Properties and application of POSS nanocomposites in aerospace

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Abstract
In recent years, polymer composites have been used in various industries. In this article, the application of polymer composites containing POSS in aerospace industries and solid composite propellants has been discussed. The studis showed that POSS nanoparticles increase the mechanical properties of polymer composites so that they can be used in harsh space conditions. POSS nanocomposites have high thermal stability and low flammability. These advantages lead to its use in thermal protection systems of space shuttles, rocket combustion chambers, missile warheads and thermal blankets on solar panels. Also, the rigid structure of POSS silica makes it useful in protective coatings against atomic oxygen, thermal cycling, orbital debris, plasma, and extreme vacuum. The low dielectric constant of POSS is another advantage of these nanoparticles, which has led to its use in electronic components of satellites, telescopes, etc. The latest findings show that solid composite propellants containing POSS increase the burning rate and the efficiency of rocket engines. These cases have made research on the properties of POSS nanocomposites in space industries very attractive.

Keywords: *"POSS", "Nanocomposite", "Propellant", "Combustion properties", "Mechanical properties".*

1. Introduction

In recent years, the world has moved towards the replacement of polymer composites instead of metals in various industries, including aerospace. Polymers have received attention due to their reasonable price, high plasticity and lightness. Space has adverse environmental conditions such as ultraviolet rays, plasma, high vacuum, ionizing radiation, meteorites, orbital debris, etc., which reduce the lifespan and performance of satellites, spaceships, and space stations. Therefore, the construction of systems with a long life and resistant to these harsh conditions has always been the focus of researchers [1]. Scientists are trying to replace the bodies of rockets and spacecraft with polymer composites, so that in addition to reducing costs, the inert weight of these systems can also be reduced. But the basic problem of polymers is their thermal stability and mechanical resistance compared to metals, which are limited in their use due to harsh spatial conditions [2]. One of the ways to improve the properties of polymers is to use additives. Nanoscale additives show better performance than conventional additives due to their high surface-to-volume (S/V) ratio and are very promising due to their low cost, high processability, and tunable properties [3]. POSS is a nanoscale additive that has attracted much attention in recent years due to the special properties it gives to polymers. POSS is a set of unique molecules with a cubic inorganic core such as Si_8O_{12} surrounded by eight organic groups (Fig. 1).

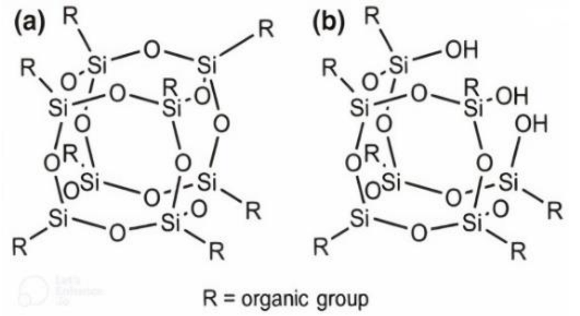

Fig. 1:POSS structure. a) cage. b) Partial cage [3]

The physical properties of POSS have been reported in different ranges due to the substitution of different organic groups. Organic groups may be H atoms or reactive or non-reactive organic groups. Reactive organic groups form chemical bonds with the polymer and are chemically mixed with the polymer. But its non-reactive type is physically mixed with the polymer (Fig. 2) [4].

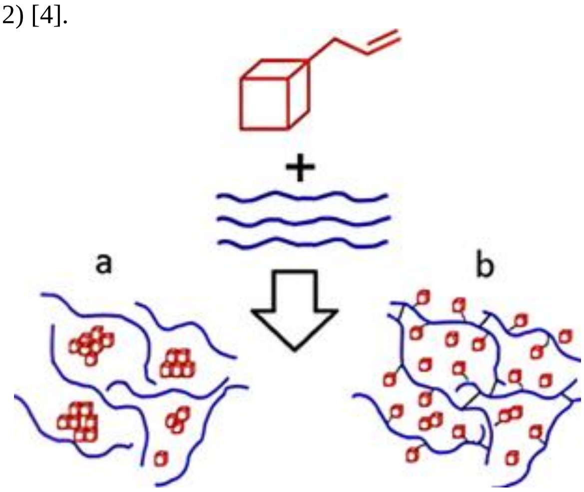

Fig. 2:(a) non-reactive POSS (b) reactive POSS [4].

