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Micro-fibre based Porous Composite Propellants with High Regression Rates

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ABSTRACT

Harnessing energy at micro-scale from high energy sources has gained significance in recent times for space propulsion and other applications. Conventional solid rocket propellants have advantages in terms of being efficient, compact and safe to handle, though with much lower regression rates as compared to solid explosives. An approach to high regression rates in composite propellants is demonstrated in the present work by the enhancement of fuel-oxidiser interaction, and by the incorporation of micro-scale porosity into the propellant grain. The porous polystyrene-ammonium perchlorate grain designed in this work, based on electrospun micro-fibres and aqueous impregnation, exhibits burning rates more than 25 times as compared to the non-porous grain. Such high regression rates using insensitive propellant compositions have practical implications in the development of micro-thrusters, and in gas generating devices such as MAV launch systems and turbine starters. Detailed preparatory procedure, characterisation techniques, and flame regression studies are included in this paper.

Keywords: Porous propellants; Composite rocket propellants; Electrospinning; micro-fibres; High burning rate

1. INTRODUCTION

Energy sources which are efficient, compact and safe to handle are always desired. Rapid gas generation using these energy sources for generating thrust or to perform some work, by adopting micro- and nano- technologies is both scientifically and technologically challenging. Of late, MEMS based micro-propulsion devices have been reported, and there have been attempts to integrate solid propellants into these systems[1]. Conventional high-energy solid propellants have several advantages in terms of their energy density, handling etc. when used as gas generator. They however have regression rates much lower (in few mm/s) compared to detonation speeds of solid explosives (in few km/s). In rocket motors, operation at higher pressures and high surface area port geometries in the propellant grains enable rates of gas generation adequate to produce meaningful thrust. Such liberties are defunct in case of micro- propulsion systems wherein the operating pressures and grain manufacturing complexities pose constraints.

While the energy availability is limited by the thermodynamic properties of the chemicals used, the kinetics can be tailored by ingenious ways of fuel-oxidiser interaction and micro-geometries. There have been significant interests in developing propellant formulations/geometries with high steady-state burning rates. In the past, micro- and nano-technologies have been adopted to have a wider range of burning rates in propellants, and thus have a control on the rate of energy release[2,3]. Of particular interest are composite solid propellant grains that are safe to handle, unlike explosives, but have energy/ gas release much higher than that of conventional rocket propellants.

The regression rate of solid propellants at a particular pressure is mainly governed by the thermal energy feedback from the flame to the burning solid surface. In case of conventional solid propellants, as per the Rankine-Hugoniot theory, the burning speeds in the regime between deflagration and detonation are considered to be forbidden. However, this theory takes into account the conductive mode of heat transfer and neglects the convective heat transfer. Though this theory is applicable for solid propellants, convective heat transfer mechanism assumes significance in case of gas-permeable porous propellants. Thus porosity has been used as a route to enter the forbidden regime of steady state burning speeds between deflagration and detonation of solid propellants[4,5]. However, such porous propellants are generally not preferred in conventional rocket motors due to their high sensitivity to operating pressure, unpredictability due to manufacturing variations and compromised mechanical properties.

In this study, we present a method of manufacturing composite solid propellants with high regression rates by introducing controlled porosity. The structural features of fuel are modified so as to incorporate micro-scale porosity in the propellant grain. Polystyrene (PS) and Ammonium Perchlorate (AP) composition was adopted for this work[6]. Micro-fibres of PS were prepared via electrospinning as a non-woven mat with about 90 per cent *v/v* porosity, followed by hydrophilic surface functionalisation. In some cases, nano-scale catalysts such as Fe_2O_3 and CuO were also introduced and uniformly distributed inside the PS micro-fibres during the electrospinning process. AP in near stoichiometric amounts (90 per cent *w/w*) was loaded inside this porous matrix using aqueous impregnation

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technique. The regression rates of these novel porous composite propellants are observed to be 25 times higher than that of comparative non-porous propellants under atmospheric conditions. The experimental methods adopted, and the results obtained are discussed in the following sections. Applicability of such prepared porous composite propellants using non-woven fuel micro-fibres, as fast gas generating systems for micro- propulsion is also discussed.

