

Structure analysis of nanoparticle dispersed in transparent resin using synchrotron X-ray scattering

A flexible transparent plastic substrate is attracting attention in the field of photovoltaic power generation and display [1,2]. Plastic substrates have not only molding processability and lightweight properties but can also easily control transmission and reflectivity of the visible light ray by changing their molecular structure and composition. Although substrates consisting of acryl and cycloaliphatic group-based polymers have a high light transmittance in general, they are difficult to employ for products such as displays and solar batteries because of their low heat resistance and high coefficient of expansion [3]. Recently, we have developed a novel transparent plastic substrate with a heat resistance of over 200°C and a coefficient of expansion under 40 ppm/°C by dispersing inorganic nanosilica particles into the substrate resin [4]. Moreover, we found that the transparency was increased by increasing the content of nanosilica particle to over 50 vol%. From the results of synchrotron small-angle X-ray scattering measurements (SAXS), it was suggested that the increased content of nanosilica particles resulted in the formation of a para-crystal structure. In this study, we elucidate the effects of the content and diameter of nanosilica particles on their regular arrangement structures in the transparent plastic substrates using a field-emission-type scanning electron microscope (FE-SEM) and synchrotron small-angle X-ray scattering (SAXS) [5].

In the experiment section, norbornene diacrylate, an isopropanol solution containing a colloidal silica of 45 and 110 nm diameters, an additive, and an initiator were mixed under vacuum. A transparent film less than 150 μm thickness was obtained by removing a solvent at 40°C and crosslinking with ultraviolet in the mold at room temperature (r.t.). An average heat coefficient of expansion from 30 to 250°C was measured by thermomechanical analysis (TMA) using

a SEIKO instruments SS6000. Haze and parallel light transmittance were measured with a haze meter using a Nippon Denshoku Kogyo Corporation NDH2000. The regular arrangement of structures of nanosilica particles was determined using synchrotron small-angle X-ray scattering at beamlines **BL08B2** and **BL03XU**. The distance and shape of the nanoparticles were observed with FE-SEM in 5 kV at r.t. using a JEOL JSM-7401.

Figure 1 shows the effect of the colloidal silica content on the light transmittance. The light transmittances have a local minimum with an increase in the content of colloidal silica of both 45 and 110 nm diameters. It indicates that the substrate becomes transparent again after becoming opaque with increasing content of colloidal silica. The film becomes transparent at a content of 55 vol% colloidal silica when the particle diameter is 45 nm, while it becomes transparent at a content of 33 vol% when the particle diameter is 110 nm. From these results, we suggest that there is a correlation between the particle diameter of the colloidal silica and re-transparence of the film.

Figure 2 shows the SAXS profile with varying content of the colloidal silica of 110 nm diameter in a resin network film. Several peaks scattered from isolated silica particles were observed in the range of q (nm⁻¹) > 0.08 in all profiles. It indicated that no cohesion of the particle was observed with the increase in the content of colloidal silica because the provided peaks were consistent with those of a dilute solution at 0.1 vol% colloidal silica. In addition, a peak due to the scattering from the interparticle distance of the colloidal silica was observed in the range of a small angle, q (nm⁻¹) = 0.02 – 0.06, where it was difficult to observe using a conventional SAXS with a rotating-anode generator. The peak was found to shift to the wide-angle side with increasing content of colloidal silica. The correlation between the content

