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# Tereunsaturated polyesters

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Four tereunsaturated polyesters (TUPs) based on terephthalic acid, maleic anhydride and polyethylene glycol, molecular weight 200 (PEG-200), have been formulated, synthesized and characterised. The effect of variation of styrene monomer and alumina trihydrate ($Al_2O_3 \cdot 3H_2O$) filler has been studied on TUP-1 which possesses promising characteristics. Based on these characteristics, TUP-1 (III) with 20% $Al_2O_3 \cdot 3H_2O$ filler has been selected for inhibition and static evaluation of double-base rocket propellants. The results indicate that it is a potential inhibitor for double-base propellants.

## 1. Introduction

The chemistry of polyethylene terephthalate (saturated polyester) is well known, and the textile industry is regarded as the main user of terephthalic acid [1–3] at the present time. However, industrial applications of terephthalic acid-based unsaturated polyesters are relatively unknown. A literature survey reveals that terephthalic acid-based unsaturated polyesters have not been used for inhibition of double-base rocket propellants [4–9]. A wide range of unsaturated polyesters (rigid, semi-rigid, flexible, semi-flexible and very flexible), based on isophthalic acid, maleic anhydride and several glycols, have recently been synthesized and evaluated for inhibition of double-base rocket propellants [10–13]. It was, therefore considered of interest to undertake a systematic study, i.e. formulation, synthesis, characterization and evaluation of terephthalic acid-based unsaturated polyesters (designated as tereunsaturated polyesters, TUPs) for inhibition of double-base rocket propellants. Further, in an attempt to improve their mechanical and heat-resistance characteristics, the effect of styrene monomer and a well-known filler, i.e. alumina trihydrate, has also been studied.

## 2. Materials and methods

Polyethylene glycol, molecular weight 200 (PEG-200), LR; terephthalic acid (TPA) minimum purity not less than 98%, melting point 300 ± 2 °C, *p*-toluene sulphonic acid; minimum purity 99.5% and melting point, 100–102 °C, and alumina trihydrate, minimum purity 99.5%, and all passing through 400 BSS, were procured from the trade and used as-received. Maleic anhydride ($MA_n$) conforming to IS-5149:1969 and styrene monomer conforming to IS-4105:1967 were also procured from the trade.

Cobalt napthanate (3% solution in methylene chloride) and methyl ethyl ketone peroxide (50% solution in diethyl phthalate), which were commercially available, were used for curing of tereunsaturated polyesters.

The double-base rocket propellant containing 2-NDPA as stabilizer was manufactured by a casting technique [14] and its composition is as given in Table I.

TABLE I Composition of the double-base rocket propellant

| | % |
|---|---|
| Casting powder (CP) | |
| Nitrocellulose | 90.5 |
| Diethylphthalate | 4.0 |
| Lead stearate | 3.0 |
| 2-Nitrodiphenyl amine (2-NDPA) | 2.0 |
| Potassium sulphate | 0.5 |
| Casting liquid (CL) | |
| Nitroglycerine | 80 |
| Diethyl phthalate | 18 |
| 2-NDPA | 2.0 |
| Ratio of CP:CL::65:35 | |

## 3. Synthesis of tereunsaturated polyesters

The tereunsaturated polyesters were synthesized by following a two-step polyesterification process and the method, in brief, is as follows. Terephthalic acid, polyethylene glycol, molecular weight 200, and 200 mg *p*-toluene sulphonic acid were charged in a four-necked flask equipped with a stirrer, condenser, thermometer pocket and bubbler, placed in an electrical heating mantle. The inert atmosphere was maintained in the flask by bubbling nitrogen gas (free from moisture and oxygen) at a slow rate throughout the reaction. The reaction mixture was then refluxed at 170–180 °C for 4 h with slow agitation, followed by removal of water of condensation using a Dean and Stark's tube. The acid value of the reaction mixture and the volume of liberated water were checked at

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TABLE II Composition of tereunsaturated polyesters (TUPs)

| Tereunsaturated polyester | Molar ratios of ingredients | | | Acid value | |
|---|---|---|---|---|---|
| | TPA | $MA_n$ | PEG-200[a] | Before addition of $MA_n$ | After addition of $MA_n$ |
| TUP-1 | 0.25 | 0.75 | 1.0 | 20.0 | 33.2 |
| TUP-2 | 0.33 | 0.66 | 1.0 | 21.8 | 34.5 |
| TUP-3 | 0.50 | 0.50 | 1.0 | 21.0 | 33.5 |
| TUP-4[b] | 0.75 | 0.25 | 1.0 | – | – |

[a] PEG-200 was taken as 10% extra in order to compensate for glycol losses.