2. EXPERIMENTAL

2.1 Preparation

Electrospinning is a versatile technique to prepare nano- and micro-fibres of polymers with controlled and reproducible porosity[2,7]. In the present study, micro-fibres of PS as fuel were electrospun to form a porous non-woven mat. The schematic of experimental setup is as shown in Fig. 1(a). In a typical procedure, a solution of PS in dimethylformamide (DMF) solvent (30 per cent *w/w*) was pushed through an emitter needle at a constant flow rate of 2.5 ml/hr. The collector was a custom made rotating cylinder. The emitter and collector were maintained at 15 kV (+*ve*) and 600 V (-*ve*) in order to achieve a sharp and stable Taylor cone as shown in Fig. 1(b), and to have a high collection efficiency. The continuous fibres ejected from the Taylor cone undergo solvent evaporation and move towards the collector due to electrostatic attraction. The fibres are then collected on the conducting rotating drum collector as a non-woven micro-fibrous mat. The process was allowed to proceed for few hours to obtain electrospun mats with thickness of about 1 mm. In some cases, Fe_2O_3 and CuO nanoparticles as catalysts were also dispersed (10 per cent *w/w* with respect to PS) in the PS solution prior to electrospinning.

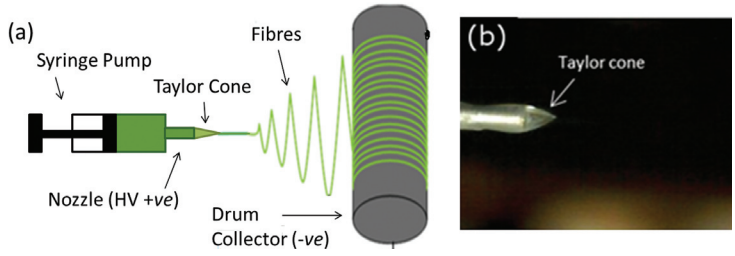

Figure 1. (a) Schematic of the experimental setup used to prepare micro-fibres of polystyrene, and (b) Close-up view of Taylor cone.

The obtained micro-fibres of PS were hydrophobic, and thus were treated with Piranha solution to functionalise them with hydrophilic groups. The porous PS mats with thickness of about 1 mm were cut into rectangular strips of 50 mm length and 10 mm width. These hydrophilic PS strips were soaked in hot saturated AP aqueous solution, and subsequently dried, so as to allow AP to be impregnated into the porous matrix. Several experiments were performed to optimise the soaking and drying conditions so as to achieve near stoichiometric loading of oxidiser (AP : PS = 90:10 per cent *w/w*).

2.2 Characterisation and Evaluation

Scanning electron microscope (FEI Quanta 200) was used to observe the structural features of the PS fibres prepared via electrospinning, and the porous propellant strips after AP impregnation. Low accelerating voltages (~ 2 kV) were used in the case of PS-AP propellant strips so as to avoid decomposition of the sample during observation. Electron dispersive spectroscopy (EDS) was used to observe the dispersion of catalysts in the PS fibres. The porosity of the PS strips before and AP impregnation was estimated using multiple volume and weight measurements. The attachment of hydroxyl functional groups to PS was observed using Fourier transform infrared spectroscopy (Perkin-Elmer FT-IR-1600). Absorption spectra of the samples prepared by KBr pellet technique were obtained in the range of 400 cm^{-1} – 4000 cm^{-1}.

The regression rates of the porous PS-AP propellant strips were estimated under atmospheric conditions, using a high speed camera (>1000 fps, Photron Fastcam SA4), and by following the flame front in the extracted sequential images. The porous propellant strips were placed between two glass slides to facilitate end burning. Due to the high intensity and corrugated nature of the flame front in case of porous PS-AP propellant strips, it was difficult to track at a resolution better than 1 mm/s. For comparison, the regression rates of propellant strips prepared by solvent-cast technique and by physical mixture of PS micro-fibres with AP were also studied under similar conditions. As a customary practice in the evaluation of novel propellants, the repeatability of burning rate data was verified by multiple experiments.