The type of POSS mixing determines the final properties of the nanocomposite. POSS nanoparticles with sizes of 1 to 3 nm are described as the smallest version of colloidal silica. Therefore, they are smaller than a macromolecule, but larger than a small molecule (the size of atoms/small molecules is below 1 nm, while

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the size of macromolecules is above 1 nm but below 10 nm). This much smaller size than conventional fillers allows dispersion of POSS between polymer chains and increases compatibility with a variety of polymers including elastomers, thermoplastics, and thermosets. which has caused its use in various industries including aerospace [5]. An example of the properties of polymer composites is collected in Table 1.

Table 1: Application of POSS nanocomposites.

Nanocomposite	Properties	Ref.
RF/OP-POSS	Thermal protection	[6]
PBZ/EP/POSS	UV resistance	[7]
EP/POSS-TiO_2	Mechanical strength	[8]
PI/POSS	Resistance to oxidation	[9]
PI/CNT/POSS	Thermal stability	[10]
Ph-POSS/PC	Flame retardant	[11]

Composite solid propellant is a polymer composite that is used as solid fuel in rocket engines and spacecraft boosters. Increasing the efficiency of these engines has always been the focus of researchers. Research results have shown that POSS nanoparticles can improve the performance of solid composite propellants due to their special properties. In this article, the effect of POSS nanoparticles on the mechanical, and dielectric properties of polymer composites and the combustion properties of composite solid propellant is investigated and its application in the aerospace industry is discussed.

2. Mechanical properties

Research has shown that the use of POSS in polymer composites increases their mechanical properties. The mechanical properties of POSS nanocomposite depend on the following factors [12]:

- POSS interaction with polymer
- POSS concentration
- Morphology
- Type and size of POSS
- Type of polymer mixing

The interaction between polymer and nanoparticles at their interface controls the mobility of the polymer chain. Therefore, the incorporation of POSS nanoparticles into the polymer can affect its mobility and change its mechanical properties. The polymer chains are adsorbed on the surface of POSS by the interaction between the organic pendant group on POSS and the polymer, which leads to the improvement of the contact surface between the surface of POSS and the polymer chains. These interactions can help POSS to bind tightly to the polymer, reduce the mobility of the polymer chains, and thus change the mechanical properties of the system. The mechanical strength of interactions, which include strong chemical interactions such as covalent/ionic bonds or weak physical interactions such as van der Waals forces/hydrophilic-hydrophobic balance/hydrogen bonds, can vary depending on the nature of POSS surface ligands [13]. The special structure of POSS has made it possible to connect different organic pendant groups on the POSS siloxane core, which allows controlling the mechanical properties of POSS in different polymer systems. The results of investigations have shown that the mechanical behavior of POSS nanocomposites is more influenced by the chemical nature of the pendant organic groups than the type of mineral cage [14]. In fact, the mechanical properties of POSS polymer nanocomposites depend on POSS pendant groups as well as the dispersion of these nanofillers in the polymer matrix [15]. If POSS has reactive pendant groups, it will form a covalent bond with the polymer, otherwise it will physically mix with the polymer. This type of mixing has caused the difference in mechanical properties in POSS nanocomposites.

Non-reactive POSS: Non-reactive POSS by being placed between polymer chains, reduce the attraction between polymer chains and increase the length of the polymer. The solid composite propellant must have acceptable flexibility so as not to be damaged by the stresses caused by transportation and storage. The mechanical properties of solid composite propellants depend on the polymer binder that holds the fuel and oxidizer. Polyurethane-based hydroxyl-terminated butadiene (PU-HTPB) is one of the most widely used binders used in solid-state propellants. The PU/HTPB polymer containing POSS increases the elongation compared to the original sample (Fig. 3). Good dispersion of nanoparticles at low loads increases elongation. By increasing the concentration of POSS in HTPB, due to the increase in the interaction of POSS, the accumulation of nanoparticles increases and as a result, the mechanical properties of the nanocomposite decrease [16].

