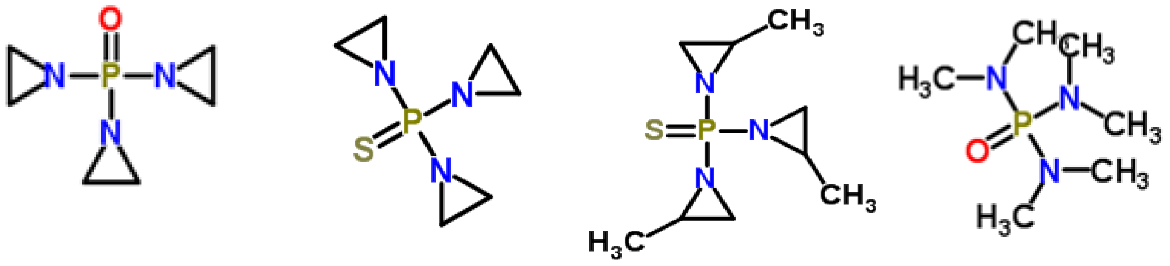
Scheme 2 – Bonding agent MAPO i.e. tris-(2-methyl-1-aziridinyl)-phosphine oxide and K54 i.e. tris-(2,4,6-dimethylaminomethyl) phenol and the trial BA tris-(pyrrolidine)-phosphine oxide (TTPT or TPPT).



BIFA (HX752) TEPAN

Scheme 3 – Bonding agent BIFA (called also HX752) i.e. 1,1-isophthaloyl-bis-(2-methylaziridine) and TEPAN i.e. reaction product between tetraethylenepentamine and acrylonitrile.

Surprisingly, among the BA used in the HTPB-based CSPR, one of the most popular is tris-(2-methyl-1-aziridinyl)-phosphine oxide (MAPO) whose application can be traced back to the fifties and sixties of the twenty century and it is still in use today. For instance, MAPO was patented as additive for fire-proof textiles in 1959, taking the advantage of its easy ring-opening reaction of the methylaziridine rings upon modest thermal treatments (22). Similarly, also the analogous tris-(aziridinyl)-phosphine oxide (APO) also known as tris-(ethylenimine)-phosporamide (TEPA) was used for the same purposes as MAPO (23). The use of MAPO in CSRP can be found for instance in a patent dated 1963 (24). The adoption of MAPO and seldom other phosphoramides as bonding agents rely on their high dipole moment, specific interaction with the oxidant of the SRP and also for their ring-opening polymerization and crosslinking tendency which is able to encapsulate the AP particles (6,25). However, there are also drawbacks in the use of MAPO, which span from processing problems in certain SRP formulations (25), to its high toxicity (26). Indeed, the search for other BA as substitutes of MAPO, it is supported also by the patent literature since long (25).



APO or TEPA ThioTEPA MethioTEPA HMPA or HMPT

Scheme 4 – (From left to right) Tris-(aziridinyl)-phosphine oxide (APO) also known as tris-(ethylenimine)-phosporamide (TEPA); the sulfur analogous of TEPA known as ThioTEPA (1,1',1''-phosphorothioyltriaziridine) and the sulfur analogous of MAPO called MethioMAPO (1,1',1''-Phosphoryltris-(2-methylaziridine) or also tris-(methylaziridinyl)-phosphine oxide) and HMPA (Hexamethyl phosphoric acid triamide).

Regarding the MAPO toxicity, the Merck Index (26) reports that it is a chemical sterilant for living organisms with the LD_{50} = 136 mg/kg (per os) in male mice, LD_{50} = 213 mg/kg (per os) in female mice, while LD_{50} = 183 mg/kg from skin absorption in mice. Furthermore, the Merck-Aldrich safety data sheet on MAPO, reports that it is a suspect carcinogen in humans (Cat 3) and carcinogen in animals (Cat 2).

From these premises, it derived our research for a safer BA than MAPO. Initially our interest focused on other phosphoramides (20). Scheme 4 shows some of the selected phosphoramides of our initial interest. First of all, APO or TEPA has the same chemical structure as MAPO but the difference is represented by the aziridine rings in place of methylaziridine rings (Scheme 4). TEPA is characterized by a high dipole moment 3.5 D (28), probably similar to that of MAPO, and it is high toxic with LD_{50} = 37 mg/kg (per os) in mice and it is used as well in chemotherapy as antineoplastic (29). Furthermore, ThioTEPA (30) and MethioTEPA present the same toxicity problems as the corresponding TEPA and MAPO since *in vivo* are oxidized to the latter two compounds respectively (31). Indeed, especially ThioTEPA it is still used as antineoplastic (30,31). Another drawback of ThioTEPA and MethioTEPA regards the very high surface tension respectively 77.8 and 57.7 dyne/cm in comparison to TEPA with 63.5 dyne/cm and MAPO with only 48.8 dyne/cm (27) which reduces considerably their ability to wet and adsorb on the AP particles. In conclusion, both TEPA, ThioTEPA and MethioTEPA, were no more considered for further studies as potential BA.