3. RESULTS AND DISCUSSION

Our approach was to modify the structural features of the fuel in a PS-AP composite propellant, so as to induce controlled porosity and enhance the regression rate. It can be seen from Fig. 2 that the PS fibres obtained after the electrospinning process have diameters less than 10 µm, and are inter-twined amongst themselves forming a non-woven porous meshwork or matrix. Though such non-woven PS fibres have high porosity, around 90 per cent *v/v*, the long range entanglement of fibres leads to their good mechanical integrity and handling properties.

Catalysts and fuel particles can be incorporated inside the micro-fibres prepared via electrospinning. As a demonstration, we incorporated nano-scale Fe_2O_3 and CuO as catalysts inside the PS micro-fibres at ~ 1 per cent with respect to AP. The dispersion of such nano-catalysts is uniform and can be seen from the EDS shown in Fig. 3.

The hydrophobic nature of as prepared PS micro-fibrous mats is as shown in Fig. 4. This is due to the inherent chemical nature of PS and due to the physical micro-scale textural

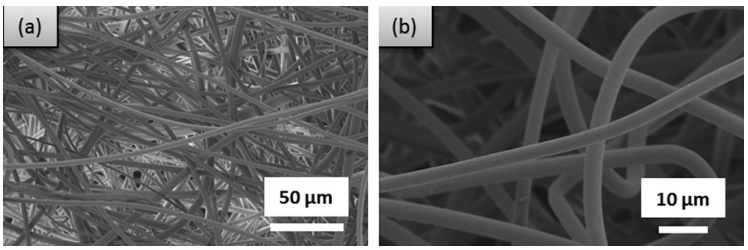

Figure 2. Representative scanning electron micrographs of the PS micro-fibres prepared via electrospinning.

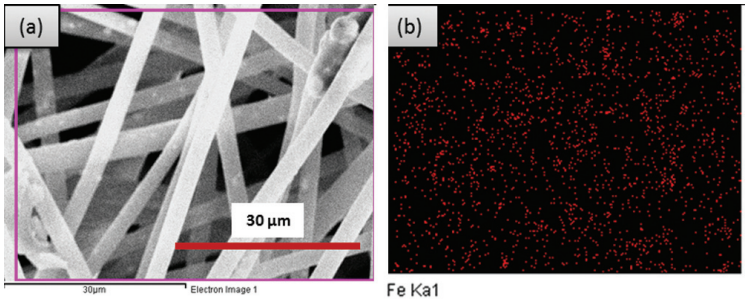

Figure 3. (a) Representative scanning electron micrograph of polystyrene microfibers containing 10 per cent w/w Fe_2O_3 nanoparticles, and (b) Corresponding energy dispersive X-Ray spectrograph showing the dispersion of Fe.

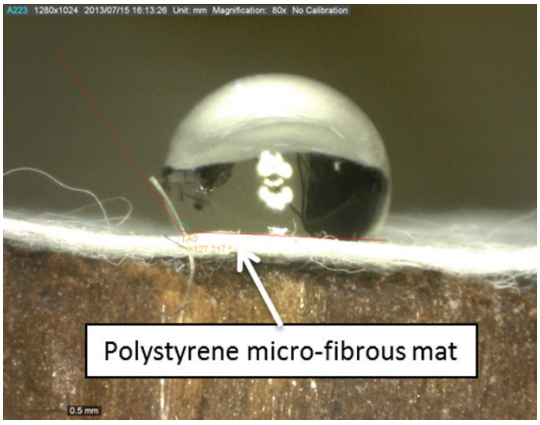

Figure 4. A water droplet placed on the as prepared polystyrene micro-fibrous mat shows the hydrophobicity.

roughness induced by the micro-fibres, and is a hurdle to aqueous impregnation of AP. A chemical treatment using Piranha solution was adopted to make it hydrophilic. After treatment of the electrospun PS fibrous mats with Piranha solution, attachment of hydroxyl (-OH) functional groups can be seen in the FTIR spectra (as shown in Fig. 5).