[b] Terephthalic acid remains unreacted during the synthesis of TUP-4 even after a long reaction time.

regular intervals and the reaction was continued until an acid value of 20 ± 2 was attained. Then, the reaction mixture was cooled and maleic anhydride was added at room temperature. This mixture was again refluxed for 2 h at 160 °C. The reaction temperature was gradually increased to 200 °C with simultaneous removal of water. The final acid value was maintained at 35 ± 2.

The traces of water and unreacted glycol were removed by applying a vacuum at 100 °C. The resin was then mixed with 0.02% (by weight of the resin) hydroquinone and 25% styrene, to obtain 75:25::resin:styrene solution. The tereunsaturated polyester was stored in an air-tight container in a cool and dark place. Similarly, four tereunsaturated polyester samples, designated TUP-1, TUP-2, TUP-3 and TUP-4, were synthesized and their formulations are given in Table II.

## 4. Characterization of tereunsaturated polyesters

The tereunsaturated polyesters were characterized for infrared (IR) spectra (smear method), gel time and exotherm peak temperature [13], tensile strength and per cent elongation [15], bond strength with propellant [16], nitroglycerine absorption [16], and flame retardance (in terms of burning rate) [13], by the methods already reported in the literature.

## 5. Results and discussion

The infrared spectra of TUP-1, TUP-2 and TUP-3 are shown in Fig. 1. It is seen that the infrared spectra of tereunsaturated polyesters are similar to a typical unsaturated polyester [17]. Various properties of TUP-1, TUP-2 and TUP-3 with 25% styrene monomer are shown in Table III.

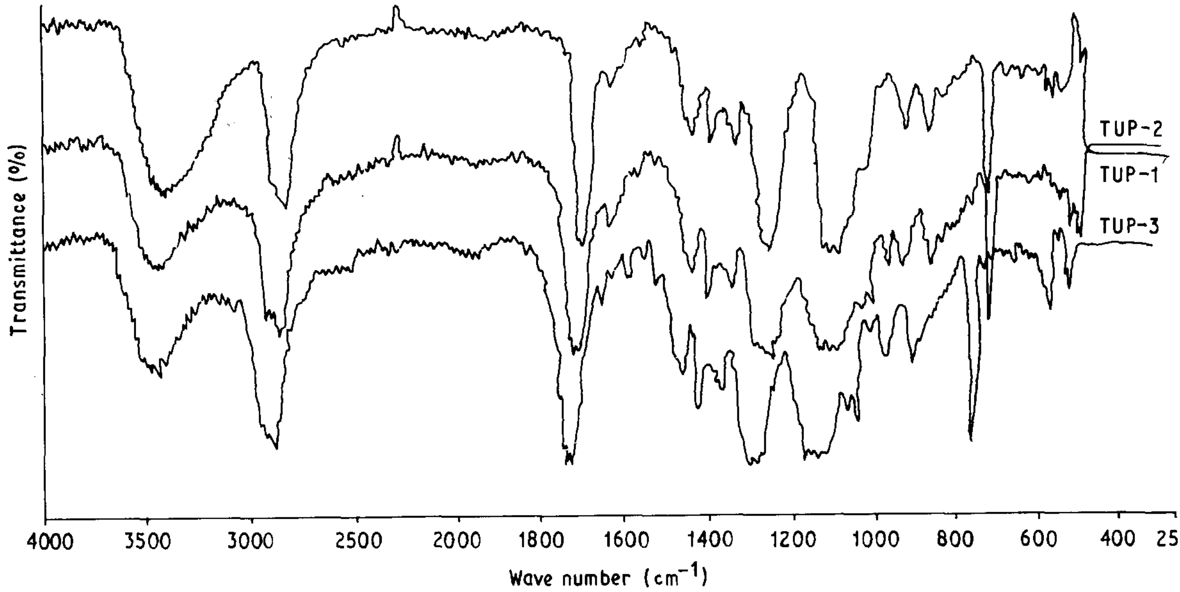

*Figure 1* Infrared spectra of tereunsaturated polyesters.