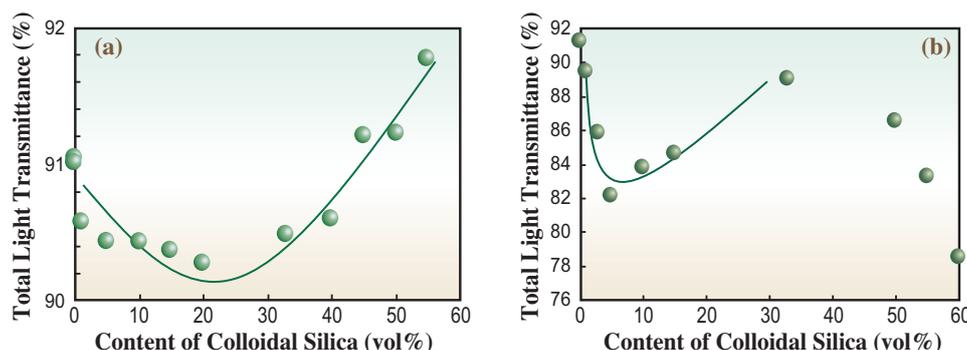


Fig. 1. Effect of colloidal silica content on light transmittance, (a) colloidal silica of 45 nm diameter, (b) colloidal silica of 110 nm diameter.

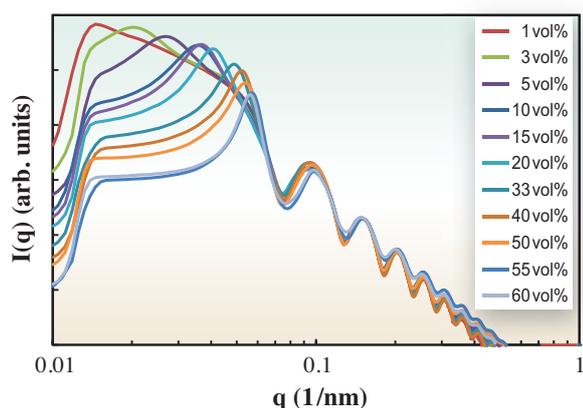


Fig. 2. SAXS profile with varying content of colloidal silica of 110 nm diameter in resin network film.

of colloidal silica and the lattice spacing calculated from the shifted peak top according to Bragg diffraction is plotted. The lattice spacing was found to decrease from 280 to 110 nm, which corresponded to the diameter of silica with increasing content of the colloidal silica. From these results, highly filled particles were suggested to exist individually in the film.

Figure 3 shows the results of SEM observations of films with varying colloidal silica contents. As the content of colloidal silica increased, their filling rate was observed to increase without the aggregation of the colloidal silica. A hexagonal close-packed structure was observed for 60 vol% colloidal silica content, which was almost equal to the theoretically predicted maximum value of the packing. Distances between particles in SEM images are consistent with the lattice spacing obtained from the SAXS profile.

In summary, highly filled nanosilica particles of 45 and 110 nm diameters resulted in a transparent film without any silica aggregation. In addition, the distances between particles calculated from SEM images agreed with those determined from the SAXS profiles. These results suggest that the SAXS measurement in SPring-8 is effective for the observation of the particle dispersion state in the nanoparticle high-filling system. A mechanism of the expression of transparency is still being elucidated from the observation of a submicron ordered structure using an ultra-small-angle X-ray scattering such as a Bonse & Hart optical system.

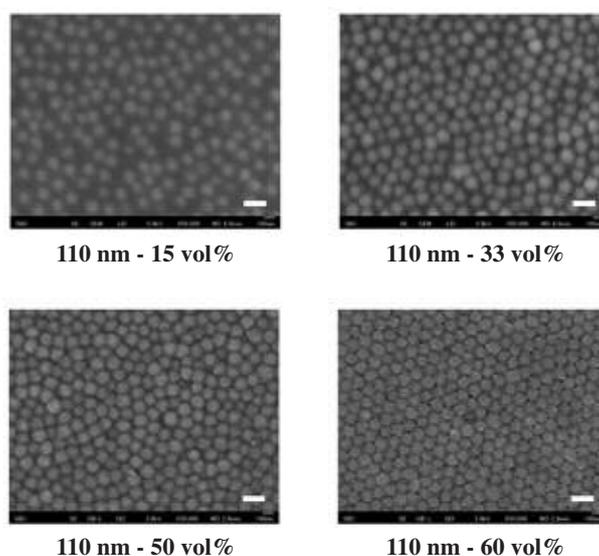


Fig. 3. SEM images with varying content of colloidal silica of 110 nm diameter in resin network film.

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