Ammonium Perchlorate was introduced into the porous PS matrix via aqueous impregnation using a near saturated solution, followed by drying. As shown in Fig. 6, AP gets crystallised on the PS fibres and in the interstitial spaces between the fibres. The weight ratio of AP was adjusted to stoichiometric amounts (90 per cent *w/w*) after multiple experiments. Though the physical dimensions and mechanical integrity of the PS strips remained similar, the porosity was found to drop from 90 per cent *v/v* to about 50-60 per cent *v/v*, before and after impregnation with AP.

The regression rates of PS-AP propellant strips prepared via electrospinning followed by aqueous impregnation, via conventional solvent-cast method, and by the physical mixtures of PS micro-fibres and AP, were measured at atmospheric conditions (Table 1). The burning speed in case of solvent-cast propellant strips was 1 mm/s. This is consistent with the values previously reported for PS-AP propellant composition[6]. In the case of physical mixtures of PS micro-fibres and AP, the regression rate was 7 mm/s, and can be attributed to the higher surface area of interaction between the fuel and oxidiser[2].

However, in the case of our novel porous PS-AP propellant strips, regression rate of 28 mm/s was observed. Also, as seen in the Fig. 7, the flame is more intense indicating a rapid energy release. High regression rates in the case of these electrospun composite propellants can be attributed to the presence of porosity, and the high surface area available for propellant gasification. Porous or gas-permeable propellant grains are known to possess high burning rates due to enhanced heat transfer via convection[4,5]. This enables much higher burning rate in the case of porous micro-fibrous PS-AP propellants, as compared to the solvent cast PS-AP wherein the burning surface regression is based on normal conduction based heat transfer.

A further increase in the regression rates are observed when nano-scale catalysts such as Fe_2O_3 and CuO are incorporated in the PS micro-fibres (Table 1). This is because of the sensitised thermal decomposition of AP in the presence of transition metal oxide catalysts, enabling higher rates of propellant gasification[3,6].

Porous composite propellants with such high regression rates are desired for several applications. Normally such regression rates can be obtained only with the addition of high energetic particles/ primary explosives in propellant formulations, heightening the sensitivity. PS-AP on the other

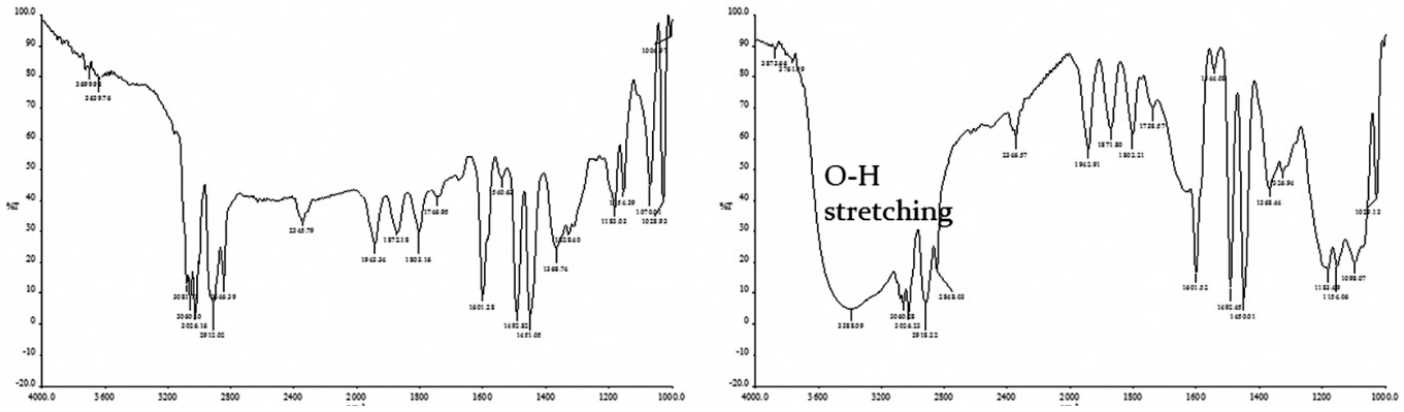

Figure 5. FTIR Spectra of the polystyrene microfibers : (a) As prepared by electrospinning, and (b) After treatment with Piranha solution.