Another well-known and easily accessible phosphoramide is the hexamethylphosphamide (HMPA or HMPT) which, shows a series of properties somewhat similar to those of MAPO. For instance, the surface tension of HMPA is 34.4 dyne/cm, even lower than that of MAPO (48.8 dyne/cm) (27). Furthermore, in terms of dipole moment, as summarized in Table 1, HMPA has μ = 5.5 D in bulk and 4.35 D in benzene, values much higher than 3.5 D reported for MAPO. Indeed, also the $E_T(30)$ value in the Reichardt's scale suggest a similar polarity with 41.4 kcal/mol measured in this work for MAPO, against the tabulated value of 40.9 kcal/mol for HMPA. However, HMPA has the drawback to be carcinogen in animals and suspected carcinogen for humans (27,28). Thus, also HMPA was not considered further in this study.

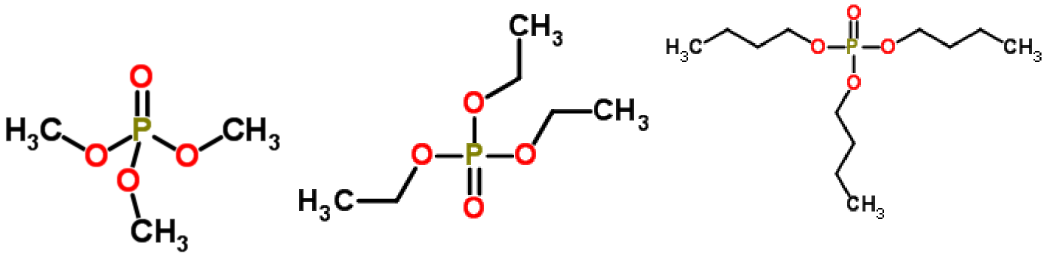
To remain in the field of phosphoramides our interest was attracted by the tris-(pyrrolidine)-phosphoramide or phosphine oxide (TTPT or TPPT) whose structure is shown in Scheme 2. First of all, this molecule appears completely safe based on the safety data sheet from Merck (32). Furthermore, it does not present the tendency to undergo ring-opening polymerization as in the case of the aziridine, methylaziridine (three membered rings) and azetidine rings (four membered ring). As already discussed previously (20), the ring-opening polymerization tendency of small rings in general is essentially driven by the strain energy of the ring. Thus, aziridine is highly strained and the strain energy of 27.1 kcal/mol is released during the ring-opening polymerization (33). For the higher homologue azetidine the ring strain energy can be estimated around 20 kcal/mol as released during the ring opening reaction, using the Van Krevelen's group increment (34). However, for pyrrolidine (five membered heterocycle) the strain energy is minimal, around 5 kcal/mol (33,34) and the ring-opening reaction is no more thermodynamically allowed and the same reasoning applies also piperidine (six-membered heterocycle) whose strain energy is nearly zero with no tendency at all to polymerize with the ring-opening mechanism. Now, the toxicity and other processing drawbacks of the phosphoramides derivatives of aziridine, methylaziridine and azetidine are linked to the ring-opening tendency especially by the action of Lewis acids and also in other conditions (20). To overcome these draw backs the first suitable member of the heterocyclic series is pyrrolidine and its phosphoramide derivative TTPT shown in Scheme 2. It must be emphasized that the mechanism of action of TTPT with AP oxidizer filler will be certain different than that of MAPO, since the ring-opening polymerization and coating of the AP granule will not occur with TTPT. Thus, the latter will act as a true plasticizer adsorbing as a liquid around the AP particles, substantially in a similar way as the conventional BA TEPAN.