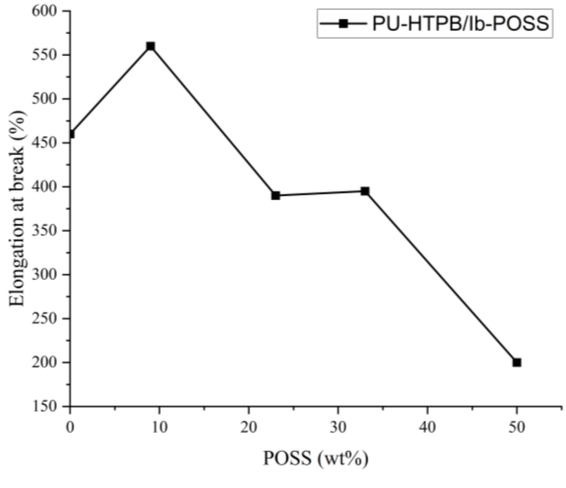

Fig. 3:Effect of POSS amount on mechanical properties of PU-HTPB [17].

Comparison of POSS with dioctyl adipate (DOA) plasticizer shows that, at equal amounts, POSS significantly increases polymer elongation compared to DOA (Fig. 4) [18].

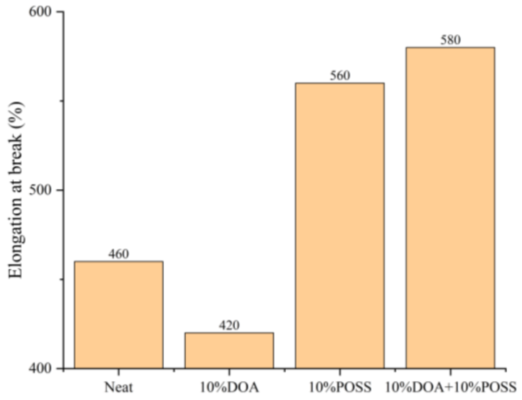

Fig. 4: Comparison of mechanical properties of Oib-POSS and DOA on PU-HTPB [18].

Polyetheretherketone (PEEK) a hard, stiff, strong polymer that excels in a variety of harsh environments, including high temperatures, chemicals and heavy loads. PEEK has low flammability, superior creep resistance, and can withstand prolonged exposure to high-pressure water and steam without degradation. It also available in a variety of grades which offer more specialized benefits for specific applications. PEEK is one of the ideal products in the aerospace industry. Due to its light weight, inert properties and relatively cheap price, it is used in the aerospace industry. This polymer is used for the exterior of the aircraft, which is in contact with atmospheric particles at low temperatures [19]. PEEK containing trisilanol phenyl-POSS (Tsp-POSS) increases the mechanical properties of the polymer. As The PEEK/POSS nanocomposite increases the hardness and mechanical strength compared to the prototype (Fig. 5) [20]. Ultra-high molecular weight (UHMW) polyethylene is a low-cost, high-strength plastic that is resistant to impact, abrasion, solvents, and fire. This polymer provides excellent performance over a wide range of temperatures. Plastic parts made from UHMW improve equipment efficiency, reduce noise and provide excellent wear resistance for parts subject to moderate wear. UHMW also has high impact resistance. very low moisture absorption; Excellent strength, stiffness and dimensional stability; And it is easily machined and made. This feature has increased its use in parts of airplanes and spacecrafts [21]. Mechanical strength and elongation of UHMW/POSS nanocomposites have increased significantly compared to pure UHMW samples. The size of the inorganic cage is fixed for POSS, so only the organic pendant groups attached to the cage determine the size of these nanoparticles. Depending on the length of the groups substituted by POSS, the stress transfer from the matrix to the core varies [14]. As the length of the pendant group increases, the mechanical properties of the system decrease. From POSS with 4-carbon (POSS4) to 9-carbon (POSS9) linear alkyl, the strain and mechanical strength of the resulting nanocomposite decreases (Fig. 6). The length of the pendant group (octamethyl, octaisobutyl or isooctyl) of POSS has a significant effect on the mechanical properties of the nanocomposite. The stress transfer from the polymer matrix to the rigid siloxane core of POSS is low in the presence of long alkyl chains. As a result, the mechanical properties of the polymer decrease [22]. Using a micromechanical model, Rico et al. showed that if the thickness of the shell (organic groups) is greater than about 25% of the radius of the rigid core, POSS does not neutralize the stress [23]. In POSS of the same length, linear substitutions have less effect on the mechanical properties of the polymer than branched substitutions. (Fig. 7) [16].

