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Applications of micro-scale combustion calorimetry to the studies of cotton and nylon fabrics treated with organophosphorus flame retardants

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ABSTRACT

Effective testing methods are critical for developing new flame retardant textiles by the industry. However, the current testing methods all have limitations. In this research, we applied micro-scale combustion calorimetry (MCC) for evaluating the flammability of the cotton woven fabric treated with a traditional reactive organophosphorus flame retardant in combination with a synergistic nitrogen-containing additive and the nylon-6,6 woven fabric treated with a hydroxyl-functional organophosphorus oligomer and crosslinkers. We found that MCC is capable of differentiating small differences among the treated fabric samples with similar flammability. MCC is able to make quantitative measurement of the peak heat release rate, the most important parameter related to fire hazard of materials, of textile whereas such analysis is more difficult using cone calorimetry due to textile fabrics' low thickness. By using the thermal combustion parameters measured by MCC, we were able to calculate the limiting oxygen index (LOI) of various treated cotton fabric samples with near-perfect agreement between the experimentally measured and the predicted LOI values of treated cotton fabrics. We also compared the capability of MCC and differential scanning calorimetry for analyzing flame retardant cotton textiles.

1. Introduction

Textile materials differ widely in construction and in chemical nature of the fibers, but most textile fibers are flammable. Flame retardant (FR) finishing is the most commonly used method to produce FR textile fabrics [1,2]. FR textiles are mainly used for protective work uniforms, firefighter apparel, military uniforms and home furnishing textiles. Recent years, the U.S. government has established new flammability requirement for mattress and upholstered furniture [3]. The demands for FR textiles have had a steady growth for the past decades, and such trend is expected to continue for years to come.

Testing and analyzing performance of FR textile samples are the most critical part in the research and development of new FR textiles by the industry, and the capability of a testing method to differentiate small differences in flame retardancy among those samples with similar flammability is vital for the success of the research and development work. However, the testing methods currently used by the industry and research community to evaluate the flammability of textiles, including limiting oxygen index (LOI), vertical fabric burning test, 45° fabric burning test, cone calorimetry, thermogravimetric (TG) analysis and differential scanning calorimetry (DSC), are generally inadequate.

LOI, a testing method for evaluating the ignition and ease of extinction of a sample, is a quantitative and reproducible method with wide spread use in both industry and academic research [4–6]. The LOI method has been developed as international standards (ASTM D2863 or BS ISO 4589-2). LOI showed good correlation to char formation and the results of other practical testing methods such as UL 94 [4]. In spite of its wide uses, the LOI method has a number of inherent deficiencies. LOI uses a downward burning configuration which is fundamentally different from that of most real fires; therefore such configuration has different heat transfer and rate of burning characteristics. LOI is run at oxygen concentration mostly higher than that of atmosphere. Moreover, research showed that LOI results were not able to predict the real fire performance in most cases [5].

Fabric vertical burning and fabric 45° burning testing methods are used to evaluating textile fabrics' flammability specified by the U.S. federal regulations 16 CFR 1615/1616 and 16 CFR 1610, respectively [7]. The vertical and 45° burning methods are also used as international standards (ASTM D 6413 and ASTM D 1230, respectively). Those methods are required for ensuring the tested fabrics in compliance with government regulations. The 45° burning testing is a qualitative method. Vertical flammability test based on a fabric specimen's char length after a standard burning procedure is probably the most frequently used textile flammability testing

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method in the industry. However, it is semi-quantitative at best, and is not very useful for screening and optimizing FR fabrics with small differences as those frequently encountered in research and development.

Thermal analysis methods, including TG and DSC, have also been used in textile flammability research [8–10]. The thermal analysis methods can be used to make quantitative measurement of a sample's weight reduction and heat release/absorption as a result of dehydration, oxidation, volatile evolution and char formation when the sample is exposed to a programmed heating procedure. The TGA and DSC data reflect the characteristics of thermal decomposition and degradation, not combustion. Therefore, TGA and DSC cannot be used to evaluate performance of FR textile samples.

More importantly, all the testing methods mentioned above are not able to provide heat release rate (HRR), the single most important parameter in characterizing flammability behaviors and predicting fire hazards of flammable materials including textiles. Research has demonstrated that HRR is the most significant predictor of fire hazard [11]. Cone calorimetry has been developed for evaluating HRR and other related parameters, and it has been widely used in predicting the fire hazard of different materials as standard international testing methods (ASTM E1354, ASTM D6113 and ISO 5660) [12]. However, the applications of cone calorimetry to textile fabrics encountered difficulties. Cone calorimeter experimental results are highly dependent on the sample thickness. Textile fabric samples are dimensionally thin; hence they are thermally thin samples. Research showed that thermally thin samples had larger maximum HRR values than thick samples [13]. The application of cone calorimetry to textile fabrics was modified by introducing a special sample mounting device. It was found that the repeatability for measuring single layer fabric specimens tested during one day was improved with such a device, but the day-to-day repeatability is still poor [14]. It was also reported that measurement of highly char-forming barrier fabrics using cone calorimetry could be complicated [15].

