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A novel hybrid PU-alumina flexible foam with superior hydrophilicity and adsorption of carcinogenic compounds from tobacco smoke

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ABSTRACT

A novel porous polyurethane (PU) hybrid foam was designed to improve the hydrophilicity of a conventional open pore PU foam, and to enhance the adsorption of carcinogenic compounds from tobacco smoke.

The hybrid foam was prepared by interdispersing ultramilled alumina particles within PU precursors to realize a PU/Al_2O_3 hybrid porous material with well controlled microstructural properties and improved hydrophilicity. The capability of the as obtained hybrid foam to adsorb toxic compounds from the mainstream of tobacco smoke was investigated by using a cellulose-active carbon-cellulose triple filter model, and the results were compared to those obtained for neat PU foam and the standard cigarette filter tip.

The results of this study showed that the ultramilled alumina particles enhanced both thermal stability and hydrophilicity of the neat PU foam. Furthermore, the as-obtained hybrid PU/Al_2O_3 foam was able to improve the adsorption of nitrosamines, acetamide, idroquinone, cresol and small aminic and aldehydic molecules, if compared to neat PU foam and standard cigarette filter tip, evidencing potential as tobacco smoke filter.

1. Introduction

Smoking tobacco is associated with a large number of adverse health effects, including cancer, cardiovascular illness and respiratory diseases. Therefore, reducing toxic compounds of tobacco smoke is one of the most important challenges of the life science in the 21st century.

The physical and chemical structure of tobacco mint smoke is rather complex. Tobacco mint consists of almost 4800 constituents, ranging from small organic and inorganic molecules to biopolymers [1–3]. During smoking, the pyrolysis of the tobacco constituents mixture occurs at temperatures up to 950 °C and in the presence of different oxygen concentrations. This thermal process generate more than 4800 different compounds, the majority of which are well-recognized to be toxic and carcinogens in humans. Among them, tobacco specific nitrosamines (TSNAs), polycyclic aromatic hydrocarbons (PAHs), nicotine and phenols represent the most toxic compounds for both smokers and passive smokers [4,5].

The design of novel functional filter tips able to selectively adsorb toxic compounds from tobacco smoke is continuously evolving and is the object of great efforts for scientific researchers. Efficient adsorbents must possess a chemical composition able to allow for a selective adsorption of tobacco smoke compounds, coupled with a suitable pore structure to accommodate these substances without undergo significant physical and chemical modifications.

Cigarette smoke filter tips were prepared by the assembly of cellulose fibers, obtained by the compaction of inorganic particles, such as activated carbon (AC), zeolites and metal oxides and, in such cases, by their combinations [2,6].

Polyurethane (PU) foams were also investigated for tobacco smoke filtering applications [6]. Indeed, PU is characterized by a large number of PAHs and cyanides binding sites, two of the most carcinogenic compounds of tobacco smoke [6]. Nevertheless, the hydrophobic nature of PU foams often requires complex physical and/or chemical treatments to improve their hydrophilicity and the corresponding ability to absorb hydrophilic molecules [7,8].

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Among inorganic materials, Al_2O_3 has received a great deal of attention for applications requiring the adsorption of hydrophilic organic and inorganic compounds, such as phenols, amines, carbon anhydride and nitro compounds [9–11]. These characteristics are due to the fact that alumina surface is considered to have both Bronsted (OH–Al) and Lewis (Al^{3+}) acid sites together with a high specific area [9]. Furthermore, if compared to other absorbents, no loss of its Lewis acidity was observed upon reduction [11]. It is also important to point out that the adsorption capability of alumina was significantly improved when submitted to ultrafine milling, a process known as 'mechanical activation', that increases its surface area and reactivity [12,13]. Alumina was also used as coating for zeolite particles in order to improve the adsorption of TSNA [10].

All these scientific results showed that by the appropriate selection of the composition and structure of the adsorbents it was possible to target the adsorption properties of the material with respect to specific tobacco smoke compounds. Nevertheless, next generation of tobacco smoke filters must be designed in order to allow for the multi-functional adsorption of carcinogenic compounds from tobacco smoke and, fabricated without using extremely complex processes that are at odds with a huge cigarette smoke filter tips production.

In this study we reported the design and fabrication of a novel hybrid porous material suitable to be used as tobacco smoke filter. The material was fabricated by incorporating ultramilled alumina particles within a flexible PU foam. The morphology and pore structure features of the hybrid foam were assessed by SEM microscopy and Image analysis, while wettability tests were performed to evaluate its hydrophilicity. Smoking tests were carried out by using a ISO machine-smoking in order to evaluate the ability of the PU/Al_2O_3 hybrid foam to improve the adsorption of toxic compounds of tobacco smoke, mainly PAHs, nicotine, TSNA, amides and phenols. In particular, these characteristics were assessed by two different approaches. First, thermogravimetric measurements (TGA/DTGA), Fourier Transform Infrared spectroscopy-(FTIR) and nuclear magnetic resonance (NMR) analysis were performed on smoked PU/Al_2O_3 samples, and the results were compared to those achieved for the neat PU foam and a standard cigarette filter tip. Simultaneously, the quantification of several toxic compounds in mainstream cigarette smoke, mainly Tar, CO, Nicotine,TSNAs, PHAs and phenols, was determined following the standard ISO 3308:2000.