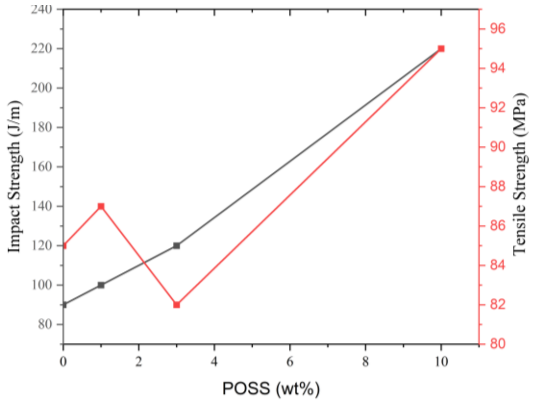

Fig. 5:effect of Tsp-POSS on the hardness and mechanical strength of PEEK [20].

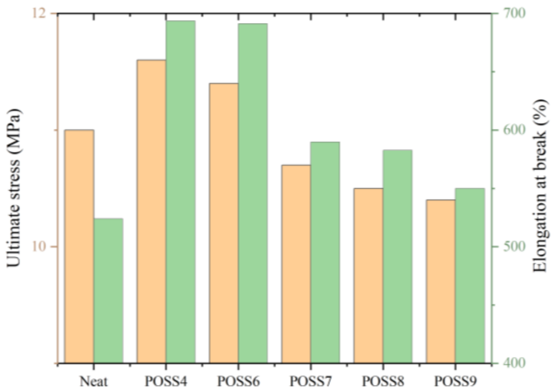

Fig. 6:Effect of POSS pendant group length on the mechanical properties of PE [22].

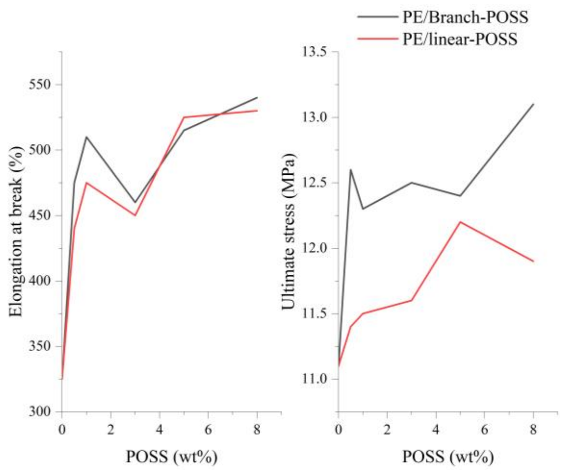

Fig. 7:Effect of the type (branch, linear) of POSS on mechanical properties of PE [16].

Reactive POSS: Meteorites, orbital debris and solar winds cause damage to space systems. Therefore, improving their mechanical strength is a priority. Research has shown that the use of reactive POSS in polymer composites increases their mechanical strength. The most effective method to increase the mechanical properties is the formation of chemical bonds at the POSS-polymer interface [24]. The hard nature of POSS significantly affects the mechanical properties, especially the modulus, hardness and tensile strength [25].The effect of reactive POSS on the mechanical properties of the system depends on the type of nanoparticle-polymer bond:

- bead configuration

In addition to flexibility and elongation, the binder of solid composite propellants must have good mechanical strength The results show that reactive POSS nanoparticles increase the mechanical strength of PU-HTPB adhesive. Trans-cyclohexane diol isobutyl-POSS and 1,2-propanediol isobutyl-POSS with two reactive groups are attached to two polymers in the form of a bead structure and act as chain extenders. PU-HTPB composites reinforced with these two POSS increase the mechanical strength of the system (Fig. 8) [17]. The increase in mechanical properties is attributed to the chemical bonding effect between POSS and polyurethane Creating a chemical bond between POSS and polymer and placing POSS nanoparticles in the hard parts of polyurethane increases the length of the polymer chains and increases its strength [26].

