©*Proc. Indian natn. Sci. Acad.*, **52**, A, No. 3, 1986, pp. 676–684
Printed in India.

MIXED GLYCOLS BASED SEMI-RIGID UNSATURATED POLYESTERS FOR INHIBITION OF DOUBLE BASE PROPELLANTS*

J P AGRAWAL**, M P CHOUK, A K SINGHAL, K S KULKARNI *and* P S VASUDEVAN

Explosives Research and Development Laboratory, Pashan, Pune 411 021, India

(*Received 17 June 1985; after revision 11 November 1985*)

Rigid unsaturated polyester based on propylene glycol has been reported to possess all the desirable properties of a good barrier layer, except the reaction time which is more (about 32–35 hours). The reaction time has been decreased by the use of mixed glycols i.e. propylene glycol and diethylene glycol. Six numbers of semi-rigid unsaturated polyesters based on isophthalic acid, maleic anhydride and propylene glycol and diethylene glycol (in different molar proportions) have been synthesised and studied for various characteristics.

Based on the data, semi-rigid unsaturated polyester-2 (SRUP-2) has been selected for inhibition of double base propellant. The successful performance of SRUP-2 is confirmed by the results of static evaluation of DB propellant sustainers inhibited with this semi-rigid unsaturated polyester-2 as a barrier coat and ERDL, EP-4 as a main inhibitor at ambient, cold (— 40 °C) and hot (+ 50 °C) temperatures.

Key Words: Semi-rigid Polyesters; Inhibition; Double-base Propellants; Insulation

1. INTRODUCTION

THE use of unsaturated polyesters[1–7] and chloro polyesters[8–10] has become popular in recent years for the inhibition of double base rocket propellants. Inhibition of double base propellants is usually done: (1) by interpositioning barrier coats, resistant to ingress of nitroglycerine (NG) before application of flexible polymerics and (2) without applying any barrier coat.

Several polymeric materials, such as rigid epoxides, rigid polyvinyl chloride, carboxy terminated polybutadiene, rigid polyesters, silicone, butyl and neoprene rubbers etc., which are useful as barrier coats, have been reported in the literature.[7]

Rigid unsaturated polyester-3 (RP-3) based on propylene glycol has been synthesised which possesses all the desirable properties of a good barrier layer, except the reaction time which is more (32-35 hours).[3]

In this study an attempt has been made to decrease reaction time by the use of mixed glycols i.e. propylene glycol and diethylene glycol. A number of semi-rigid unsaturated polyesters based on isophthalic acid, maleic anhydride and

*Paper presented at the 3rd seminar on '*High Energy Materials*' at ERDL, Pune, Nov. 1984.
**To whom all correspondence should be addressed.

propylene glycol and diethylene glycol (in different molar proportions) have been synthesised and studied for gel time, exotherm peak temperature, tensile strength, per cent elongation, bond strength with DB propellant (containing 2-NDPA, 2-Nitrodiphenyl amine, as a stabiliser), nitroglycerine and water absorption, heat resistance and flame retardance. The results of inhibition and static evaluation trials are also incorporated in this paper.

2. Materials and Methods

The materials required for the work

Propylene glycol, (BDH, LR)

Diethylene glycol, (BDH, LR)

Isophthalic acid, (mp 340–345 °C, purity 98 per cent min.)

Maleic anhydride, technical (mp 51 ± 2 °C, purity 98.5 per cent min.)

Styrene monomer, (bp 145 ± 2 °C, sp. gr. 0.9055 at 25 °C)

and other miscellaneous chemicals were procured and used as such.

2.1 *Synthesis of Semi-rigid Unsaturated Polyesters*

Semi-rigid unsaturated polyesters were prepared by a two step process in accordance with the method described in our earlier communication.[3] The compositions and the acid values of these polyesters are depicted in Table I.

Table I

Compositions and acid values of semi-rigid unsaturated polyesters

Semi-rigid unsaturated polyester (SRUP)	*Molar compositions*				*Acid value*+		*Reaction time (Hours)*
	Isophthalic acid	*Maleic anhydride (MAn)*	*Diethylene glycol**	*Propylene glycol**	*Before adding MAn*	*After adding MAn*	
SRUP-0	1/3	2/3	0.0	1.0	49.0	41.0	32–35
SRUP-2	1/3	2/3	0.2	0.8	50.5	39.0	24–25
SRUP-4	1/3	2/3	0.4	0.6	50.0	41.5	22–23
SRUP-6	1/3	2/3	0.6	0.4	50.0	39.0	18–19
SRUP-8	1/3	2/3	0.8	0.2	51.0	39.0	16–17
SRUP-10	1/3	2/3	1.0	0.0	50.0	42.0	12–14

*Glycols are taken 20 per cent extra by weight to compensate glycols losses.