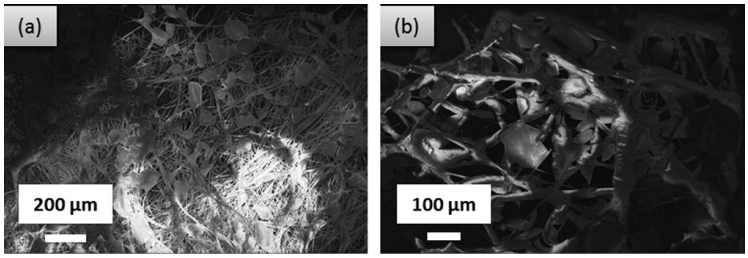

Figure 6. Representative scanning electron micrographs of the porous composite propellant strips after impregnation of the oxidizer at stoichiometric ratio.

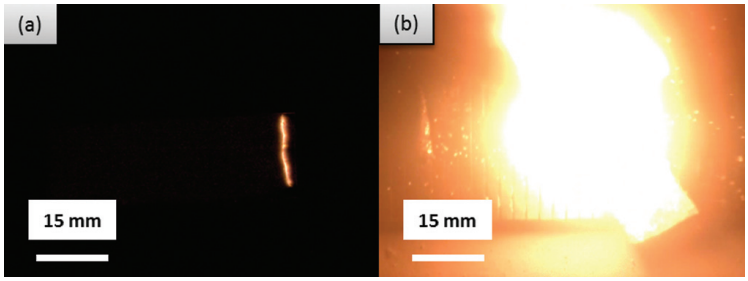

Figure 7. Representative images showing the flame propagation through (a) Solvent-cast propellant, and (b) Porous propellant strips (top view).

hand is an insensitive composition. Though volumetric energy density of such porous propellants is lower that of solid cast propellants by about 50 per cent, there are applications that require high-regression rates and wherein volumetric constraints are not so severe. The porous PS-AP composite propellants prepared in this work can be used in applications wherein a rapid energy release or gas generation is required, such as in micro-propulsion systems/thrusters, micro-scale actuators, air-bag inflation systems, turbine starters, MAV launch systems and so on.

Table 1. Burning rates of PS-AP composite propellants. PS: AP w/w ratio was maintained at 10:90. Sample no. 4 and 5 contained CuO and Fe_2O_3 nanoparticles as catalyst (1 per cent w/w with respect to AP)

Sample	Burning rate (mm/s)
Solvent cast AP + PS	1 ± 0.1
Physical mixture of PS micro-fibers + AP	7 ± 1
Porous PS micro-fibers + AP	28 ± 3
Porous PS micro-fibers + AP + CuO	43 ± 4
Porous PS micro-fibers + AP + Fe_2O_3	52 ± 4

4. CONCLUSIONS

Emerging micro-scale propulsion and gas generating systems would benefit from solid propellants with high regression rates. In this work, we report a novel method to prepare micro-porous solid propellant grains. A Polystyrene (PS) – Ammonium Perchlorate (AP) composition was adopted for this work. Porous PS non-woven mats were prepared using electrospinning technique. Since polystyrene is hydrophobic, a surface modification for invoking hydrophilic nature for proper adhesion to ionic oxidiser salt was carried out. The surface modified porous polymeric mat was subsequently loaded with oxidiser AP through an aqueous impregnation technique, at a solid loading close to stoichiometric proportion, necessary for high combustion performance. These prepared porous PS-AP composite propellants were found to regress more than 25 times faster, than the comparative non-porous propellant. Though the volumetric energy density is compromised in case of such porous propellants, their insensitivity and high regression rates make them suitable for several applications such as micro-scale thrusters and gas generating systems.

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He was also involved in conceptualisation of the work, planning of experiments, data interpretation, and manuscript review.