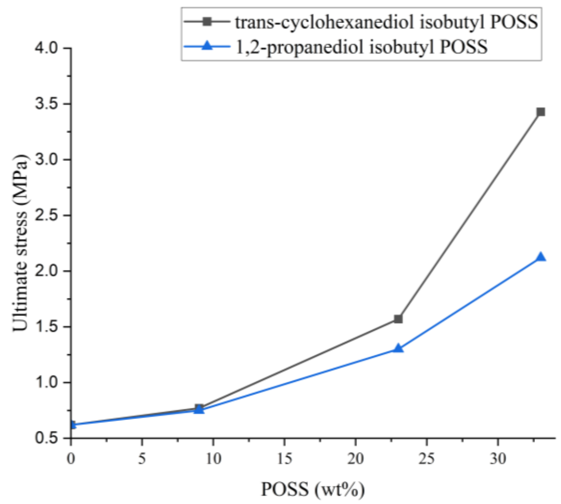

Fig.8:Effect of reactive POSS with bead configuration on the mechanical properties of PU-HTPB [17].

- Star configuration

methyl methacrylate (PMMA) polymer is widely used in the aerospace industry due to its special properties, including transparency (light transmission up to 92%) and its high resistance compared to glass. This polymer is used in making the windows of fighter and passenger planes. Increasing its mechanical resistance allows its use in more advanced industries such as space stations and astronaut suits [27]. The results show that PMMA/POSS nanocomposites have high strength compared to the original sample. Octavinyl-POSS (V-POSS) and propyl-octa(methacryloxy)-POSS (M-POSS) have eight reactive groups and are mixed with PMMA in a star configuration and form cross-links. Studies on the effect of POSS on mechanical properties have confirmed that the greatest increase is observed when cross-linking between POSS and polymer [28]. The results show that in addition to increasing the mechanical strength, the strain of the resulting nanocomposites has increased (Fig. 10). The increase in nanocomposite strain is attributed to the placement of POSS through covalent bonds between polymer chains and the increase in the free volume of the system. Also, these covalent bonds in the nanocomposite increase the mechanical strength of PMMA. M-POSS with ethyl, methyl acrylate groups has a structure similar to PMMA compared to V-POSS with vinyl groups. This similarity forms a uniform network structure in the nanocomposite. The cross-linking density of the composites prepared with M-POSS significantly increases the mechanical strength compared to V-POSS [24].

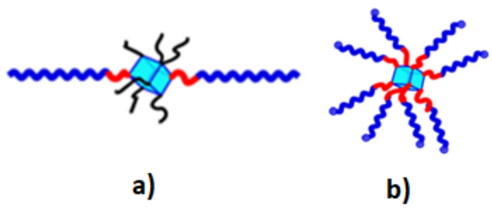

Fig.9: a) bead configuration. b) Star configuration [29].

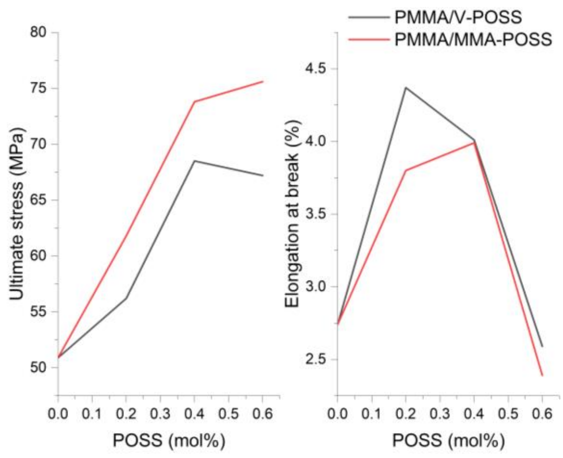

Fig.10:Effect of reactive POSS with star configuration on mechanical properties of PMMA [24].

