ORIGINAL ARTICLE

Characteristics of novel transparent poly(methyl methacrylate)/silica nanoparticle hybrid film prepared based on entanglement-agglomeration transition mechanism

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Using polydisperse poly(methyl methacrylate) (PMMA) and SiO₂ nanoparticles with an average particle diameter of ~ 15 nm, transparent PMMA/SiO₂ hybrid films could be fabricated based on the agglomeration mechanism of nanoparticles in the suspension. The calculated distance between the particles in the transparent films was ~ 30 nm, corresponding to the actual measured value of 31 nm obtained from the small-angle X-ray scattering intensity. Upon heating the transparent hybrid films to 140 °C, above the glass-transition temperature of PMMA, the transmittance of UV light decreased significantly with the heating time for hybrid films with $M_w = 9.6 \times 10^4$ and a critical molecular weight (M_c) of 3×10^4 or greater, at which PMMA chains show effective entanglement. However, for hybrid films with $M_w = 0.3 \times 10^4$ and with the M_c or a lower molecular weight, the initial high transmittance was sustained over the entire wavelength range even after a long period of heating, and no agglomeration of the SiO₂ nanoparticles was observed. Such molecular weight dependence was also observed for monodisperse PMMA/SiO₂ hybrid films, leading to an examination of the difference in the rates of polymer chain entanglement and disentanglement. *Polymer Journal* (2015) **47**, 311–319; doi:10.1038/pj.2014.130; published online 14 January 2015

INTRODUCTION

Because nanoparticles, such as metals and metal oxides with dimensions on the nanoscale, have significantly larger specific surface areas than micrometer-sized particles, the development of new functions is anticipated. However, the Derjaguin and Landau, Verwey, and Overbeek theory suggests that irreversible aggregation occurs because of the attractive forces generated between particles when the distances between them are on the subnanometer scale.¹⁻⁵ Although nanoparticles such as those of silica (SiO₂), titania and zirconia are generally synthesized by the sol-gel reaction of their respective precursors, aggregation resulting from the formation of a hydrogen bond between particles tends to occur because nanoparticles possess OH (hydroxyl groups) in such instances. Composites of these nanoparticles evenly dispersed stable in a polymer matrix without agglomeration, namely, polymer nanohybrids, have been widely studied in recent years.⁶⁻⁸ Polymer hybrids can be prepared using a simple industrial method of direct blending of both ingredients in the molten state. However, it is extremely difficult to disaggregate the secondary agglomeration of nanoparticles and then disperse them evenly as primary particles in the polymer owing to the reasons described above.

Many efforts have been made to prevent the agglomeration of nanoparticles in the preparation of polymer nanohybrids. As a result, it has been revealed that modifying the surface of nanoparticles by considering the affinity to the matrix polymer is an effective method. As a successful example, Sugimoto et al.9 synthesized polymerizable SiO₂ nanoparticles by chemical modification of the SiO₂ surface containing -OH and then prepared transparent polydisperse poly (methyl methacrylate) (PMMA)/SiO2 nanohybrids by in situ bulk copolymerization using a radical initiator with methyl methacrylate. Polymerizable SiO₂ nanoparticles, prepared by a urethanization reaction between silanol groups on the surface of SiO₂ particles measuring 12 nm in diameter dispersed in ethyl acetate and 2-(methacryloyloxy)ethyl isocyanate, were incorporated into the PMMA main chain by copolymerization with the methyl methacrylate monomer. PMMA nanohybrids with a maximum SiO₂ nanoparticle content of 50 wt% showed high transmittance without agglomeration. The preurethanized SiO₂ nanoparticles used in this study had their surface -OH slightly converted to methyl groups in advance and then dispersed and stabilized in the polar organic solvent ethyl acetate. Meth et al.¹⁰ reported the successful synthesis of an organic solvent

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blend by skillfully using organic solvents. To evenly disperse and stabilize the SiO₂ nanoparticles spread in the organic solvent dimethylformamide in polystyrene or PMMA, the surface was capped with phenyl groups via the sol-gel reaction between the phenyltrimethyl methoxysilane and the silanol groups on the surface of the SiO₂ nanoparticles, which had an average particle diameter of 28.6 ± 0.3 nm. These phenyl-modified SiO₂ nanoparticles could be dispersed evenly at a relatively high concentration in dimethylformamide containing a trace amount of water. After stirring and blending the organo-SiO₂ nanoparticles and either the two types of highmolecular-weight PMMA or the two types of high-molecular-weight polystyrene with a roller mill, the suspension was cast onto a glass plate or a polyimide (Kapton) sheet; the solvent was then removed under vacuum conditions at a surface temperature of 110 °C. Few changes in the glass-transition temperature (T_g) owing to the dispersion and stabilization of the SiO₂ nanoparticle content up to 50 vol% were observed because the thickness of these composite films was 5-20 µm and the specimens containing SiO₂ nanoparticles had a high molecular weight.

