FLAME RETARDANT EFFECTS OF AEROGEL AND NANOSILICA ON ENGINEERED POLYMERS

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Introduction

Aerogels are typically manufactured via high temperature and pressure-critical-point drying of a colloidal metal oxide gel filled with solvents. Aerogel materials derived from silica materials represent a structural morphology (amorphous, open-celled nanofoams)¹ rather than a particular chemical constituency. Aerogel is not like conventional foams in that it is a porous material with extreme microporosity and composed of individual features only a few nanometers in length with a highly porous dendritic-like structure.

This unique substance has unusual properties such as low thermal conductivity, refractive index and sound suppression; in addition to its exceptional ability to capture fast moving dust.² The highly porous nature of the aerogel's structure provides large amounts of surface area per unit weight. For instance, a silica aerogel material with a density of 100 kg/m³ can have surface areas of around 800 to 1500 m²/g depending on the precursors and process utilized to produce it.

To take advantage of the unique properties of silica aerogels, especially the ultra light weight and low thermal conductivity, their composites with various engineering polymers were prepared and their flammability was investigated by Cone Calorimetry. The flammability of various polystyrene/silica aerogel nanocomposites were measured. The combination of these nanocomposites with a NASA patented flame retardant SINK³ were also studied. The results were compared with the base polymer to show the differences between composites with different forms of silica.

Experimental

Materials and Sample Preparation

This work examines several important combinations of flame retardant systems to understand the combination effects of flame retardant nanocomposite materials. Polymer/aerogel composites were prepared using a twin-screw extrusion approach, while polystyrene/silica nanocomposites were prepared by a single-screw technique⁴. The resulting materials were subjected to comprehensive studies on their flammability. Three types of Cabot hydrophobic silica aerogels were investigated in this project: 4 mm nanogel granules, ball-milled nanogel granules, and 80 micron beads. Nanoscale fumed silica material, Aerosil® 972 (16 nm, surface area is $110\pm20 \text{ m}^2/\text{g}$) (an organo-silica where the surface is covered by methyl groups), was provided by Degussa.

Cone Calorimetry Evaluation

Heat and visible smoke release rates of composites were evaluated at irradiance of 35 kW/m² with a Custom Scientific Cone Calorimeter according to modified ASTM E1354. Testing samples were made in triplicate of two conjunctive 2 x 4 x 1/16 inch strips instead of 4 x 4 x 1 inch samples. Analyses included peak heat release rate (PHRR), total heat release (HR), mass loss rate (MLR), and total time to ignition (TTI). The standard derivation was within 5 percent.

Results and Discussion

The Cone data of the nanocomposites from different types of aerogel and engineering polymers are shown in Table 1. It was found that the addition of 10 wt% ball-milled aerogel to Versify[®] propylene-ethylene copolymers from Dow Chemical did not alter the flammability, as indicated by the PHRR of 970 kW/m² for Versify[®] versus 957 kW/m² for 10% ball-milled aerogel filled Versify[®]. On the other hand, the PHRR was dramatically reduced to 645 kW/m² when 10 wt% of aerogel granules were used. Therefore, it is suggested and somewhat expected that the milling destroyed the mesoporous aerogel particles trapped air and reduced the heat transfer to the base polymer, thus delaying or reducing the PHRR. When aerogel beads

were introduced to Polyamide 66 (PA66), the PHRR of PA66 was reduced from 872 to 501 kW/m². For PA66 with 24% GF (glass fiber) composite, the addition of aerogel further reduced the PHRR of composite from 555 to 406 kW/m², while simply increasing the amount of GF in composites resulted in higher PHRR (645 kW/m² for 30% GF composite). These results suggest that combination flame retardant effects between aerogel and GF occurred in PA66.

Table1. Cone Results of Ae	rogel Based Composites
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Material	PHRR	TTI (s)	Total HR	MLR
Versify	970	38		17.9
Versify-Aerogel-ball mill	957	28		19.1
Versify-Aerogel-granules	645	18		10.7
Polyamide 66	872	39	21.4	12.4
Polyamide 66-Aerogel- beads	501	12	19.1	10.2
Polyamide 66 /24% GF	555	14	24	18.9
Polyamide 66 /30% GF	645	14	16.6	72
Polyamide 66/24% GF/Aerogel	406	14	24	18.9

As for nanosilica based polymer nanocomposites, the addition of nanosilica also reduced the PHRRs. For instance, 20% SINK in Polystyrene (PS) reduced the PHRR of PS from 1212 to 838 kW/m² (-31%); 10% silica reduced it from 1212 to 1060 kW/m² (-13%), while the combination of silica aerogel and SINK reduced it to 530 kW/m² (-56%), Table 2.

Table2. Cone Results of Polystyrene/Silica Nanocomposites.

Material	PS	PS/ SINK- 20	PS/ silica-10	PS/silica- 10/SINK-20
PHRR	1212	838	1060	532
TTI (s)	. 43	22	26	25
Total HR	3.25	3.04	3.31	2.75
MLR	29.6	16.5	30.2	14.8
Residue	2.1	6.4	11.6	20.1

The strong combination effect of nanocomposites with SINK-filled polystyrene was observed with silica nanocomposites, as shown in Figure 1. The combination of silica and SINK reduced the PHRR to 530 kW/m² (-56%). Similar to nanocomposites with attapulgite⁵, the addition of silica broadens the burning time span, significantly reduces the mass loss rate, total heat released, and enhances residue.



Figure 1. HRR of polystyrene/silica nanocomposites.

Conclusions

The Cone results of silica aerogel based composites materials indicated that aerogel is effective in enhancing the flame retardancy of various engineering polymers, while the flammability of the resulting composites were affected by the type of aerogel. Combination effects of aerogel with other additives in reducing flame retardancy are observed. Moreover, results of nanocomposites suggested that fumed silica had similar combination flame retardant effects. Therefore, it is clear that factors other than chemical composition of additives have significant effects on the flammability of engineered polymeric materials.

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