3. Dielectric properties

Materials with low dielectric constant (ε) are widely used in electronic and telecommunication components, including satellites, space telescopes, etc. [30]. The use of POSS nanocomposites in electronic components reduces their ε. Factors affecting the reduction of ε of electronic components containing POSS are:

- POSS large surface
- POSS nanoscopic structure
- A change in the internal electric field (pole) due to the presence of POSS

The hollow cage structure, high symmetry and low density of POSS make air permeability in it and reduce ε. However, the pore volume of POSS nanoparticles is exaggerated to reduce ε. Because the 0.54 nm POSS core in a 1.5 nm POSS molecule is only 4.8% of the total POSS volume, and its porosity is negligible compared to the POSS volume [31]. Therefore, it can be concluded that the porosity of POSS is not the main reason for the reduction of ε in the material. The real reason for the large decrease in ε is that due to the rigidity and large size of POSS, molecular voids are created in the material. However, for some cases, although the free volume caused by POSS nanoparticles is negligible, the ε of the nanocomposite decreases. Scientists believe that there is probably another mechanism to reduce ε of POSS nanocomposites [32]. Liu et al proposed a new mechanism for the dielectric properties of POSS nanocomposites. POSS molecules tend to aggregate and crystallize in polymers due to their high adhesion energy. The composition of these nanoparticles changes the mechanical, rheological or electrical properties of polymers through the surface effect. It can be assumed that the surface effect can possibly change the dielectric properties. They found that the aggregation of POSS nanoparticles decreases the polarity and ε of the composite [33].

4. Combustion properties of propellants

In 2021, for the first time, Ren et al used POSS in a HTPB-based solid composite propellant. OctaPhenyl POSS (OPS), OctaAminophenyl POSS (OAPS) as neutral POSS and OctaNitroPhenyl POSS (ONPS), OctaDiNitroPhenyl POSS (ODNPS) as energetic POSS were used in this propellant formula (table. 2) [34].

Table. 2: Formulations of propellants in mass fraction (wt%).

Components	H0	H1	H2	H3	H4	H5
HTPB binder	14	14	14	14	14	14
AP	68	67	67	67	67	67
Al	18	18	18	18	18	18
OPS	-	1	-	-	-	-
ONPS	-	-	1	-	-	-
ODNPS	-	-	-	1	-	-
OAPS	-	-	-	-	1	-
Fe_2O_3	-	-	-	-	-	1

POSS nanoparticles showed good compatibility with HTPB-based propellant components. The results showed that POSS compounds can increase the burning rate of these propellnts (Fig. 10). At high temperature, the POSS compounds in the propellant are decomposed and by forming porous SiO_2 structures, they increase the AP decomposition reaction level (Fig. 11). The burning rate of Iron(III) oxide (Fe_2O_3) catalyst is higher than that of POSS due to larger specific surface area and more active sites. ODNPS has a higher burning rate than Fe_2O_3. The reason can be attributed to its high porosity compared to other POSS (Fig. 11). Therefore, high-energy POSS can be proposed as a possible alternative for the burning rate catalyst of solid composite propellants. Aluminum (Al) is used as a metal fuel in solid composite propellants. In the combustion process of the engine, Al is easily accumulated, causing incomplete combustion of Al and creating multi-phase currents in the nozzle of the rocket engine and reducing the propellant efficiency. In general, common burning rate catalysts, such as Fe_2O_3, cannot prevent aluminum accumulation in addition to increasing the burning rate. But the POSS compounds decompose before the melting temperature of Al and form a nanoscale porous structure that binds to the Al surface and improves their dispersion and reduces the possibility of their aggregation. POSS increases the contact surface between Al and the oxidizer, thereby reducing the content of C and Al elements and increasing the Oxygen (O) content in the products, which leads to more production of Carbon dioxide (CO_2), Carbon monoxide (CO), and Aluminium oxide (Al_2O_3) and increases the combustion efficiency. SEM images show that POSS porous structures reduce the size of combustion products (Fig. 12). As shown in the Fig. 13, POSS reduces the erosive burning in the rocket engine by reducing the amount of large size products. In dynamic images taken from engine combustion, it is clear that POSS gives the size of solid particles of combustion products (Fig. 14). These cases make it possible to introduce POSS as a promising additive in solid compound propellants.