Organic solvent blending is an effective method for preparing transparent polymer nanohybrids in which the nanoparticles used are evenly dispersed and stable in a matrix polymer. The surface modification of the SiO₂ nanoparticles is believed to enhance the affinity with the polymer used and leads to dispersion stability in an organic solvent. The depletion effect has been discussed for many years and applied to explain the agglomeration of colloidal particles in suspensions using polymers that generate no strong interactions such as hydrogen bonds with the colloidal particles dispersed in an organic solvent, and are rarely adsorbed onto the particles.^{11,12} This theory is based on a simple model in which the polymer chains (random coil) between colloidal particles or plates undergo elastic deformation and are expelled from between the colloids when a certain driving force moves them closer, causing the colloids to come into contact with one another. Therefore, this theory has been widely applied because the agglomeration of colloidal particles is predicted to be related to the size of the dissolved polymers, that is, the diameter (radius of gyration $\times 2$) of the polymers. In particular, Vrij et al.13,14 evaluated the critical polymer concentration (C^*) at which the agglomeration of SiO₂ nanoparticles occurred owing to the depletion effect and the molecular weight dependence using a cyclohexane suspension of spherical SiO₂ nanoparticles and monodisperse polystyrene with different molecular weights.^{15,16} The results revealed that the critical concentration occurred more frequently at low concentrations as the molecular mass, or the radius of gyration, becomes greater. The authors also showed that the depletion effect becomes apparent when increasing the size of the SiO₂ nanoparticles and the initial concentration, thus causing the agglomeration to be more evident. However, there have been no clear experimental results or discussions on the polymer solution theory concerning the critical polymer concentration (C^*) that induces the depletion effects and the limitations of the depletion effect.

We evaluated the agglomeration behavior of SiO₂ nanoparticles in a hybrid suspension of PMMA/SiO₂ randomly dispersed in tetrahydrofuran (THF) to comprehend the effects of polymer properties on the nanoparticle dispersion-agglomeration transition in polymer/nanoparticle hybrids. This study resulted in the discovery of the unique molecular weight dependence of C^* at which the SiO₂ nanoparticles rapidly agglomerate despite the fact that the specimens used were polydisperse PMMA.¹⁷ We also analyzed the molecular weight dependence of C^* in the unique dispersion-agglomeration transition with monodisperse PMMA based on polymer solution theory. Furthermore, we investigated the limitations of the depletion aggregation theory and developed a new agglomeration theory called 'Entanglement-Agglomeration Transition Mechanism of Polymer Chains'.^{17,18}

This research presents a new method for preparing a transparent PMMA/SiO₂ nanoparticle hybrid film based on the entanglement-agglomeration transition mechanism previously proposed by our group.¹⁷ Moreover, it is revealed that the molecular weight dependence of PMMA relating to the agglomerating behavior of evenly dispersed SiO₂ nanoparticles in the acquired transparent hybrid film when heated at the $T_{\rm g}$ of PMMA or higher corresponds to that of SiO₂ nanoparticles observed in suspension.^{17,18}

EXPERIMENTAL PROCEDURE

Materials

 SiO_2 nanoparticles. Fuso Chemical Company's high-purity colloidal SiO_2 (surface: unmodified, average diameter φ : 15 nm, shape: spherical/cocoonshaped/aggregated) prepared by the sol-gel method was selected for study, and a suspension with 12 wt% of SiO₂ dispersed in isopropyl alcohol was utilized. Data concerning the shapes, diameters and surface modification conditions of these SiO₂ nanoparticles, provided by Fuso Chemical Co. Ltd (Osaka, Japan) have been detailed in our previous report.¹⁷ The abbreviation '-non' indicates that the silanol groups that exist on the surface of the SiO₂ nanoparticles are unmodified, whereas 'spherical', 'cocoon-shaped' and 'aggregated' are described as 'PL-2SL-', 'PL-1SL-' and 'PL-1-', respectively.