+Synthesis of Semi-rigid Unsaturated Polyester is a two-step process.

1st Step Reaction—Mixed glycols + Isophthalic acid $\xrightarrow[(-H_2O)]{\text{Heat}}$ Low Mol. Wt. Esters (A.V. = 50) (Before Adding MAn)

2nd Step Reaction—Reaction product of 1st step + MAn $\xrightarrow[(-H_2O)]{\text{Heat}}$ SRUP (A.V. = 40). (After Adding MAn)

2.2 *Characterization of Semi-rigid Unsaturated Polyesters*

Semi-rigid unsaturated polyesters were characterized for the following properties :—

- Gel time and exotherm peak temperature.[4]
- Tensile strength and per cent elongation.[11]
- Bond strength[12] with DB propellant (containing 2-NDPA as a stabilizer).
- Nitroglycerine absorption.[12]
- Water absorption.[13]
- Heat resistance.[14]
- Flame retardance.[4]

2.3 *Inhibition and static evaluation trials*

The cast double base propellant sustainer (containing 2-NDPA as a stabilizer) was machined to 108mm diameter and 120mm length. The inhibition of the propellant was done with SRUP-2 as barrier coat and ERDL, EP-4 and styrene as main inhibitor similar to the method already described.[3] The inhibition thickness was kept 2.75 to 3.0mm. Similarly three propellant sustainers were inhibited and statically evaluated one; each at ambient, cold (−40 °C and hot (+50 °C) temperatures after conditioning.

3. Results and Discussion

3.1 *Gel Time and Exotherm Peak Temperature*

The gel time and exotherm peak temperature data are presented in Table II and time versus temperature curves (exotherms) obtained are shown in Fig. 1. It is observed that as the short chain glycol (propylene glycol, PG) is replaced by the long chain glycol (diethylene glycol, DEG), gel time gradually increases and exotherrm peak temperature decreases. The gel time and exotherm peak temperature for SRUP-0 are 22min and 129 °C respectively whereas for SRUP-10 are 74min and 70 °C. This may be explained on the basis of molecular weight per unsaturated acid. As the PG is replaced by DEG, the molecular weight per unsaturated acid will increase and consequently the number of polyester chains will decrease in order to maintain the same mol. wt. (the no. av. mol. wt. $\bar{M}n$ is of the same order for all semi-rigid unsaturated polyesters, as acid values are practically same). Since the long chain polyester molecules are less reactive, it is expected that the gel time will increase as the PG is replaced by DEG.

The bond energy of a carbon-carbon double bond (C=C) is 100kcal/mole and that of a carbon-carbon single bond (C—C) is 58.6kcal/mole.[15] The unsaturated polyester chains are linked to one another through the conversion of double bonds into single bonds during polymerization and as a result, 17.2kcal/mole (2 × 58.6–

TABLE II

Characteristics of semi-rigid unsaturated polyesters

Semi-rigid Unsaturated Polyester (SRUP)	Gel time* (min) ± 1 min	Exotherm Peak* temperature 0 °C ± 5 °C	Tensil Strength kg/cm²	Percentage Elongation	Bond Strength kg/cm²	Rate of Burning (mm/sec)
SRUP-0	22	129	229.0	8	85.0	0.29
SRUP-2	32	114	166.5	10	62.0	0.33
SRUP-4	43	108	137.0	13	60.7	0.34
SRUP-6	50	100	123.2	14	55.0	0.37
SRUP-8	56	96	118.0	18	48.0	0.39
SRUP-10	74	70	115.0	20	45.0	0.40

*1 per cent Accelerator and 1 per cent catalyst and at 40 °C.

100 = 17.2) energy is liberated. As the number of polyester chains decreases with the replacement of PG by DEG, it is expected that the amount of heat liberated during gelling will decrease from SRUP-0 to SRUP-10 or exotherm peak temperature will gradually decrease from SRUP-0 to SRUP-10.