2. Experimental

2.1. Chemicals

Polyether polyol and Metilen Diphenyl di-Isocyanate (MDI) were purchased from Huntsman (Italy) and used as received. Distilled water was used to control foaming. Al_2O_3 powder was provided from Sigma–Aldrich (Italy). Trade cigarettes were purchased from local market.

2.2. Preparation of the PU and PU/Al_2O_3 hybrid foams

The PU foam was prepared by mixing polyol and additives for two minutes and, subsequently by adding MDI under continuous mixing for 30 s. The as obtained mixture was poured within a $10 \times 10 \times 3\ cm^3$ mould to allow foaming, and further cured at 50 °C for 24 h. Before the preparation of the PU/Al_2O_3 hybrid foam, the alumina powder was milled by using an Ultra-centrifugal mill (Z100, RETSCH, Germany) equipped with a 80 μm grind size, and selecting a milling speed of 14,000 rpm. The as-obtained activated powder was mixed with the reagents, and foaming achieved following the previously described procedure. The polyol/MDI/water/Al_2O_3 composition was 66/33/1/0 for neat PU foam and 33/16.5/0.5/50 wt.% for PU/Al_2O_3 hybrid foam.

2.3. Physical characterizations

The thermal degradation of the foams was investigated by thermogravimetric (TGA) and derivative TGA (DTGA) analyses. The tests were carried out on a TGA2950 (TA Instruments, USA) over a 30–700 °C temperature range, at 10 °C/min and under inert atmosphere.

The morphology of the foams was analyzed by SEM (S440, LEICA, Germany) at an accelerating voltage of 20 kV, while gravimetric measurements and image analysis were used in order to assess the porosity and the pore size distribution of the scaffolds, as described in a previously reported work [14].

Energy Dispersive Spectroscopy (EDS, INCA 200, Oxford, UK) and trypan blue staining analyses were performed on PU and PU/Al_2O_3 foams in order to assess their elemental composition and to examine the distribution and exposure of the HA particles on the pore walls of the PU/Al_2O_3 foam. For trypan blue staining, the samples were soaked with a 1% w/v water solution for 10 min, washed twice in 100% ethanol and analyzed by an optical microscope.

Wettability tests were performed by a Contact angle System OCA20 (Dataphysics, Italy) in order to determine the effect of the Al_2O_3 particles on the hydrophilicity of the PU foam. A 3 μL water droplet was poured onto the surface of the foams, and the time required for the complete fluid penetration (wetting time), measured. Twenty measurements were performed for each sample.

2.4. Smoking tests and chemical characterizations

Smoking tests were carried out to assess the ability of PU and PU/Al_2O_3 hybrid foams to be used as cigarette smoke filters. As shown in the scheme of Fig. 1, the tests were performed by using a cellulose/active-carbon/cellulose triple filter of a trade cigarette. In particular, the active-carbon (AC) of the triple filter ($d = h = 7$ mm) was replaced with the PU or PU/Al_2O_3 foam, and the obtained cigarette smoked according to the ISO smoking protocol (ISO 3308:2000) by harmonized Borgwaldt LM1 smoking machine (Borgwaldt KC GmbH, Hamburg, Germany).

The adsorption properties of the samples were assessed by the analysis of the compound retained within the filter and those present within the cigarette smoke. For the first evaluation, FTIR and NMR spectroscopies were used. In particular, FTIR analysis of smoked samples was carried out by using a Nexus-Nicolet spectrophotometer working at a wavenumber resolution of 4 cm^{-1} and 64 scans. The FTIR spectra, in the 4000–600 cm^{-1} wavenumber range were collected in absorbance mode on transparent pellet obtained by dispersing the crumbled samples in KBr (2% wt./wt.). Spectra deconvolution was also performed to clarify the contributions of the different functional groups by using the best fits by Gaussian sum, and normalized considering as un-variant peak the adsorption at 1230 cm^{-1}. PU and PU/Al_2O_3 samples before smoking were tested for proper comparison.

For NMR analysis, proton NMR spectra were recorded on a Bruker 600Avance spectrometer operating at 600.13 MHz and at 300 K by a High Resolution Magnetic Angle Spinning (HR-MAS) microprobe. The analysis was performed on the liquid samples obtained by extracting the smoked filters with two solvent: fully deuterated dimethylsulfoxide (DMSO-d_6) and a mixture of deuterated water/dimethylsulfoxide (D_2O/DMSO-d_6) in order to collect highest number of trapped compounds. The spectra were collected with a 90° pulse of 8 μs, relaxation delay of 2 s, spinning rate 6 kHz and 1024 scans. The water signal was suppressed by presaturation