Poly(methyl methacrylate). As mentioned in our previous report,¹⁷ the polydisperse PMMA specimens were prepared by radical polymerization in principle. Because the critical molecular weight (M_c), at which the entanglement effect of the PMMA chain occurs has been reported to be ~ 3×10^4 based on the molecular weight dependence of the zero shear melt viscosity,¹⁹ we used the two following PMMA samples: PMMA with a weight-average molecular weight (M_w) of 9.6×10^4 ($MW_{max} = 120 \times 10^4$) containing polymer chains with a molecular weight greater than M_c and a polydispersity (M_w/M_n) of 1.9 and PMMA with $M_w = 0.3 \times 10^4$ ($MW_{max} = 1.3 \times 10^4$) comprising polymer chains with a molecular weight less than M_c and $M_w/M_n = 1.3$. MW_{max} indicates the maximum molecular weight of the polymer chain contained in the specimens acquired from gel permeation chromatography. Commercially available monodisperse PMMA (Scientific Polymer Products, INC., New York, NY, USA) specimens were used.

Preparation of hybrid suspension and film: blending method

Figure 1 shows the preparation method for the hybrid suspension and hybrid film (blending method). The weights of PMMA and SiO₂ nanoparticles were



Figure 1 Preparation of hybrid suspension and hybrid film. A full color version of this figure is available at Polymer Journal online.

measured to obtain a weight ratio of 100/5. THF was added to achieve the prescribed polymer concentration, and the mixture was then stirred to prepare the intended hybrid suspension. The concentrations of both the polymer and SiO₂ nanoparticles changed simultaneously through this method. UV-vis spectra (transmittance) were measured using this hybrid suspension. Subsequently, the hybrid suspension was added in small amounts to n-hexane to reprecipitate PMMA. The reprecipitate was filtered and thoroughly dried at room temperature and under reduced pressure to remove the remaining organic solvent and to obtain a hybrid powder. The weight ratio of PMMA and SiO₂ nanoparticles in the hybrid film was confirmed to remain constant from the time that the hybrid suspension was prepared, based on the residual weight ratio at 800 °C on the thermogravimetry curve. This powder was then heated to 190 °C for 5-10 min with a heat press machine. After visually confirming that the polymer had been melted, it was pressurized and depressurized at 40-50 MPa ~ 10 times for deaeration. Finally, the polymer was heated for 1 min at 25 MPa and then slowly cooled down to the intended temperature to prepare the hybrid film. The thickness of the films was ~ 250 µm in all cases.

The physical properties of these (PMMA/SiO₂) hybrid films were evaluated through thermogravimetry, UV-vis spectroscopy, transmission electron microscopy (TEM) and small-angle X-ray scattering measurements.

Measurement

TEM micrographs were provided by Kuraray Co. Ltd (Tokyo, Japan) using a JEOL JEM-100CX transmission electron microscope at an accelerating voltage of 100 kV. RuO_4 was used to stain the composite specimens, which were cut into ultra-thin sections at room temperature using an ultramicrotome.

Transmittance of the hybrid suspension and hybrid film was measured with a light path length of 10 mm in quartz cells at room temperature using an ultraviolet-visible spectrophotometer (UV-vis, model V630 manufactured by JASCO Corporation).

Small-angle X-ray scattering was performed using beamline BL-10C at the Photon Factory of the High Energy Accelerator Research Organization in Tsukuba City, Japan. The wavelength of the X-rays used was 0.1488 nm, and the scattering intensity was detected using a one-dimensional position-sensitive proportional counter with 512 channels. The measurements were carried out using the same method described in our previous paper.²⁰



Figure 2 Changes in transmittance of PMMA/PL-2SL-non SiO₂ (100/5) hybrid suspension in THF and hybrid film as a function of polymer concentration at the time the hybrid suspension was prepared. (Wavelength: 400 nm; $M_{\rm W}$ =9.6×10⁴, $M_{\rm W}/M_{\rm n}$ =1.9).