As shown in Table 1 the candidate TTPT shows a considerably higher polarity either in the $E_T(30)$ scale with 52.6 kcal/mol with respect to 41.4 kcal/mol of MAPO as measured by us (see Table 1). These results with the Reichardt's scale are corroborated by the high dipole moment of TTPT measured at 7.3 D in bulk and at 5.53 D in benzene (35), considerably higher than that of MAPO observed at 3.5 D. Even the dielectric constant of TTPT results much higher than that of MAPO (45.1 vs 14.6 respectively, see Table 1). From these data it is

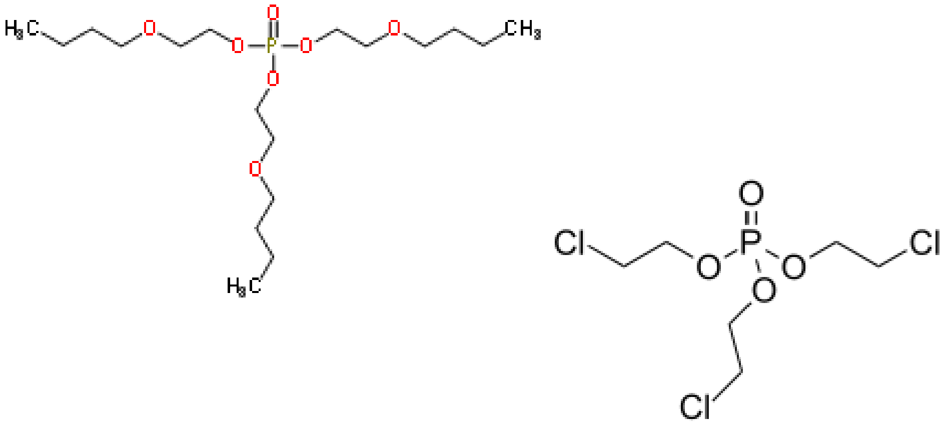
doi:10.20944/preprints202209.0017.v1

definitively demonstrated that MAPO (and APO) do not have any especially high polarity and any especially high donicity (20, 21). The unicity of MAPO as BA regards its mechanism of action with AP as summarized by other authors (6) and definitely involving the ring-opening polymerization mechanism on the AP surface. Regarding TTPT, the lack of ring opening polymerization is certainly compensated by the higher $E_T(30)$, µ and ε values with respect to MAPO.

In addition to TTPT as new candidate BA, we have considered also a selection of alkylphosphates shown in Scheme 5. The phosphates may resemble the phosphoramides with the substitution of nitrogen atoms with oxygen and are all characterized by $\mu > 3$ D (see Table 1). In general phosphate are indeed used as plasticizers for plastics and rubbers and used also as special selective solvents for certain electrolytes. The Reichardt's E_T (30) scale shows that TMP with 43.6 kcal/mol and TCEP with nearly similar value are very close to the conventional BA polyamine called TEPAN (see Scheme 1). On the other hand, TEP shows an E_T (30) value of 41.2 kcal/mol closer to the conventional BA named K54 (see Table 1). TBUOP in its turn is closer to MAPO in the E_T (30) scale (41.1 vs 41.4 kcal/mol respectively). Only TPP and TBP, being composed by long aliphatic chains have lower values in the E_T (30) scale. Based on these results, it would be worth to evaluate TMP and TCEP as replacement of TEPAN, TEP as replacement of K54 and TBUOP as potential replacement of MAPO in a CSRP. However, for the time being it was decided to give preference to potential BA which are characterized by very high E_T (30) values i.e. TTPT and TEA.



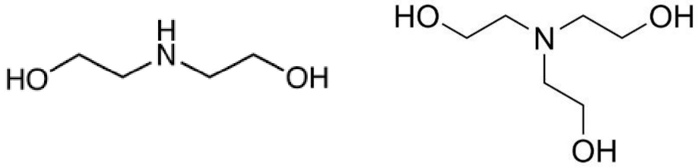
Trimethylphosphate (TMP) Triethylphosphate (TEP) Tributylphosphate (TBP)



Tris-(2-butoxiethyl) phosphate (TBUOP) Tris-(2-chloroethyl)phosphate (TCEP)

Scheme 5 – Chemical structures of a series of alkylphosphates consideres as potential BA.

As shown in Table 1, it turned out that the alcohol-amine BA called TEA (see Scheme 6 for structure) shows the highest $E_T(30)$ value with 53.5 kcal/mol among the selected liquids, although previous measurements have suggested a slightly lower $E_T(30)$ value of 49.6 kcal/mol (10,11). TEA is followed by BIFA (or HX752) in the $E_T(30)$ scale and TTPT is just in the middle between these two BA. BIFA is also an azirdinyl derivative as shown in Scheme 3 also with its mechanism of interaction with AP may remind MAPO.



