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Short communication

Thermal degradation of transparent poly(methyl methacrylate)/silica nanoparticle hybrid films

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ABSTRACT

Using thermogravimetric (TG/DTG) analysis, we evaluated the thermal degradation characteristics of transparent poly(methyl methacrylate) (PMMA)/silica nanoparticle hybrid films obtained by well dispersing surface-unmodified silica (SiO_2) nanoparticles, of average particle size approximately 15 nm, in poly(methyl methacrylate), of weight-average molecular weight (M_w) 9.6 × 10^4 as synthesized by radical solution polymerization of methyl methacrylate (MMA). The TG/DTG curve of a secondary aggregated opaque hybrid film, comprising SiO_2 nanoparticles of size greater than several hundreds of nanometers, was in substantial agreement with that of pure PMMA. What was surprising, however, was that in the transparent hybrid, weight reduction due to cleavage of head-to-head bonds in PMMA occurring around 200 °C was nearly completely absent, and DTG peaks originating from cleavage of head-to-tail bonds and allylic-position cleavage of terminal vinylidene double bonds increased. These thermal degradation behaviors can be explained by the hypothesis of a specific chemical reaction between tertiary terminal macroradicals produced by cleavage of head-to-head bonds and silanol (SiOH) on the SiO_2 nanoparticle surface.

1. Introduction

Because nanoparticles of metals or metal oxides of a size on the order of nanometers collectively have a much larger surface area than particles on the order of micrometers, they are anticipated to demonstrate new functionality. Nanoparticles of silica (SiO_2), titania (TiO_2), zirconia (ZrO_2), and the like are generally synthesized by a sol–gel reaction of their precursors, but in such cases, aggregation by hydrogen bonding between particles readily occurs because the nanoparticles have hydroxyl (OH) groups on the surface. In recent years, there has been a great deal of research on dispersion-stabilized blends, namely, polymer nanohybrids, in which these nanoparticles do not aggregate in the polymer matrix [1–3]. Polymer nanohybrids can be prepared using a simple industrial method of directly blending nanoparticles into a polymer matrix in the molten state; however, for the abovementioned reasons, it is extremely difficult to de-aggregate secondary aggregates of nanoparticles and uniformly disperse them in the polymer as primary particles.

Much effort has been directed at averting aggregation of nanoparticles in the preparation of polymer nanohybrids. Organic solvent blending is an effective method for preparing a transparent polymer nanohybrid in which nanoparticles are uniformly dispersion-stabilized in a matrix polymer [4]. To understand the influence of polymer characteristics on the dispersion-aggregation behavior of nanoparticles in polymer/nanoparticle hybrids, we assessed the aggregation behaviors of SiO_2 nanoparticles in poly(methyl methacrylate)/silica (PMMA/SiO_2) hybrid suspension randomly dispersed in tetrahydrofuran (THF). We discovered that despite using samples consisting of polydisperse PMMA, the critical polymer concentration, C^*, at which SiO_2 nanoparticles rapidly aggregated, was specifically dependent on molecular weight [5]. As

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a result, we have also published a logical discussion of the molecular weight dependence of C^* in the dispersion–agglomeration transition behavior using monodisperse PMMA based on polymer solution theory [6]. We were able to elucidate the limits of the depletion aggregation theory [7,8], which supports the newly proposed theory of agglomeration called the "polymer chain entanglement agglomeration mechanism" [5,6]. Furthermore, based on this entanglement agglomeration theory, the characteristics of transparent PMMA/SiO_2 nanoparticle hybrid films prepared at concentrations at C^* or lower, we further found that the specific molecular weight dependence of C^* observed in hybrid suspensions also appears in hybrid films too, and that SiO_2 nanoparticles rapidly agglomerate due to entanglement of polymer chains [9].

In the present study, we proposed that the thermal degradation characteristics of transparent PMMA/SiO_2 nanoparticle hybrid films, in which, based on the polymer chain entanglement agglomeration mechanism, could be interpreted by assuming the reaction of the well-dispersed SiO_2 nanoparticles in the PMMA matrix with the tertiary terminal macroradicals produced by the cleavage of the weak linkages of the head-to-head bonds in PMMA chains.

2. Experiments

2.1. Samples

2.1.1. Silica nanoparticles

The SiO_2 used was high-purity colloidal SiO_2 prepared by the sol–gel method by Fuso Chemical Co., Ltd. (Japan). It was used in the form of a suspension of surface-unmodified cocoon-shaped nanoparticles of average particle size 15 nm dispersed in a proportion of 20.1 wt% in water. Fig. 1 shows a transmission electron microscopy (TEM) image provided by Fuso Chemical Co., Ltd. [5].