RESULTS AND DISCUSSION

SiO₂ nanoparticle dispersion-agglomeration transition of hybrid films with polydisperse PMMA: transmittance and TEM images

Figure 2 shows a plot of the changes in transmittance at 400 nm for the hybrid suspension and hybrid film obtained by blending PMMA $(M_w = 9.6 \times 10^4, M_w/M_n = 1.9)$ and spherical unmodified organosilica sol (PL-2SL-non, average particle diameter: 15 nm) at a weight ratio of 100/5 and by adjusting the polymer concentration with THF in relation to the polymer concentration in the suspension. The hybrid suspension showed high transmittance up to a polymer concentration of ~ 5 wt%, indicating that PMMA/SiO₂ nanoparticles were evenly dispersed. However, the transmittance rapidly declined once the polymer concentration exceeded 5 wt%. This phenomenon corresponded to the dispersion-agglomeration transition behavior observed in our previous study (the polymer addition method).¹⁷ The critical polymer concentration (C^* value) was also 5 wt% (SiO₂ concentration: 0.25 wt%) in the case of the blending method in which the initial concentration of SiO₂ changed, as shown in Figure 2.

For all polymer concentrations, the transmittance of the hybrid film showed lower values than those for the original PMMA film and hybrid suspension. Hsu et al.21 proved that a smoother surface can preserve the transmittance; thus, the decrease in transmittance may be due to surface roughness. A secondary agglomeration of PMMA/SiO2 may have occurred to some extent during the reprecipitation, but the C^* value for the hybrid film was observed to be the same as that for the hybrid suspension. Figure 3 shows TEM images of the hybrid film, which were acquired from the suspension prepared with polymer concentrations of 2 and 8 wt%. As the figure clearly shows, SiO₂ nanoparticles in the film obtained with 2 wt% (below C^*) were generally primary particles 15 nm in diameter and were evenly dispersed. At a content of 8 wt%, on the other hand, the TEM images clearly indicate that the secondary agglomeration of SiO₂ nanoparticles had progressed and agglomerates in the micrometer size range were being generated. These findings show that it is feasible to maintain nearly the same dispersion-agglomeration condition of the hybrid suspension by selecting appropriate polymer precipitants (nonsolvents). Figure 4 shows the polymer concentration dependence of the suspension used in the measurement of transmittance (400 nm) in the UV-vis spectra for hybrid films prepared using SiO2 nanoparticles with varied shapes. As the figure clearly shows, C^* appeared at ~ 5 wt% for all shapes. This observation was made because the C^* value (Figure 2) for the suspension prepared by the blending method adopted in this study was ~ 5 wt% regardless of shape, similar to the polymer addition method reported previously.17

These findings show that it is possible to prepare transparent hybrid films by collecting hybrid powders from the transparent hybrid suspension prepared with a polymer concentration of C^* or below and submitting the powders to the heat press process. Because the PMMA chains in the transparent hybrid film existed as isolated chains (random coils) without forming any entanglements in the suspension with a polymer concentration of C^* or below, PMMA chains in the film could be considered to consist of aggregated single-molecular chains with almost no entanglements (single-molecular chain aggregate). Accordingly, SiO₂ nanoparticles were assumed to be evenly dispersed in the PMMA single-molecular chain particle aggregates.

SiO₂ nanoparticle dispersion-agglomeration transition of hybrid films: distance between particles and small-angle X-ray scattering analysis

 SiO_2 nanoparticles used for the preparation of the hybrid film detailed in Figure 2 were spherical in shape with an average particle diameter of



Figure 3 TEM images of PMMA/PL-2SL-non SiO₂ (100/5) hybrid films with polymer concentrations of 2 and 8 wt%. ((a): 2 wt%; (b): 8 wt%).

15 nm. Because SiO₂ nanoparticles in the hybrid film prepared at or below *C*^{*} were evenly dispersed as described above, the distance between the SiO₂ nanoparticles can be calculated if the volume fraction in the matrix polymer PMMA is known. For instance, when assuming a system in which spherical nanoparticles of radius *r* with a specific gravity of 1 are dispersed evenly in a matrix with a volume fraction *V* and at a distance *d* between each particle, then *d* is given by $[(4\pi 2^{1/2}/3 V)^{1/3}-2]r$ and the total surface area *A* of all the particles in the system is given by 3 *V*/100*r*.²² If the values *r* = 40 000 nm (40 µm), 400 nm and 4 nm are used for spherical particles with *V*=0.02, for instance, the total relative surface areas (r.a.) of the particles are 1, 100 and 10 000, respectively, whereas the distances between the particles are *d*=160 000 nm (160 µm), 1,600 nm (1.6 µm) and 16 nm, respectively. When the commonly known respective specific gravities of 1.2 and 2.2 for PMMA and SiO₂ nanoparticles are applied, PMMA/SiO₂ nanoparticles with a weight ratio of 100/5 yield a volume ratio of 83.33:2.27. Accordingly, the volume fraction of the SiO₂ nanoparticles in the matrix polymer PMMA can be estimated to be 0.027 (2.7 vol%). In this case, therefore, the distance between SiO₂ nanoparticles is estimated to be ~ 30 nm. Figure 5 shows the plot for the Lorentz-corrected small-angle X-ray scattering intensity $I(q)q^2$ of the hybrid film shown in Figure 2 with respect to the scattering vector *q*. PMMA is amorphous and the scattering intensity decreases monotonically with respect to *q*, but a clear peak ($q_{max} = 0.2 \text{ nm}^{-1}$) appears on the smaller angle side with a *q*-value of 1 nm⁻¹ or less for hybrid films. Although the peak does not change until the PMMA concentration reaches *C*^{*} (5 wt%), it gradually shifts toward the wider