Diethanolamine Triethanolamine

Scheme 6 – Chemical structures of diethanolamine and triethanolamine

In the results section it was already explained the rationale behind the selection of TTPT and TEA to be tested as BA in a standard CSRP. Essentially the selection fell on two potential BA characterized by high $E_T(30)$ values (among the liquids considered here). The phosphates were excluded this time from the evaluation because of a restricted number of CSRP compounds scheduled. As reference, MAPO was used because it is a universal reference BA in CSRP compounds with its special mechanism of interaction with AP, while TEPAN was selected because it is a polyamine with relatively high $E_T(30)$ value but mechanism of interaction with AP definitely different with respect to MAPO.

The results of CSRP evaluation reported in Fig. 5 suggest that the selection of TTPT was really successful. Because of its high polarity, it is able to compensate the MAPO ring-opening polymerization over AP granules probably with an excellent AP-TTPT dipolar interaction which may recall solvation. After all, AP is fully soluble either in MAPO or in TTPT at room temperature (36). The results in Fig. 5 are showing that TTPT is able to match in full the CSRP mechanical properties of MAPO both in terms of tensile strength and elongation at break. On the other hand, TEPAN and TEA are instead able to supply higher elongation at break to the CSRP compound at the expenses of a relatively lower tensile strength.

Conclusions

MAPO is the standard bonding agent used on CSRP but it is highly toxic to handle and it is also too reactive. It was shown that using the Reichardt's $E_T(30)$ scale it was possible to study the polarity of a selection of conventional liquid BA including MAPO and then, using the same $E_T(30)$ scale, also new potential BA were selected. The most remarkable new BA found in this study is TTPT which is safer than MAPO since it is not toxic and it does not undergo hazardous polymerizations. Once tested in CSRP compound as substitute of MAPO, the new bonding agent TTPT is able to match in full the mechanical properties of the CSRP compounded with MAPO.

With the present work, a new dimension has been added in the selection and evaluation of the BA for CSRP, the effective use of the Reichardt's $E_T(30)$ scale of polarity.

Author Contributions: Conceptualization, F.C.; methodology, F.C.; software, F.C.; validation, F.C.; formal analysis, F.C.; investigation, F.C.; resources, F.C.; data curation, F.C.; writing—original draft preparation, F.C.; writing—review and editing, F.C.; visualization, F.C..

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Acknowledgments: none

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mason, B. P.; Roland, C. M. Solid propellants. *Rubber Chem. Technol.* **2019**, *92*, 1-24.

2. Koch, E.C. *High Explosive, Propellants, Pyrotechnics*. W. De Gruyter GmbH, Berlin, **2021**.

3. Varghese, T. L.; Krishnamurthy, V. N. *The Chemistry and Technology of Solid Rocket Propellants*. Allied Publishers, New Dehli, **2017**.

4. Lysien, K.; Stolarczyk, A.; Jarosz, T. Solid propellant formulations: A review of recent progress and utilized components. *Materials*, **2021**, *14*, 6657.

5. Cheng, T. Review of novel energetic polymers and binders–high energy propellant ingredients for the new space race. *Design. Monom. Polym.* **2019** ,*22*, 54-65.

6. Gan, J.; Zhang, X.; Zhang, W.; Hang, R.; Xie, W.; Liu, Y.; Luo, W. ;Chen, Y. Research progress of bonding agents and their performance evaluation methods. *Molecules*, **2022** ,*27*, 340.

7. Nguyen, T. T.; Phan, D. N.; Nguyen, D. C.; Do, V. T.; Bach, L. G. The chemical compatibility and adhesion of energetic materials with several polymers and binders: a study. *Polymers*, **2018**, *10*, 1396.

8. Naseem, H.; Yerra, J.; Murthy, H.; Ramakrishna, P. A. Ageing studies on AP/HTPB based composites solid propellants. *Energ. Mater. Front.* **2021** ,*2*, 111-124.

9. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*. 3rd edition. Wiley-VCH, Weinheim, **2003**.

10. Reichardt, C. Pyridinium-N-phenolate betaine dyes as empirical indicators of solvent polarity: Some new findings. *Pure Appl. Chem.* **2008** ,*80*, 1415-1432.

11. Welton, T.; Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*. 4th edition. John Wiley & Sons, New York, **2011**.

12. Wielgus, M.; Zaleśny, R.; Murugan, N. A.; Kongsted, J.; Ågren, H.; Samoc, M.; Bartkowiak, W. Two-photon solvatochromism ii: experimental and theoretical study of solvent effects on the two-photon absorption spectrum of Reichardt’s dye. *ChemPhysChem*, **2013**, *14*, 3731-3739.

