THERMAL PROPERTIES OF AUTOMOTIVE POLYMERS I. THERMAL GRAVIMETRIC ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY OF SELECTED PARTS FROM A DODGE CARAVAN

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Abstract

Thermal properties of polymeric materials were measured to obtain phase changes and decomposition characteristics as the materials are heated through their decomposition temperatures. Twenty two components, consisting of seventy one polymeric parts used on the Dodge Caravan, were studied. These components were chosen because they could play a role in car fire propagation as a result of their large size and/or location on the vehicle. The polymers used for making these parts were all identified using mainly Fourier transform infrared spectroscopy (FTIR). Filler content and type as well as specific gravity for all components were also determined.

A high resolution thermal gravimetric analysis (TGA) instrument was used to calculate thermal decomposition temperatures, and rates of decomposition. TGA runs were conducted in nitrogen and air atmospheres. We found that cross linked systems have, in general, lower thermal decomposition rates than thermoplastic systems. Most polymers exhibited a higher rate of decomposition in nitrogen than in air. The chemical structure of the polymer had a profound effect on the mode and rate of degradation. For the different polymers investigated the ranges of decomposition temperatures were between 233 °C and 522 °C in nitrogen, and 240 °C to 565 °C in air. We also used TGA to determine the amounts of organic residues including carbon black, and the amounts of inorganic fillers found in the different compositions.

The differential scanning calorimetry (DSC) measurements were conducted using a modulated unit. Melting points, glass transition temperatures, heat capacities, and heats of fusion were calculated. These variables measure the amount of heat absorbed or evolved during heating of the sample and, as such, have a significant influence on the flammability characteristics.

Purpose

The work described in this report is being done under Project B.10 (Study of Flammability of Materials) of the GM/DOT Settlement Agreement. The overall objective is to study the flammability of materials, including engine compartment fluids (other than gasoline), and vehicle exterior and interior materials using existing laboratory test methods as appropriate, as to their flammability properties and limits. For selected materials, efforts will be made to identify or devise cost effective, less flammable substitutes which will not compromise other important physical properties.

Conclusions

Thermal decomposition behavior of selected automotive polymers has been quantified under well controlled conditions. The results will be used to interpret the potential flammability behavior of these polymers. Also thermodynamic properties including

melting behavior, heat of fusion, glass transition, and heat capacity were all determined for these materials and will be used to quantify ignition and fire propagation behavior.

Significance

The information developed in this study will contribute towards quantifying the flammability of polymeric compositions and will help in identification and characterizationof less flammable substitutes.

Introduction

Several complementary research projects for studying different aspects of the flammability characteristics of polymeric materials used in passenger vehicles and light trucks are being conducted at the National Institute for Science and Technology (NIST), Factory Mutual Research Corporation, and at the General Motors Research and Development Center. Four segment leader vehicles were chosen for the investigation; namely: a passenger van (Dodge Caravan), a utility sport vehicle (Ford Explorer), a front wheel drive vehicle (Honda Accord) and a rear wheel drive vehicle (Chevrolet Camaro). This particular study deals with the investigation of thermal characteristics of twenty two polymeric components used on the 1996 Dodge Caravan. The parts were identified by visual inspection and from observation and data obtained on car burning experiments being conducted on pre-crashed vehicles under Project B.3 (Fire Initiation and Propagation Tests). The thermal properties investigated using thermal gravimetic analysis include decomposition temperatures and rates of decomposition of polymeric component under nitrogen and air atmospheres. These values are related to ignition temperatures and flame spread in a fire situation under oxygen rich and oxygen starved atmospheres. We also used the differential scanning calorimeter to determine melting points, heats of fusion, glass temperatures, and heat capacities of the polymers. These variables measure the amount of heat absorbed or released by the polymer in a fire situation. Also the melting points and glass transition temperatures will be a measure of the temperatures at which softening and dripping would be expected.

Experimental

Polymer Composition Analysis: The compositions of most of the polymeric parts chosen for this investigation were not known. For most parts there was no label to identify the type of resin or other additives used to make the part. For this reason all parts were analyzed to identify their composition. Several analytical techniques were used. A Nicole Magnum-IR. 550 Fourier transform infrared spectrometer (FTIR) was used to identify the nature of the polymer and in some cases identify the type of additive used. For solid samples a micro analysis technique was used by placing the sample in a diamond cell and

conducting the analysis on small areas under a microscope. The diamond cell is used because it does not get scratched or damaged by solid samples, and also because diamond has a high refractive index and it is transparent to infrared light. The visible/infrared light microscope is used pick up the area of the sample to be analyzed, and for focusing the infrared beam on that area for micro analysis. For further confirmation some samples were also extracted with chloroform, and the FTIR spectrum of the extract was obtained.

Thermal gravimetric analysis was used to determine the amount of inorganic filler used in the polymer compositions. Samples were heated in a thermal gravimetric analysis (TGA) cell under a programmed heating rate in an air atmosphere to 1000°C. Under these conditions all organic materials in the sample burn and volatilize. The amount of residue left behind can be used to calculate the inorganic filler concentration in the parent material.

Qualitative and semi-quantitative elemental analysis of fillers was conducted by X-ray fluorescence spectroscopy. This technique is capable of identifying all elements with atomic numbers greater than nine. In some instances the crystalline structure of the filler, determined by X-ray diffraction, was used for identifying the filler type.

High Resolution Thermal Gravimetric Analysis (TGA): All thermal analysis was conducted using aTA 2100 controller (TA Instruments, Inc.). The TGA unit is a TA 2950 operated in high resolution mode where suppression of heating rate is automatically applied when degradation of the polymer proceeds at a fast rate. The heating rate was set at 50 °C/minute, and the resolution factor was set at an intermediate value of 4. All samples were heated from room temperature to 980 °C. For each sample decomposition temperatures and the maximum rates of decomposition were determined.

Modulated Differential Scanning Calorimetry (MDSC): The cell used for conducting these measurements is the TA 2920. Measurements were conducted at temperatures of -62 °C to 270 °C. The heating rate was set at 5°C /minute. The degree of modulation was set at +/- 0.531 °C, every 40 seconds. Glass transition temperatures, melting points, heats of fusion, and heat capacity values were all determined from these measurements.

Density Measurements: Specific gravity values of all solid samples except foams were determined from weight in air divided by weight in water. For sponge samples the density was determined from measurements of weight and volume of uniform cylinders cut from these samples.

Results & Discussion

Location of Polymeric Parts on the Vehicle:
The locations of the selected polymeric components on a Dodge Caravan are schematically shown in Figure 1. These include the following passenger compartment components: headliner, instrument panel shelf, instrument panel console, kick panel insulation (silencer), and steering column boot. Selected exterior and under hood

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