Figure 4 Transmittance in UV-vis spectra of PMMA/PL-2SL-non SiO₂ (100/5), PMMA/PL-1SL-non SiO₂ (100/5) and PMMA/PL-1-non SiO₂ (100/5) hybrid films as a function of polymer concentration at the time the hybrid suspension was prepared. (Wavelength: 400 nm; $M_{\rm W}$ =9.6×10⁴, $M_{\rm W}/M_{\rm n}$ =1.9).

angle side once it exceeds C^* , and the concentration increases as well. The relationship between q and the lattice interplanar spacing d (Bragg's law) is expressed by equation (1).

$$d = \frac{2\pi(n)}{q} \ n = 1, 2, 3... \tag{1}$$

When *d* is calculated using the value of q_{max} by setting n=1, *d* becomes 31 nm for $q_{\text{max}} = 0.2 \text{ nm}^{-1}$ at C^* and below, where the SiO₂ nanoparticles are dispersed and stabilized in the matrix polymer. This result corresponds to a distance of 30 nm between the SiO₂ nanoparticles obtained from the spherical model mentioned above. Moreover, the distance becomes 19 nm when exceeding C^* and reaching 8.0 wt% ($q_{\text{max}} = 0.38 \text{ nm}^{-1}$). The spacing is believed to have become narrower on average owing to the agglomeration of SiO₂ nanoparticles. When the concentration of PMMA exceeded 5 wt% in the suspension, the domain in which SiO₂ nanoparticles were agglomerated increased. This result is believed to have caused the value of q_{max} to gradually shift toward the wider angle side.

$\rm SiO_2$ nanoparticle agglomeration in polydisperse PMMA/SiO_2 nanoparticle transparent hybrid films

Isopropyl alcohol-dispersed SiO₂ nanoparticles are dispersed and stabilized in the hybrid suspension as they are solvated by isopropyl alcohol. As the degree of solvation changes owing to THF dilution, no agglomeration occurs. As mentioned in our previous report,¹⁷ however, when PMMA is added, solvent molecules are consumed in dissolving PMMA, and the solvation of SiO₂ nanoparticles collapses with increasing PMMA concentration. Then, a rapid agglomeration occurs owing to the formation of entanglements of PMMA chains at the critical polymer concentration C^* . To clarify the dispersionagglomeration transition behavior caused by the formation of entanglements with the two components (SiO2 nanoparticles-PMMA) without using a solvent, a continuous heating experiment of the transparent hybrid films was conducted. As previously described, because M_c is ~ 3×10⁴ ¹⁹ when effective entanglement effects appear for PMMA, a hybrid suspension was prepared with a polymer concentration of C^* or below the concentration at which no



Figure 5 Plots of $I(q)q^2$ versus q for PMMA/PL-2SL-non SiO₂ hybrid films with different polymer concentrations and PMMA.

entanglements are formed with a PMMA/SiO₂ weight ratio of 100/5 (volume fraction ratio: 97.3:/2.7) by using PMMA and SiO₂ nanoparticles (PL-1-non, average particle diameter: 15 nm) with $M_{\rm w} = 9.6 \times 10^4$, which is greater than or equal to $M_{\rm c}$, or $M_{\rm w} = 0.3 \times 10^4$, which is less than or equal to $M_{\rm c}$. A transparent hybrid film with almost no development of entanglements was prepared by applying the heat press process to the hybrid powder acquired from the reprecipitation of the suspension. The agglomeration behavior of the SiO₂ nanoparticles caused by the formation of entanglements in the molten polymer was evaluated based on the time dependence of UV-vis spectra (transmittance) by consecutive heating at 140 °C, which is at or above the $T_{\rm g}$ (generally 120 °C) of PMMA.

