



Polymer/clay aerogel composites with flame retardant agents: Mechanical, thermal and fire behavior



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ABSTRACT

Aerogel is a class of material characterized by its high void content and extreme lightness. Different polymer/clay aerogels have been prepared by a simply freeze–thaw process from a suspension with poly(vinyl alcohol) (PVOH) and clay (Na⁺-MMT). Low density polymer/clay aerogels modified with flame retardant agents were prepared using a similar approach. The addition of flame retardant agents slightly increased the apparent density of the final composites whereas the compression properties were reduced due to the decrease in the polymer/clay interfacial bonding. An exception was the sample containing Al(OH)₃ that exhibited higher modulus and stress at maximum deformation. Regarding thermal properties, the presence of ammonium polyphosphate (APP) or silica gel (SG) significantly slowed the rate of aerogel decomposition at the temperature range from 250 °C to 500 °C while the onset of polymer decomposition was not affected. Fire behavior was analyzed through cone calorimeter suggesting that either the presence of Al(OH)₃ or APP reduced the heat release rate of PVOH/clay systems.

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1. Introduction

Due to its associated energy and cost savings in product development and performance, the lightening of heavy structures and the use of weight-reduced solution has been a key objective for many industries. More recently, the growing concern about the global warming has driven research interest through the mass reduction of vehicle components, packaging items or consumed goods as a way to meet economy and carbon reduction targets. Among the different materials, polymers are very attractive due to its intrinsically low density. In addition, further reductions on the polymer apparent density are possible by means of foaming, which at the same time allows acquiring other interesting attributes [1]. Through improving key properties i.e. energy absorption or fire resistance, polymer foams can be expanded from traditional sectors like construction or packaging to high technological industrial sectors.

Aerogel was first described by Kistler, who reported the preparation of silica aerogel [2]. It is known to be one of the lightest foamed materials with a typical density ranging from 0.01 to 0.1 g/cm³. Though most of them are based on silica, recent works have shown a novel method to fabricate polymer/clay aerogel composites [3,4]. In this process, smectic clays are gelled in water and combined with a hydrophilic polymer capable of creating interfacial interactions with clays. When this clay/polymer

solution is frozen, the ice crystallization growth causes a rearrangement of the clay platelets being possible to achieve three-dimensional structures. The infiltration of such a structure with the polymer covering the particles produces a foam-like robust material. The polymer/clay ratio is of great importance and allows obtaining large variations in the specific properties [5,6]. Others factors, such as filler [7,8], polymer type [9,10] and freezing conditions [11,12], also have an influence on the aerogel performance.

Due to its relative low cost, high solubility in water, and strong interaction with clays, poly(vinyl alcohol) (PVOH) is an excellent candidate for making aerogels. The resulting properties are similar to those of conventional expanded polystyrene foam, or polyurethane foams. Although PVOH/clay composites systems have been already characterized [13], some aspects, such as the flame retardancy and the impact behavior have not been yet studied. Furthermore, the effect of the addition of fillers as a way to modify properties is still a matter that needs to be investigated. PVOH is a flammable polymer with a low limiting oxygen index value of 19.7 which results in a significant restriction of its fields of application. It was previously studied that flame retardant properties of PVOH can be improved by the incorporation of different types of additives. Potassium carbonate and silica gel were selected according to the results of Gilman et al. [14] who demonstrates that the flammability of PVOH can be reduced by the presence of relatively small quantities of these fillers in compression moulded disks. In another study [15], phosphorous–nitrogen compounds and ammonium polyphosphate were combined to form an intu-

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mescent flame retardant agent for PVOH. However, there is no report on the flammability of PVOH aerogels.

In this work, in an attempt to improve the properties of PVOH/clay composites, different flame retardant agents were added into the clay–polymer colloidal system to produce modified aerogel composites via the freeze-drying method. The mechanical, thermal, impact and fire behaviors of the resultant composites have been characterized.

2. Experimental details

2.1. Materials

Poly(vinyl alcohol) (PVOH) 98% hydrolyzed with an average molecular number of 40,000 g/mol, density 1.26 g/cm³, was purchased from Sigma Aldrich. Sodium Montmorillonite (Na⁺-MMT), PGW grade, density 2.6 g/cm³, was purchased from Nanocor Inc. Aluminium hydroxide(Al(OH)₃), Martinal OL-111/LE, *d*₅₀ = 0.7–1.2 μm was obtained from Albemarle Corporation. Ammonium polyphosphate (APP) compound, Budit3079, was received from Budenheim Ibérica. Silica gel (SG) and Potassium Carbonate (PC) (99% purity) were purchased from Panreac. All ingredients were used without further purification.