Micro-scale combustion calorimetry (MCC) is a pyrolysis-combustion flow calorimetry with dynamic capability to measure HRR and other related parameters of polymers using samples of a few milligrams [16]. MCC first heats a sample in a controlled pyrolysis state under nitrogen (or a mixture of oxygen and nitrogen) gas flow, then rapidly oxidizes the pyrolyzate in excess oxygen at a high temperature (e.g., 900 °C) to simulate combustion. Thus, MCC reproduces both the solid phase state (pyrolysis) and gas phase state (combustion) chemical processes of polymeric materials, and determines HRR based on the quantity of oxygen consumed in a non-flaming oxidation process [16–18]. The MCC method has also been established as a standard testing method (ASTM 7309) in 2007. Good correlations were observed between the data of cone calorimetry and those of MCC for flame retardant polyolefin [19].

In our previous research, we found that MCC is capable of determining HRR and other flammability parameters of different textile fabrics [20]. In this research, we applied MCC to measure the flammability of cotton and nylon fabrics treated with phosphorus-based flame retardants, and also compared the MCC parameters with the LOI and thermal analysis data.

2. Experimental

2.1. Materials

Two cotton woven fabrics were used in this study: (1) a twill weave fabric (242 g/m^2) dyed with vat dyes supplied by Milliken, Blacksburg, South Carolina; and (2) a nylon-6,6 woven fabric (124 g/m^2) supplied by Testfabrics Inc., West Pittiston, Pennsylvania. The flame retardant N-methylol dimethylphosphonopropionamide (MDPA) with the commercial name of "Pyrovatex CP New®" (CA Registry No. 20120-33-6) was supplied by Ciba Specialty Chemicals, High Point, North Carolina. The hydroxy-functional organophosphorus oligomer with the trade name of "Fyroltex HP" (formerly "Fyrol 51", CA Registry No. 70715-06-9) was supplied by Akzo Nobel Chemical Corporation, New York. Dimethyloldihydroxyethyleneurea (DMDHEU) with the commercial name of "Freerez 900®" and trimethylolmelamine (TMM) with the commercial name of "Aerotex M-3®" were supplied by Noveon, Cleveland, Ohio. The catalyst based on NH_4Cl with the commercial name of "Catalyst RD®" was supplied by Eastern Color & Chemical, Greenville, South Carolina.

2.2. Fabric treatment

The woven cotton fabric was immersed in a solution containing a flame retardant and other additives, passed through a laboratory padder with two dips and two nips, then dried at 90 °C for 3 min and finally cured in a Mathis curing oven at 165 °C for 2.5 min. The wet pick-up of the cotton twill fabric was 87 ± 2%. The nylon-6,6 fabric was treated similarly, dried at 90 °C for 1.5 min and cured at 165 °C for 2 min. The wet pick-up was 80 ± 2%. After curing, the treated woven fabrics were subjected to one home laundering cycle before testing. All concentrations presented in this study were based on weight of bath (w/w, %).

2.3. LOI measurement

The LOI of the cotton woven fabric was measured according to ASTM Standard Method D2863.

2.4. MCC measurement

The MCC measurement was conducted using a micro-scale combustion calorimeter (model "MCC-2") produced by Govmark, Farmingdale, New York, according to ASTM D7309 (Method A). To improve sample uniformity, the textile fabrics were first ground in a Wiley mill to form homogeneous powders. The sample thus prepared (~5 mg) was heated to a specified temperature using a linear heating rate (1 °C/s) in a stream of nitrogen flowing at 80 cm^3/min. The thermal degradation products of the sample in nitrogen were mixed with a 20 cm^3/min stream of oxygen prior to entering the 900 °C combustion furnace. Each sample was run in three replicates and the MCC parameters were the averages of the three measurements. The combustion of fuel gases in the mixture of 20% O_2 and 80% N_2 at 900 °C for 10 s is a very conservative condition to ensure complete oxidation of the fuel gases. It has been reported that 2% O_2 concentration in the mixture was sufficient for complete oxidation of fuel gases formed by the degradation of plastics samples [17].

2.5. Determination of phosphorus concentration on the treated fabrics

Approximately 2 g of a fabric sample taken from five different parts in a treated fabric was ground into a powder using a Wiley mill to improve sample uniformity. 2 ml concentrated H_2SO_4 was added to 0.1 g of solid fabric powder in a beaker. 10 ml 30% H_2O_2 was added drop-wise into the beaker, allowing the reactions to subside between drops. The reaction mixture was then heated up to 250 °C to digest the powder and to evaporate the water until a dense SO_3 vapor was generated. The completely digested sample as a clear and homogenous solution was transferred to a 50 ml volumetric flask, and then diluted with de-ionized water. The solution thus prepared was analyzed using a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer