Thermal and Flammability Properties of a Silica-PMMA Nanocomposite

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Introduction

The properties of a polymer composite material depend not only upon the properties of the individual components, but also upon the polymer's phase morphology and interfacial properties with the other component. If the area of the interface between the two components becomes significantly large, the latter consideration, or interphase, becomes of primary importance in determining the overall properties of the composite material[1]. For example, polymers filled with nanoscale silica particles generated a second glass transition that was much higher than that of the polymer resins[2]. This phenomenon was accounted for by the formation of tightly and loosely bound polymer chains around the particles[3]. Other studies reported an improvement in physical properties[4,5] and also some improvement in thermal stability[6]. An improvement in flammability properties of polymers using the concept of enhanced interfaces with layered silicates has been demonstrated for clay-nanocomposites[7,8,9]. In this study, the use of nanoscale silica particles as a flame retardant additive in a polymer nanocomposite is investigated with regard to improvements in both the flammability properties and the physical properties of poly(methyl methacrylate) (PMMA). In contrast, conventional flame retardant additives, such as brominated compounds and hydrides, improve flammability of polymers but tend to reduce their physical properties.

Experimental‡

Methyl methacrylate (MMA, 99%, inhibited with 10 ppm monomethyl ether of hydroquinone), and 2,2-dimethoxy-2-phenylacetophenone (99%, DMPA) were purchased from Aldrich. Colloidal silica (12 nm, 30 mass% in methyl ethyl ketone; MEK-ST) was donated by Nissan Chemical. A Digital Instruments Dimension 3100 atomic force microscope (AFM) was operated in tapping mode in laboratory air conditions using a commercial silicon microcantilever probe. Manufacturer's values for the probe tip radius and probe spring constant are in the ranges of 5 nm to 10 nm and 20 N/m to 100 N/m, respectively. Topographic and phase images were obtained simultaneously using a resonance frequency of approximately 300 kHz for the probe oscillation, a scan rate of 0.6 Hz, a free-oscillation amplitude of approximately 50 nm, and a set-point amplitude of approximately 30 nm. Phase images are presented without any offsetting, planefitting, or filtering applied to the image data. Bright field transmission electron microscopy (TEM) images of polymethylmethacrylate (PMMA)-nanosilca nanocomposites were obtained at 120 kV, under low-dose conditions, with a Phillips 400T electron microscope. The PMMA-SiO_2 nanocomposite was ultramicrotomed with a diamond knife at 23 °C to give ~70 nm thick sections. The sections were transferred from water to carbon-coated Cu grids of 200 mesh. Thermal gravimetric analysis (TGA) data were collected from 30 °C to 700 °C at 10 °C/min under N_2 using a TA Instruments SDT 2960.

Preparation of PMMA-Silica Nanocomposites:[10] To 1.0 g of the MEK-ST solution was added 9.0 g of MMA. The combined solution was stirred with a magnetic stirbar and allowed to concentrate at 23 °C until the residual mixture was approximately 3.0 g. Assuming that most of the excess methyl ethyl ketone had been removed by co-evaporation with the excess of MMA, the final mixture consisted of 0.3 g or 10 mass% colloidal silica dispersed in 2.7 g of MMA. This mixture was placed in a clear glass vial and activated for photopolymerization with 0.7 mass% DMPA. The glass vial containing the activated mixture of MMA/SiO_2 was sealed and allowed to photo-polymerize at 25-27 °C for 6 h by exposure to natural sunlight. A clear, hard solid formed in the vial which was unsealed and placed in a vacuum oven at 100 °C and a pressure of 2.7 kPa for 30 h. The cylindrical composite plug was removed by carefully fracturing the glass vial. As a control, the same polymerization procedure was conducted on 3.0 g of DMPA-activated MMA without the presence of the MEK-ST.

Results and Discussion

Tapping mode atomic force microscopy (AFM) images were taken of a smooth surface of a molded PMMA sample to examine the dispersion of the silica particles in the PMMA resins.

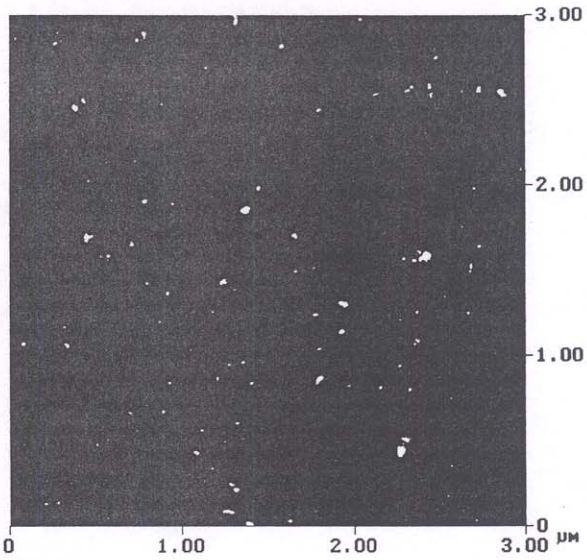

Figure 1. AFM image of the PMMA-SiO_2 sample: 3 µm x 3 µm area. The color scale from black to white represents a phase difference of 30°.