2.2. Aerogels preparation

Aerogels were prepared by combining clay gels and polymer solutions. Na⁺-MMT gels were made by dispersing 10 g clay in 100 ml of deionised water. Then the flame retardant agents were added to the gels in different amounts. The resultant suspension was blended at 6000 rpm using an IKA Ultra-turrax disperser. At the same time, 10 g PVOH was dissolved in 100 ml of deionised water at 80 °C via magnetically stirring for 2 h. Finally, polymer solution and clay/filler gel were mixed and stirred at low speed to avoid bubble formation. The even-dispersed resulting sol with a concentration of 5 wt% of PVOH, 5 wt% of clay (5PVOH5clay) and flame retardant agents were poured in cylindrical vials of 30 mm diameter, frozen at –80 °C in an ethanol/solid CO₂ bath for 30 min before lyophilized in a lyophilizer (Telstar Lyoquest) for 72 h. Once dried, samples were removed from the vials and kept in a vacuum desiccator prior to be tested. For the mechanical characterization, each aerogel specimen was cut and polished to form a flat cylinder of 25 mm diameter and 25–30 mm height. Control samples without flame retardant agent were also prepared following the same procedure. All the components were noted by its weight ratio to 100 ml of deionised water as shown in Table 1. For example, sample 5P5C2APP means that the weight ratios of PVOH, clay and APP are 5%, 5% and 2% respectively.

2.3. Characterization

2.3.1. Apparent density

The experimental apparent density (ρ_{app}) was calculated by measuring the mass of the specimen on a Cobos balance (Cobos,

Spain, +0.01 mg precision) and the aerogel cylinder dimensions. Five replicas were taken for each composition.

2.3.2. Morphology

The microstructure of the aerogels was investigated using a Scanning Electron Microscopy (SEM, Jeol 5610, Japan) at 10 kV. Prior to its observation, the samples were cryofractured and sputter-coated with a thin gold layer.

2.3.3. Compression testing

Low strain rate compression testing was performed using a Galdabini (Italy) universal testing machine at a crosshead rate of 1 mm/min and maximum strain of 70% following ISO 604 standard [16]. High strain rate compression was carried out in instrumented Dartvis 16000 (Ceast, Italy) impact tester, using a 50 mm diameter flat headstock and a total mass of 2 kg that was dropped from a position 100 mm height. The maximum impact energy was of 1.962 J. All the compressive experiments were done at room temperature. To avoid frictional effects, a thin layer of molybdenum disulfide grease was painted in the contact areas between support and sample.

2.3.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/DSC1 equipment. Samples were loaded in alumina pans and heated at a rate of 10 °C/min from 30 to 900 °C under dry air atmosphere.

2.3.5. Cone calorimetry

A cone calorimeter (Ineltec BECC model, Spain) was used to study the fire behavior of the aerogels following ISO 5660 procedure [17]. Square samples (100 × 100 mm) with an average thickness of 7 mm were located in a steel support to be exposed to an external heat flux of 50 kW/m².

3. Results and discussion

3.1. Apparent density and morphology

The apparent density of a porous solid is a measure that includes both the volume of the solid as well as the one of the voids either open or closed type. Table 1 shows the results of different aerogel composites. The presence of additives slightly raises the density as expected due to the higher presence of solids as well as a result of increasing the viscosity of the precursor solution. When a solution with a high viscosity is frozen, the growth rate of ice crystals slows down because of the higher resistance. Smaller ice crystals are generated and thus the volumetric expansion of the aerogel reduces.

Morphological studies of the aerogel composites are displayed in Fig. 1. Previous studies [4,13] indicate that the poly(vinyl alcohol) molecular chains can strongly interact with the clay platelets by hydrogen bonds, creating a three-dimensional polymer/clay network which is exemplified in Fig. 1a. It is clear that the polymer

Table 1
Mechanical property of flame retardant agents modified aerogels.

Samples	Density (g/cm ³)	Low strain rate		High strain rate	
		$\sigma_{10\%}$ (MPa)	<i>E</i> (MPa)	σ_{Max} (MPa)	ϵ_{Max} (%)
5P5C	0.105	0.088 ± 0.018	2.3 ± 0.5	0.66 ± 0.06	47 ± 3
5P5C5Al(OH) ₃	0.148	0.119 ± 0.011	2.1 ± 0.4	0.54 ± 0.01	34 ± 2
5P5C2APP	0.115	0.048 ± 0.004	0.8 ± 0.2	0.46 ± 0.01	62 ± 3
5P5C0.5SG	0.106	0.041 ± 0.010	0.8 ± 0.3	0.44 ± 0.01	51 ± 5
5P5C0.5SG0.3PC	0.110	0.060 ± 0.014	0.9 ± 0.2	0.51 ± 0.01	49 ± 2
5P5C1SG	0.112	0.065 ± 0.016	1.1 ± 0.2	0.55 ± 0.01	45 ± 3
5P5C1SG0.6PC	0.119	0.057 ± 0.007	1.0 ± 0.4	0.50 ± 0.03	44 ± 1

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