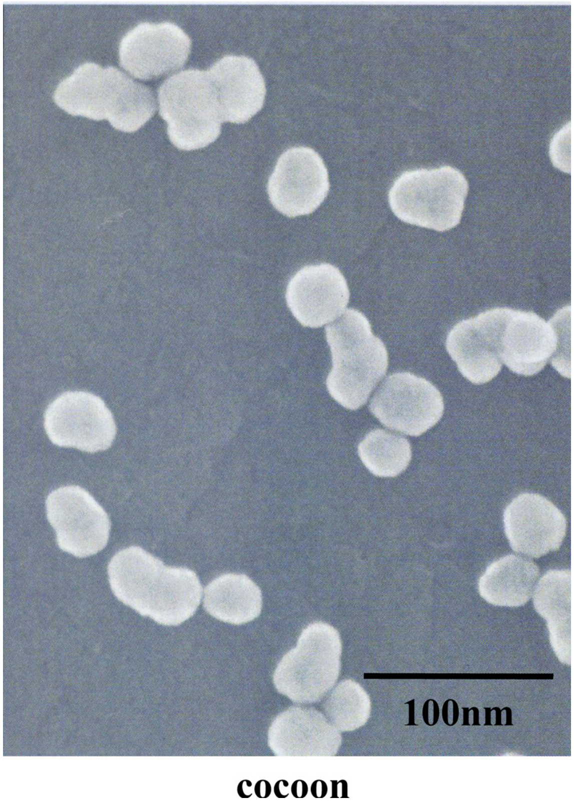

Fig. 1. TEM image of an SiO_2 nanoparticle used in this experiment.

Fig. 2 shows the TG curve of the SiO_2 nanoparticles vacuum-dried at room temperature to remove water. In Fig. 2, a weight reduction of approximately 5 wt% from room temperature to about 200 °C occurred due to the evaporation of water adsorbed to silanol (SiOH) groups on the SiO_2 nanoparticle surface, and a weight reduction of approximately 2 wt% from about 400 °C to 800 °C occurred due to evaporation of water produced by a dehydration condensation reaction between SiOH groups. We believe that SiOH groups substantially retained their structure in the temperature region of interest in the present study (200 °C–400 °C).

2.1.2. Poly(methyl methacrylate)

The PMMA used was synthesized by radical solution polymerization. The monomer and solvent were commercially-available methyl methacrylate (MMA, Wako Pure Chemical Industries, Ltd., Japan) and 2-butanone (methyl ethyl ketone, MEK, Kanto Chemical Co., Inc., Japan), respectively, each used without further purification. The polymerization initiator was α,α'-azobisisobutyronitrile (AIBN, Kanto Chemical Co., Inc., Japan), used after purification with methanol. Polymerization was performed by mixing 80 g of MMA, 0.1323 g of AIBN, and 200 mL of MEK in a four-necked flask and stirring for 24 h at 80 °C in a nitrogen atmosphere. After polymerization, the solution in the flask was diluted with 800 mL of MEK, and then added dropwise to an excess quantity of n-hexane to re-precipitate PMMA. The obtained precipitated powder was filtered, and the recovered substance was vacuum-dried for one week at room temperature. The polymerization rate was approximately 70%. The molecular weight of the obtained radical-polymerized PMMA sample was measured by gel permeation chromatography (GPC, HLC-8220GPC, Tosoh; column: Tosoh TSKgel GMHxL–G3000HxL–G2000HxL column system) with a differential refractometer using THF as the eluent, calibrated using commercially available monodispersed PMMA (Scientific Polymer Products, INC., New York, USA) specimens. The molecular weight characteristics of the polymerized PMMA were number average molecular weight (M_n) 5.0×10^4, weight average molecular weight (M_w) 9.6×10^4, and dispersity (M_w/M_n) 1.9.

2.2. Preparation of hybrid suspensions and films

PMMA and SiO_2 nanoparticles in a proportion of 100/10 parts by weight were together diluted with THF (Kanto Chemical Co., Inc.,

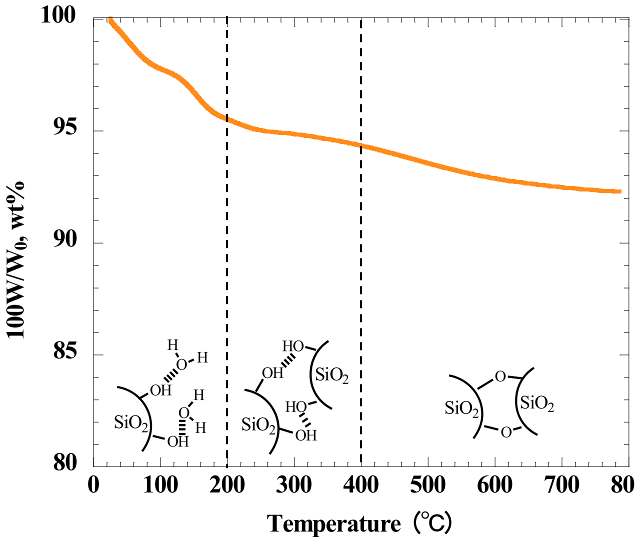

Fig. 2. TG/DTG curve of SiO_2 nanoparticles used in this experiment.