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Material Behaviour

Effect of pre-strain during ageing on the maximum elongation of composite solid propellants and its modelling

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ABSTRACT

In this study, the effects of accelerated ageing under pre-strain on the maximum elongation of composite solid propellants were investigated. The maximum elongation of aged composite solid propellants at different ageing times, temperatures and pre-strains were determined. An ageing model was developed to analyse the effects of pre-strain and temperature on model parameters. Results show that pre-strain can increase the maximum elongation significantly during accelerated ageing, and the increasing amplitude exhibits a linear relationship with ageing temperature and pre-strain. The physical tension effect caused by pre-strain is a cumulative effect of the stress on samples and shows obvious characteristics of stress relaxation. The relaxation time is independent of pre-strain and exhibits an exponential relationship with ageing temperature. The effect of pre-strain on chemical ageing is related to a critical temperature T_C. For the HTPB propellant investigated in this study, the T_C is between 65 °C and 70 °C. When the ageing temperature is below T_C, pre-strains have almost no effect on the ageing rate constant for maximum elongation k_ε; however, at temperatures above T_C, they may promote chain scission reactions and decrease k_ε.

1. Introduction

Composite solid propellants (CSPs) have been used widely in various solid rocket motors (SRMs) due to their excellent mechanical performance, high energy and mature product technology [1–4]. However, the mechanical capabilities of CSPs may change due to chemical reactions and physical processes caused by external factors during storage (e.g. temperature, strain), and generally result in the loss of grain structural integrity [5]. Ageing studies are, therefore, important for the assessment of the reliable and safe use of propellants. Most propellant applications call for storage time as long as possible. However, the degradation processes are usually too slow at ambient temperatures to conduct normal ageing studies in a reasonable time. Thus, accelerated ageing procedures are generally used in an attempt to reduce the time scale [6].

Many studies have focused on accelerated ageing under zero-strain ageing conditions. However, these are not sufficient to reflect actual storage conditions of SRMs. In a case-bonded SRM, solid propellant grains are subjected to a variety of strains that are introduced during curing and cooling of the grains due to differential thermal expansion between the propellant and the case material [7]. These strain conditions can significantly alter the ageing processes, ultimately affecting the mechanical properties of the propellants [8]. Therefore, it is necessary to study the ageing properties of CSPs under pre-strain conditions.

In recent years, much research has examined the mechanical properties and network characteristics of CSPs during pre-strain ageing. Layton [9] studied the accelerated ageing of PBAN propellant at different strain levels. He observed that strains up to 10% during ageing had no effect on the gel content; in other words, ageing strain does not alter the rate of chemical cross-linking between the polymer chains. However, the samples aged with various strains up to 12% consistently had a lower relaxation modulus than unstrained samples. Wang et al. [10] investigated the ageing behaviour of HTPB propellant under constant strain conditions. They discovered that strain during ageing had almost no effect on the total strain at 50 °C, but it reduced at 25.8 °C and it increased at 70 °C. Myers [11] found that the ageing strain increased the ageing rate of CTPB propellant significantly at 145 °F(≈63 °C), but only slightly at 70 °F(≈21 °C). This effect was obvious in the gel content. Chang et al. [12] demonstrated that strains up to 11.4% had virtually

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Nomenclature

ε_m	Maximum elongation, that is the elongation value corresponding to the maximum tensile strength in uniaxial tensile test, %
$_{\varepsilon}0$	Applied pre-strain elongation amplitude, kept constant during ageing, %
T	Ageing temperature, K
T	Ageing time, *d*
ε_p	Increase of ε_m caused by physical tension effect, %
ε_c	Maximum elongation related to chemical ageing, %
ε_v	Increasing amplitude of ε_m caused by physical tension effect, %
ε_{ini}	Maximum elongation of unaged propellant, %
k_ε	Ageing rate constant of ε_m, %/*d*
τ_0,τ	Relaxation time, *d*
σ	Relaxation stress, MPa
σ_0	Relaxation stress at the beginning, MPa
k_{gel}	Ageing rate constant of gel content, %/*d*
α_T	Temperature sensitive coefficient, %/K
$\alpha_{\varepsilon 0}$	Strain sensitive coefficient, 1/%
α_τ	Temperature coefficient, 1/K