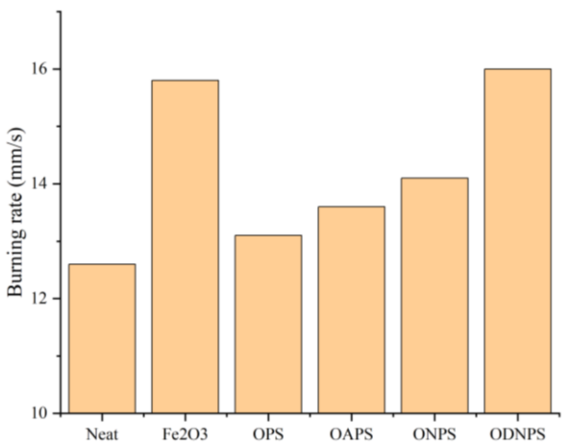

Fig. 10:Effect of POSS and Fe_2O_3 on the burning rate of composite solid propellant based on HTPB in 10 MPa pressure [34].

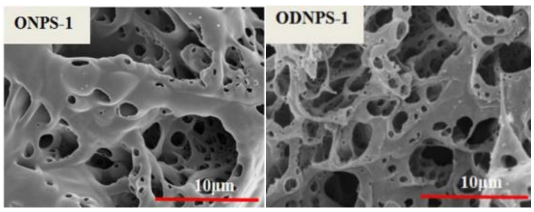

Fig. 11:SEM images of ONPS and ODNPS combustion residues [34].

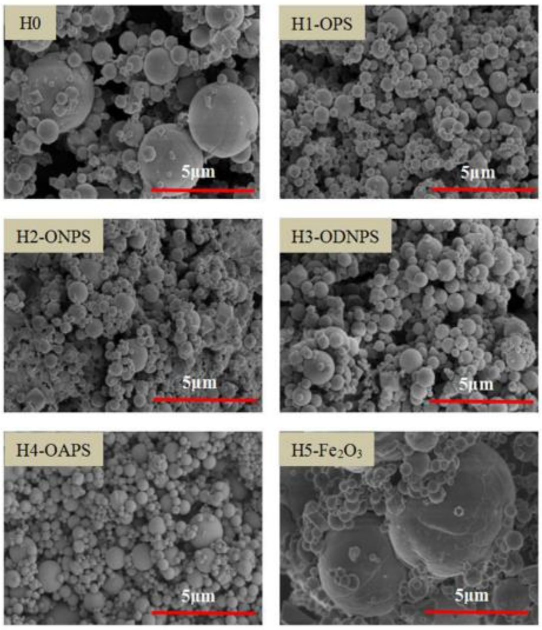

Fig. 12:SEM images of combustion products [34].

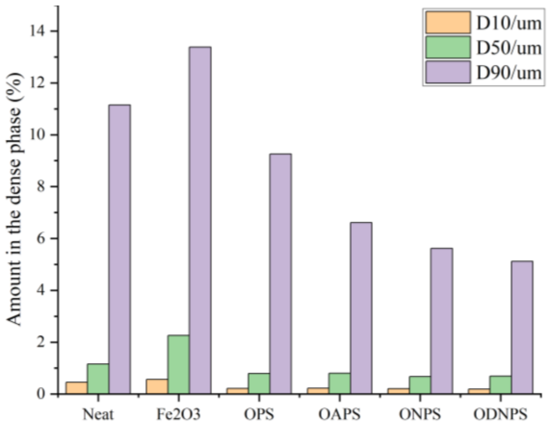

Fig. 13:Particle size of combustion products [34].

Fig. 14: Dynamic burning surface of three propellants [34].

5. Conclusion

POSS nanoparticles increase the mechanical strength, elongation, thermal stability and fire resistance of the polymer. Therefore, they enable polymers to be used in various parts of spacecraft, satellites and telescopes. Polymer composites containing The low dielectric constant of these materials has increased their use in electronic and telecommunication components. Using POSS as an additive in solid composite propellants increases the burning rate and improves its combustion performance. In high-energy POSS, the increase in burning rate was more evident. These characteristics have caused POSS nanoparticles to be widely used in the aviation and missile industries in recent years. But the main problem of POSS is its high price compared to other additives. Therefore, their use is only economically justified in expensive systems such as rocket, satellites and space telescopes. It is still too early to decide whether POSS nanoparticles can be used and replaced by other materials or not, and more research is needed to confirm the results and use them on an industrial scale [34].

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