13. Cerón-Carrasco, J. P.; Jacquemin, D.; Laurence, C.; Planchat, A.; Reichardt, C.; Sraïdi, K. Solvent polarity scales: determination of new ET (30) values for 84 organic solvents. *J. Phys. Org. Chem.* **2014** ,*27*, 512-518.

14. Reichardt, C. Solvation effects in organic chemistry: a short historical overview. *J. Org. Chem.* **2021** ,*87*, 1616-1629.

15. Cataldo, F. Ozone solvatochromism in selected solvents. *J.Mol. Liq.*, **2018** ,*265*, 733-739.

16. Mchedlov-Petrossyan, N. O.; Vodolazkaya, N. A. Protolytic equilibria in organized solutions: ionization and tautomerism of fluorescein dyes and related indicators in cetyltrimethylammonium chloride micellar solutions at high ionic strength of the bulk phase. *Liquids*, **2021** ,*1*, 1-24.

17. Spange, S.; Weiß, N.; Schmidt, C. H.; Schreiter, K. Reappraisal of empirical solvent polarity scales for organic solvents. *Chemistry-Methods* **2021** ,*1*, 42-60.

18. NourEldin, A.F.; Adel, W.M.; Attai, Y.A.; Ismail, M.A. *IOP Conf. Ser.: Mater. Sci. Eng.* 2020, *973***,** 012030.

19. Boshra, I.K.; Lin, G.; Elbeih, A. Influence of different crosslinking mixtures on the mechanical properties of composite solid rocket propellants based on HTPB. *High Perf. Polym.***2021**, *33*, 52–60

20. Cataldo, F. A revision of the Gutmann donor numbers of a series of phosphoramides including TEPA. *Eur. Chem. Bull.* **2015**, *4*, 92-97.

21. Gal, J. F.; Maria, P. C.; Yáñez, M.; Mó, O. On the Lewis basicity of phosphoramides: A critical examination of their donor number through comparison of enthalpies of adduct formation with $SbCl_5$ and BF_3. *ChemPhysChem*, **2019**, *20*, 2566-2576.

22. Chance, L.H.; Drake, G.L. Jr.; Reeves, W.A. “Flame resistant organic textiles and method of production” U.S. Patent No. 2,891,877. Jun. 23, **1959**.

23. Pearce, E. (Ed.) Flame Retardant Polymeric Materials. Plenum Press, New York, **1975**.

24. Hudson, P.S.; Bice, C.C. “Solid composite propellants containing aziridinyl curing agents” U.S. Patent No. 3,087,844. Apr. 30, **1963**.

25. Obert, A. “Bonding agents for HTPB-type solid propellants”. U.S. Patent No. 5,417,895. May 23, **1995**.

26. O’Neal M.J. (Ed.) *Merck Index* 14ª ed., Merck Research Laboratories, Whitehouse Station, NJ, **2006** paragraph 5936.

27. Data from Chemspider website: http://www.chemspider.com/

28. Bollinger, J. C.; Yvernault, G.; Yvernault, T.; Julg, A.; Rajzmann, M. Moments dipolaires et conformations de l'hexaméthyl-phosphotriamide (HMPT) et des dérivés aziridinylés correspondants. *J. Mol. Struct.*, **1980** , *69*, 273-288.

29. O’Neal M.J. (Ed.) *Merck Index* 14ª ed., Merck Research Laboratories, Whitehouse Station, NJ, **2006**, paragraph 9672.

30. O’Neal M.J. (Ed.) *Merck Index* 14ª ed., Merck Research Laboratories, Whitehouse Station, NJ, **2006**, paragraph 9673.

31. Heath, D.F. *Organophosphorus Poisons Anticholinesterases and Related Compounds*. Pergamon Press, Oxford, UK, **1961**.

32. TTPT safety data sheet from Merck website: https://www.sigmaaldrich.com/IT/en/sds/aldrich/93404

33. Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*. Academic Press, London, **1970**, p. 574.

34. Van Krevelen, D. W. *Properties of Polymers. Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*. Elsevier, Amsterdam, **1990**, Chapter 20.

35. Ozari, Y.; Jagur-Grodzinski, J. Donor strength of N-substituted phosphoramides. *J. Chem. Soc. Chem. Comm.* **1974**, 295-296.

36. Cataldo, F. (2015). Unpublished results.