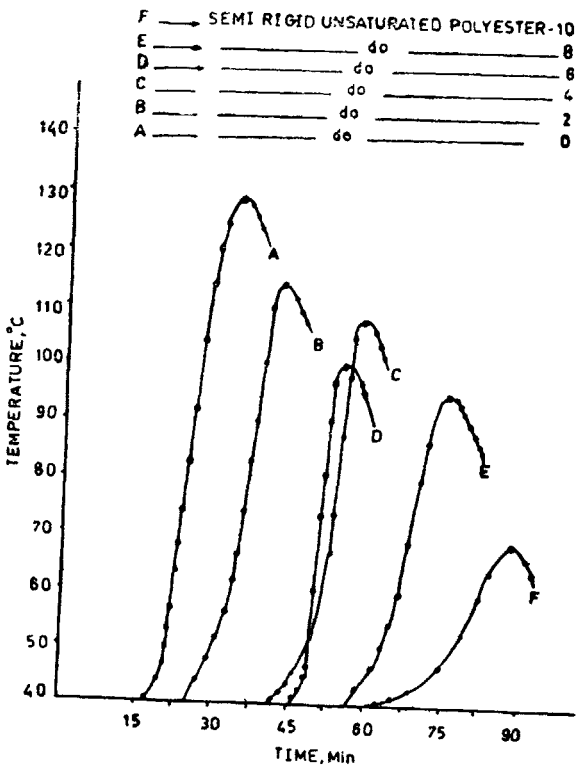

FIG 1 Exotherms for semi-rigid unsaturated polyester.

3.2 *Tensile Strength, Percentage Elongation and Bond Strength*

The mechanical properties of semi-rigid unsaturated polyesters are presented in Table II. As the molar proportion of diethylene glycol is increased from SRUP-0 to SRUP-10, tensile strength as well as bond strength decreases while percentage elongation increases. This is in accordance with the observation made by us in case of chloropolyesters (based on mixed glycols and tetrachloro phthalic anhydride) that crosslink density and tensile strength are interlinked and if one increases, other also increases.[16] This may also be explained on the basis of analogy of the gel time and exotherm peak temperature. As propylene glycol (PG) is replaced by diethylene glycol (DEG), the number of unsaturated polyester chains will decrease in order to have the same molecular weight. Since the polyester chains are linked to one another through the unsaturated linkages and as the number of polyester chains are gradually decreasing, the crosslinking density will also decrease, resulting into decrease in tensile strength and increase in percentage elongation from SRUP-0 to SRUP-10.

The bond strength with the double base propellant decreases as propylene glycol (PG) is replaced by diethylene glycol (DEG). The reason for this is not well understood. However, it is observed that flexible and slow curing polyesters have a weak bond with 2-NDPA containing propellant whereas rigid and fast curing polyesters have strong bond. It is perhaps due to migration of nitroglycerine (NG) and other nitrobodies such as 2-NDPA from the propellant to the inhibitor, which interfere with the polymerization/curing/crosslinking process, resulting into incomplete curing and weaker bond. As the gel time increases with the increase in diethylene glycol molar proportion, the quantum of interference as a result of migration of NG and nitrobodies increases and therefore, bond strength decreases.

3.3 *Nitroglycerine and Water Absorption*

Nitroglycerine and water absorption data are compiled in Table III and Table IV respectively. It is observed that water absorption is the highest in the case SRUP-10. This is due to two reasons.[15]

i. The increased flexibility of the cured product caused by the ether linkages in diethylene glycol.

ii. The increased hydrophilicity due to the polarity of the ether oxygen.

The liquid absorption is minimum in the case of SRUP-0 due to the greater rigidity of the molecular structure. The rigidity decreases as PG is replaced by DEG and therefore NG and water absorption increase from SRUP-0 to SRUP-10. This is also supported by the data of Parker and Moffett.[17]

3.4 *Heat Resistance*

Heat resistance has been measured in the form of volatile losses at 150 °C and data are given in Table V.