Abbreviation

HTPB	Hydroxyl-terminated polybutadiene, binder prepolymer
CSP	Composite solid propellant
SRM	Solid rocket motor
PBAN	Polybutadiene acrylo-nitrile acrylic acid
AP	Ammonium perchlorate
Al	Aluminium powder
DOS	Dicapryl sebacate, used as a plasticiser
TDI	Toluene diisocyanate, a curing agent
DPPD	Diphenyl-p-phenylenediamine, an antioxidant
MAPO	Tris 1(2 methylazirindinyl) phosphine oxide, a bonding agent
CTPB	Carboxyl-terminated polybutadiene

no effect on the maximum elongation of HTPB propellant at ageing temperature of 70 °C.

For ageing of CSPs, changes in mechanical properties are of primary interest in most studies focusing on decrease in the elongation. The elongation is a crucial mechanical property parameter for CSPs because it will have a significant decline in storage for long periods of time, which will compromise the structural integrity of solid rockets and lead to service life constraints [13]. With this in mind, our research is mainly focused on the changes in maximum elongation during pre-strain ageing. A major challenge is that the changes in maximum elongation for CSPs are highly complex during pre-strain ageing because it is obvious that the physical and chemical processes are connected. In previous studies, the effects of pre-strain on mechanical properties of CSPs during the ageing process have been largely limited. The mechanism of pre-strain ageing has not been sufficiently studied, and existing ageing models do not include the effects of pre-strain.

Therefore, the pre-strain ageing mechanism and effects of pre-strain and ageing temperature on the maximum elongation of CSPs were studied in this paper. The organization of the paper is as follows. A detailed description of accelerated ageing experiments under different pre-strain conditions is provided in Section 2. The test results of maximum elongation are discussed in Section 3. Development and parameterization of the pre-strain ageing model of the maximum elongation for CSPs are presented in Section 4. The effects of pre-strain and ageing temperature on model parameters are analysed in Section 5. Finally, the conclusions are summarized in Section 6.

2. Experimental

2.1. Sample preparation

The CSP investigated was HTPB-based solid propellant. It has the following chemical composition: 68 mass-% of AP, 17 mass-% of Al, 11.78 mass-% of HTPB, 2.5 mass-% of DOS, 0.378 mass-% of TDI, 0.091 mass-% of DPPD, 0.058 mass-% of MAPO and 0.193 mass-% of other additives. AP size distribution: coarse particles (80%) in the range 140–160 μm and fine particles (20%) in the range 70–80 μm. The size of Al was in the range of 5–15 μm. All formulations were prepared in a vertical kneader and cured in a cabinet oven for 7 days at 50 °C. Samples of freshly mixed and cured HTPB propellant were cut into dumbbell shaped specimens with dimensions of 140 mm × 48 mm × 10 mm.

2.2. Accelerated ageing experiments

Accelerated ageing experiments were carried out in air-circulating ovens (accurate to ±1 °C) with strain grids to elongate the samples to 3, 6, and 9% pre-strain levels. The samples were aged at elevated temperatures and then removed according to the scheduled times of the test matrix shown in Table 1.

2.3. Tensile tests

The aged samples were put into a dryer until they no longer shrunk, and the geometrical dimensions were constant. This can avoid the influences of viscoelastic recovery and moisture on their mechanical behaviour. The samples were then cut into standard dumbbells with a gauge length of 70 mm suitable for tensile tests. Tensile tests were performed on an Instron 5567 machine equipped with pneumatic grips; an extensometer clamped on the sample allowed maximum elongation values to be obtained. Testing was conducted at a strain rate of 100 mm/min. Five repeat samples were typically tested for each ageing condition (temperature, time and pre-strain), and the average value of the maximum elongation is reported.

2.4. Gel content test

The gel content of the propellant samples was determined using a solvent-extraction method according to the ASTM D-2765 [14]. The solvent used was methylbenzene. The samples used for gel content test were from the scrap of tensile samples. The gel content was calculated using the following:

$$\%\,\text{Gel content} = 100 - \frac{W_s - W_d}{f_{binder} W_s} \times 100 \qquad (1)$$

where W_s is the mass of the specimen being tested, W_d the mass of dried solid compositions, f_{binder} the fraction of binder system (the ratio of the mass of the HTPB binder in the formulation to the total mass of the formulation).