TABLE III Various properties of tereunsaturated polyesters

| Tereunsaturated polyester | Tensile strength (kg cm$^{-2}$) | Elongation % | Gel time (min) | Exotherm peak temperature (°C) | NG absorption (%) after 96 h | Bond strength (kg cm$^{-2}$) | Burning rate (mm s$^{-1}$) |
|---|---|---|---|---|---|---|---|
| TUP-1 | 16.0 | 12.5 | 19.0 | 52.0 | 17.20 | 1.60 | 0.57 |
| TUP-2 | 12.9 | 16.0 | 21.0 | 55.0 | 14.56 | 1.45 | 0.52 |
| TUP-3 | 7.0 | 20.0 | 24.0 | 57.0 | 22.70 | 1.27 | 0.51 |

TABLE IV Effect of variation of styrene monomer on mechanical properties of tereunsaturated polyesters

| Characteristics | 25% styrene | | | 35% styrene | | | 45% styrene | | | 55% styrene | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TUP-1 (I) | TUP-2 (I) | TUP-3 (I) | TUP-1 (II) | TUP-2 (II) | TUP-3 (II) | TUP-1 (III) | TUP-2 (III) | TUP-3 (III) | TUP-1 (IV) | TUP-2 (IV) | TUP-3 (IV) |
| Tensile strength (kg cm$^{-2}$) | 16.0 | 12.5 | 7.0 | 26.5 | 18.0 | 11.0 | 52.0 | 36.0 | 22.0 | 83.0 | 61.0 | 48.0 |
| Elongation (%) | 12.5 | 12.9 | 7.0 | 20.0 | 22.0 | 30.0 | 23.0 | 27.0 | 39.0 | 16.0 | 19.0 | 44.0 |
| Bond strength (kg cm$^{-2}$) | 1.60 | 1.45 | 1.27 | 2.70 | 3.10 | 11.00 | 5.00 | 5.00 | 18.00 | 8.20 | 10.00 | 22.00 |

The gel time data show that it increases from TUP-1 to TUP-3. This is because the molar proportion of maleic anhydride, which is mainly responsible for the reactivity of unsaturated polyesters, decreases from TUP-1 to TUP-3 (Table II) as reported in the literature [18]. It is seen from the Table III that TUP-1 has the highest tensile strength (TS) and it decreases from TUP-1 to TUP-3. This decrease in TS is also attributed to the maleic anhydride content which decreases from TUP-1 to TUP-3 and as a result, the availability of cross-linking sites decreases, leading to a lowering of the tensile strength [18]. Further, the NG absorption data show that it increases from TUP-1 to TUP-3. This is attributed to the decrease in tensile strength (indicative of the extent of cross-linking) [19] and if TS decreases in this order, NG absorption increases accordingly from TUP-1 to TUP-3. In other words, as the molecular rigidity decreases from TUP-1 to TUP-3, the NG migration increases. The NG (molecules being small in size) can easily seep into the molecular structures of tereunsaturated polyesters, similar to unsaturated polyesters and chloropolyesters and, therefore, the extent of NG migration is inversely related to the molecular rigidity, as observed experimentally.

The tensile strength, per cent elongation, bond strength between inhibitor and propellant and NG absorption, are very important properties of polymeric material and a compromise among them is made in such a way as to ensure successful performance during static evaluation of inhibited propellant at ambient, cold and hot temperatures. The tensile strength of propellant and inhibitor should be as close as possible in order to minimize differential expansion between them during storage. As the inhibited rocket propellant is required to work successfully over a wide range of temperature i.e. − 40 to + 50 °C, it should possess elongation of a high order. At the same time, the bond between propellant and inhibitor must be strong enough and should not give way at the time of combustion of the propellant.

The tensile strength of TUP-1, TUP-2 and TUP-3 is not comparable with that of double-base rocket propellants. The bond strength between propellant and different TUPs is also not sufficiently high. In an attempt to enhance tensile strength and bond strength, the effect of variation of styrene monomer on these properties was studied and the data are shown in Table IV. The data show that the tensile strength and bond strength increase as the concentration of styrene monomer increases [20]. The per cent elongation also increases, showing the availability of cross-linking sites in TUP-1, TUP-2 and TUP-3, even after addition of 25% styrene.