TABLE III

Effect of time on nitroglycerine absorption of semi-rigid unsaturated polyesters

Semi-rigid Unsaturated Polyester (SRUP)	Nitroglycerine Absorption, per cent (Wt/Wt)							
	days							
	1	2	4	6	8	10	12	14
SRUP-0	1.29	1.68	1.85	2.75	2.98	3.14	3.18	3.22
SRUP-2	1.33	1.81	2.37	2.78	2.99	3.42	3.48	3.60
SRUP-4	1.61	2.04	2.70	3.13	3.40	3.68	3.97	4.15
SRUP-6	1.65	2.30	3.00	3.40	3.75	3.95	4.15	4.30
SRUP-8	2.98	3.64	4.54	5.17	5.45	5.85	6.20	6.47
SRUP-10	4.57	Specimens broke into pieces						

TABLE IV

Effect of time on water absorption of semi-rigid unsaturated polyesters

Semi-rigid unsaturated polyester (SRUP)	Water Absorption, per cent (Wt/Wt)					
	days					
	1	2	3	4	5	6
SRUP-0	0.47	0.69	0.76	0.92	1.02	1.12
SRUP-2	0.48	0.75	0.90	1.11	1.25	1.30
SRUP-4	0.54	0.82	1.04	1.21	1.37	1.43
SRUP-6	0.61	0.94	1.20	1.32	1.45	1.58
SRUP-8	1.30	1.96	2.32	2.72	3.01	(+)
SRUP-10	2.15	2.61	2.99	(+)	(+)	(+)

(+) Specimens broke into pieces.

TABLE V

Heat resistance (volatile losses) of semi-rigid unsaturated polyesters at 150 °C

Semi-rigid Unsaturated Polyester (SRUP)	Loss in weight, per cent					
	hours					
	1	2	3	4	5	6
SRUP-0	0.38	0.48	0.66	0.83	0.87	1.02
SRUP-2	0.40	0.56	0.70	0.90	0.99	1.18
SRUP-4	0.42	0.60	0.75	0.94	1.12	1.34
SRUP-6	0.44	0.65	0.85	1.01	1.24	1.42
SRUP-8	0.84	1.31	1.70	1.99	2.20	2.36
SRUP-10	1.37	2.26	3.10	3.62	3.82	3.86

Loss in weight increases with time of exposure for all semi-rigid polyesters and loss is minimum in case of SRUP-0 and maximum in case of SRUP-10. This shows that polyester based on DEG is more susceptible to heat degradation. As explained earlier crosslinking density is maximum in case of semi-rigid unsaturated polyester-0 (SRUP-0) based on PG and the extent of crosslinking decreases with the replacement of PG by DEG. Once the extent of crosslinking (rigidity of the molecular structure) is decreasing from SRUP-0 to SRUP-10, it is expected that the loss in weight will also increase in this direction, which is observed experimently. In other words, heat resistance decreases from SRUP-0 to SRUP-10.

3.5 *Flame Retardance*

The flame retardance of semi-rigid unsaturated polyesters has been reported in terms of burning rate, which has been depicted in Table II. The data shows that the burning rate is progressively increasing as propylene glycol is replaced by diethylene glycol. This can be explained if we assume that polymer degradation governs the regression rate. It has already been explained under tensile strength and per cent elongation data (shown in Table II) that the crosslinking density decreases as PG is replaced by DEG. It means that SRUP-0 possesses maximum crosslinking density which decreases progressively from SRUP-0 to SRUP-10. Therefore, SRUP-0 requires greater energy for breaking the polymer chains as compared to other semi-rigid polyesters to give degradation products responsible for the flame reactions. Thus, the burning rate increases as the crosslinking density decreases from SRUP-0 to SRUP-10. This is similar to the data reported[18] in the literature in case of composite propellants.

3.6 *Reaction Time*

The reaction time required for synthesis of these semi-rigid unsaturated polyesters is also depicted in Table I. It is seen that the reaction time decreases as the short chain glycol (PG) is replaced by long chain glycol (DEG). The reaction time for the synthesis of SRUP-0 is 32–35 hours and it comes down to 24–25 hours on replacement of 20mol per cent of PG by DEG.

The tensile strength, percentage elongation, bond strength and nitroglycerine absorption are very important properties of polymeric materials and a compromise among these properties is made to ensure successful performance during static evaluation at ambient and extreme temperatures while selecting for inhibition of rocket propellants.