The contrast in the image (**Figure 1**) is likely caused by repulsive tip-sample interactions for the nanosilica, resulting in a positive phase that shows up as bright, and an attractive tip-sample interaction for the PMMA, resulting in a negative phase that shows up as dark. In the figure, many small agglomerates of perhaps between 2 and 6 particles are observed along with what appear to be single particles with diameters of approximately 12 nm. Note that the AFM image is of the sample surface and the bright phase contrast indicates lateral positions of nanosilica at or very near the surface.

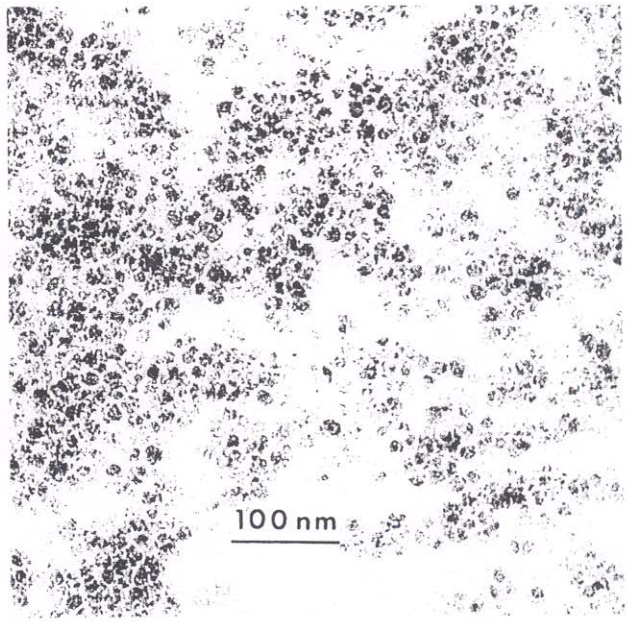

Figure 2. TEM image of PMMA-SiO_2 sample

The TEM analysis of the PMMA-SiO_2 material at high magnification shows the 12 nm silica spheres clearly (**Figure 2**), but also shows areas of

greater silica concentration. This image, combined with the broader area analysis from AFM (**Figure 1**) indicates that the PMMA-SiO_2 nanocomposite has some non-uniformity of SiO_2 dispersion.

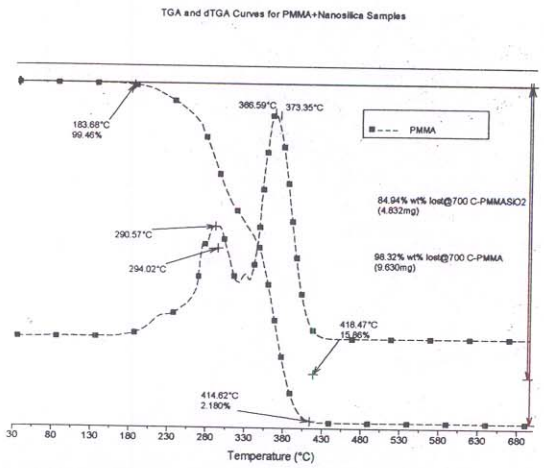

Figure 3. TGA and derivative TGA (dTGA) curves for PMMA + SiO_2 nanocomposites. Standard deviation for the wt% loss at 700 °C is: 0.167 for PMMA+SiO_2, 1.59 for PMMA.

The TGA data (**Figure 3**) show that the PMMA+SiO_2 nanocomposite has a higher residue yield (about 16% of residue mass – 10% silica mass = about 6% organic residues/char) and higher thermal stability when compared to the control PMMA sample. The observed three peaks at about 210 °C (a shoulder instead of a peak), 290 °C, and 366 °C appear to be initiated by scissions of head-to-head linkages, by scissions at the chain-end from vinylidene ends, and by random scission within the polymer chain, respectively[11]. The peak height of the second peak of the PMMA+SiO_2 nanocomposite is less than that of the control PMMA sample and the third peak is shifted toward higher temperature by about 7 °C for the nanocomposite sample compared to the control PMMA sample. This indicates that the bound polymer chains near silica particles might have higher thermal stability or/and the nanosilica may be providing a barrier which prevents release of evolved degradation products, thus trapping the products which recombine to form thermally stable residues/char. Since the thermal stability of polymeric materials have significant influence on their flammability properties[12], it is quite feasible that the flammability properties of the nanocomposite sample would be significantly improved compared with those of the control sample.

Scaled up preparations of these types of nanocomposites are under way to improve the dispersion of the nanoscale silica particles in PMMA and to be able to make larger samples for the measurement of flammability properties. The results will be presented at the meeting.

Conclusions

The feasibility of the preparation of a nanocomposite sample consisting of PMMA and nanoscale silica particles was demonstrated using a relatively simple procedure of photopolymerization of MMA with the colloidal silica. The reasonably good dispersion of the particles was confirmed by AFM and TEM except in a few areas where significant agglomeration is observed. TGA data show an improvement in thermal stability and enhanced formation of organic residues/char for the nanocomposite sample compared to the control PMMA sample. The preparation of other monomers with well-dispersed nanosilica fillers to give their corresponding nanocomposites by simple ambient polymerization methods also should be feasible.

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