The bond strength data (Table IV) indicate that these resins are not suitable for direct bonding applications because of their poor bond strength. However, these resins may be used for main inhibition after application of a barrier coat of Acrolite-471, a rigid and fast-curing unsaturated polyester (Proprietary product of Acropolymer Ltd, New Delhi). In view of the desired combination of tensile strength, per cent elongation and bond strength, TUP-1 (III) was selec-

TABLE V Different properties of unfilled and filled TUP-1 (III)

| Tereunsaturated polyester | Gel time (min) | Exotherm peak temperature (°C) | Tensile strength (kg cm$^{-2}$) | Elongation (%) | NG absorption after 96 h (%) | Burning rate (mm s$^{-1}$) |
|---|---|---|---|---|---|---|
| TUP-1 (III) | 9.0 | 90 | 52.0 | 23.0 | 8.0 | 0.50 |
| TUP-1 (III) + 20% $Al_2O_3 \cdot 3H_2O$ | 8.25 | 84 | 65.0 | 20.5 | 3.8 | 0.40 |
| TUP-1 (III) + 40% $Al_2O_3 \cdot H_2O$ | 8.0 | 55 | 69.0 | 9.0 | 3.4 | 0.21 |
| TUP-1 (III) + 60% $Al_2O_3 \cdot 3H_2O$ | 7.5 | 52 | 98.5 | 5.5 | 2.1 | self-extinguishing |

ted for studying the effect of $Al_2O_3 \cdot 3H_2O$, a well-known filler. The effect of variation of alumina tri hydrate on various characteristics of TUP-1 (III) is depicted in Table V. It is observed that the exotherm peak temperature decreases on the addition of alumina trihydrate from 0% to 60%. This is because of the fact that the quantity of resin which is the only source of heat liberation on polymerization decreases [21]. As the amount of resin decreases, the heat liberated also decreases resulting in a decrease in the exotherm peak temperature from TUP-1 (III) + 0% alumina trihydrate to TUP-1 (III) + 60% alumina trihydrate. However, there is no significant effect of alumina trihydrate on gel time.

The tensile strength data show a regular increase from 0%–60% filler concentration. This is due to the reinforcing action of $Al_2O_3 \cdot 3H_2O$ in the polyester matrix which is a three-dimensional network. Similar to tensile strength, there is also a specific trend in elongation,. which decreases from 0%–60% filler, which is well known.

NG absorption data show a decrease from unfilled TUP-1 (III) to TUP-1 (III) + 60% $Al_2O_3 \cdot 3H_2O$. This is also due to the fact that the amount of resin which is mainly responsible for NG absorption, decreases as the amount of filler increases. This is in accordance with the findings of Agrawal *et al.* [22] in case of polyesters [21] and chloropolyesters [22].

The data on flame retardance in terms of burning rate are also shown in Table V. It is seen from the burning rate data that at 20% filler concentration, there is no marked difference in burning rate. However, at 40% filler concentration the burning rate becomes 0.21 mm s$^{-1}$, whereas at 60% concentration the system becomes self-extinguishing. As reported earlier [23], alumina trihydrate decomposes endothermically, releasing its water of hydration and inducing an overall cooling effect on the burning polymer. This overall cooling effect becomes significant, especially at higher loadings of alumina trihydrate and the temperature is lowered to such an extent that the flame does not propagate further.

Based on various characteristics, it is seen that TUP-1 (III) with 20% $Al_2O_3 \cdot 3H_2O$ possesses desirable combination of properties of an ideal inhibitor for double-base rocket propellants. This inhibition system was therefore used as the main inhibitor for a double-base propellant after application of three barrier coats of Acrolite-471 for inhibition of double-base rocket propellant. The inhibited propellants were conditioned at + 27 °C (for 24 h), − 30 °C (for 20 h) and + 50 °C (for 8 h) and statically evaluated. The *P-t* profiles (Fig. 2) which are flat and neutral, indicate a constant surface area throughout the combustion duration. In other words, it is concluded that TUP-1 (III) + 20% alumina trihydrate is a promising inhibition system for inhibition of double-base rocket propellant after application of barrier coats of Acrolite-471.

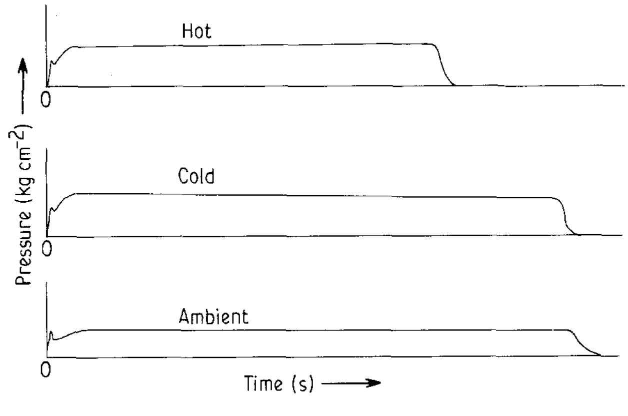

*Figure 2* Pressure–time profiles for double-base rocket propellant sustainers inhibited with TUP-1 (III) -20% $Al_2O_3$ at ambient, cold and hot temperatures.

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