The data of these properties for SRUP-2 are :

Tensile strength, kg/cm^2	166.5
Percentage elongation	10.0
Bond strength, kg/cm^2	62.0
Nitroglycerine absorption, (per cent age) (after 14 days by Liquid Absorption Method)	3.60

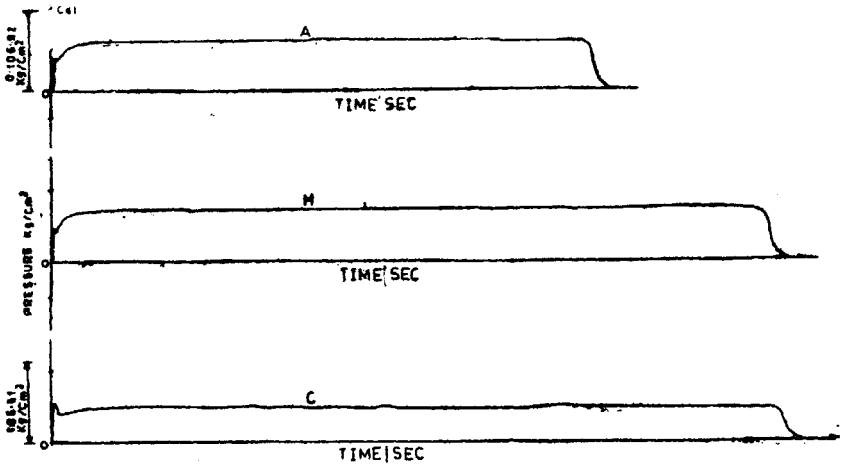

FIG 2 Pressure—time profiles for double base rocket propellant sustainer inhibited with semi rigid unsaturated Polyester-2 as sarrier coat and ERDL, EP-4 as main inhibitor.

A—Ambient
H—Hot
C—Cold

The semi-rigid unsaturated polyester possessing these properties i.e. SRUP-2 is considered suitable as a barrier coat during the inhibition of DB propellants.

The inhibited, machined and X-rayed propellant sustainers are statically fired at ambient, cold (−40 °C) after conditioning for 16 hrs, and hot (+50 °C) after conditioning for 6hr and pressure-time profiles are shown in Fig. 2. The pressure level is 70.7kg/cm² as against 71.0kg/cm² theoretically calculated throughout the duration of combustion. The combustion duration is 16.8 seconds as against 16.75 seconds theoretically calculated at ambient temperature. As the combustion duration and pressure experimentally observed compare well with the theoretically computed combustion duration and pressure data, it is concluded that no extra surface is exposed during combustion and in other words, SRUP-2 works satisfactorily as a barrier coat.

ACKNOWLEDGEMENT

The authors wish to thank Dr K R K Rao, Director, Explosives Research and Development Laboratory, Pune 411 021 for his very keen interest, encouragement and helpful discussions in this work.

REFERENCES

1. B Hans *Ger Pat* 1206 340 (to Nitro chemie GmbH Aschan) 2 December 1965; *C A* **64** (1966) 6395
2. H Berding Jahrostag Inst Chem Trieb Explosiustoffe Fraunhofer Ges 1971 (Publ 1972) 359–374

3. J P Agrawal and M P Chouk *Res Ind* **27** (1982) 19 Propellants Expssves, Pyrotee
4. J P Agrawal M P Chouk and R S Satpute *Br Polymer J* **14** (1982) 29
5. J P Agrawal M P Chouk and V M Kate *Indian J Tech* **22** (12) (1984) 460
6. J P Agrawal M P Chouk R S Satpute and K S Kulkarni *Propellants, Explosives and Pyrotechnics Germany* **10** (1985) 77
7. R Stenson *ERDE UK Tech Note* No. 48 (1971)
8. M Caire-Maurisier and J Transchant *Propellants Explos* **2** (1977) 101
9. J P Agrawal and K S Kulkarni Paper presented at the 34th Congr int astronaut Fed Budapest (1983)
10. J P Agrawal K S Kulkarni and S S Deo *J Hazardous Mater Netherlands* **10** (1985) 43
11. *ASTM Standards on Plastics* ASTM Designation D 638–44 T
12. J P Agrawal and R D Pokharkar *J scient ind Res* **39** (1980) 633
13. *ASTM Standards on Plastics* ASTM Designation D 570-42
14. P Robitcchek and B C Thomas *Ind Engng Chem* **46** (8) (1954) 1629
15. H V Boenig *Unsaturated Polyesters : Structure and Properties* Elsevier Publishing Co London (1964)
16. J P Agrawal and K S Kulkarni Paper presented at the 9th Europe Conf Flammability and Fire Retardants Austria May 9–10 (1985)
17. E E Parker and E W Moffett *Ind Engng Chem* **46** (8) (1954) 1615
18. K Kishore and R S Yadva *Indian J Tech* **8** (11) (1970) 429