Figure 6 shows the effects of heating time on the UV-vis spectra (transmittance) of the hybrid film. Figure 6a illustrates a PMMA specimen with a molecular weight $(M_w = 9.6 \times 10^4)$ above M_c , whereas Figure 6b shows a PMMA specimen with a molecular weight $(M_{\rm w} = 0.3 \times 10^4)$ below $M_{\rm c}$. As Figure 6a clearly shows, the transmittance of hybrid films prior to heating at 400 nm was 85% for the PMMA specimen with a molecular weight greater than or equal to M_c . However, the overall transmittance started to decrease after 45 min of heating at 140 °C and it (400 nm) decreased to 50% and 40% after 24 and 48 h, respectively, causing the entire film to become cloudy, such that the characters 9.6×10^{4} under the film were not visible. Because the transparent hybrid film was prepared with the hybrid powder obtained at a concentration of C^* or below, which existed in a random coil (isolated) conformation with no polymer chain entanglements at the time the suspension was prepared, the PMMA chains in the transparent hybrid films are believed to have been in a state in which single-molecular chains, where PMMA chains had hardly started to form, were aggregated. When this film was heated to a temperature of T_{g} or above, the molecular chains began to intrude upon each other because the thermal motion of the PMMA chain and entanglements started to progress with an increase in the heating time. The formation of the entanglements acted as a strong driving force to expel SiO₂ nanoparticles from the PMMA chain domain where the SiO₂ nanoparticles were evenly dispersed in the matrix PMMA at a volume fraction ratio of ~0.027. As a result, it can be assumed that the local

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Figure 6 Effect of heating time on the UV-vis spectra (transmittance) of the polydisperse PMMA/PL-1-non SiO₂ hybrid films. ((a): $M_w = 9.6 \times 10^4$; (b): $M_w = 0.3 \times 10^4$).

concentration of the SiO₂ nanoparticles increased and they rapidly came into close contact and collided with one another, inducing secondary agglomeration and causing the hybrid film to become cloudy. For transparent hybrid films that use PMMA $(M_w = 0.3 \times 10^4)$ with a molecular weight below M_c (as shown in Figure 6b), the figure clearly shows that the transmittance of the hybrid film did not decline over the entire wavelength range after 56 h and remained at nearly the same level as that measured prior to the heating process. Similar to PMMA with a large molecular weight of M_c or above, polymer chains in the hybrid films comprising PMMA chains with a molecular weight of M_c or below, prepared at polymer concentrations of C^* or below, are also believed to be in a state in which no effective entanglements are formed even though they come into contact with one another as an aggregation of single-molecular chain particles. When the transparent hybrid film is heated to 140 °C, the low-molecular-weight PMMA chains (97.3 vol%) with lower T_g and the SiO₂ nanoparticles (2.7 wt%) display Brownian motion mutually and randomly. However, agglomeration does not occur as SiO₂ nanoparticles do not come into contact with one another because PMMA chains with a low molecular weight of M_c or below do not form any effective entanglements and have an overwhelmingly greater number of molecules compared with that contained in the PMMA chains with a large molecular weight.

Thus, it became evident that no agglomeration of SiO_2 nanoparticles occurred in the transparent hybrid films prepared using the PMMA specimens, comprising polymer chains with a low molecular weight of M_c or below even when heated to T_g or above while maintaining the dispersed condition. SiO₂ nanoparticles are believed to exist in an evenly dispersed condition in the single-molecular chain aggregates in which isolated (random coil) chains with a low molecular weight in the transparent hybrid film agglomerate.

SiO₂ nanoparticle agglomeration in monodisperse PMMA/SiO₂ nanoparticle transparent hybrid films

A similar experiment was conducted using monodisperse PMMA with a narrow molecular weight distribution to examine the details of the molecular weight dependence for the dispersion-agglomeration transition behavior of SiO₂ nanoparticles owing to the heating of transparent hybrid films, comprising polydisperse PMMA (with a high molecular weight of M_c or above and a low molecular weight of M_c or below) and SiO₂ nanoparticles mentioned in the previous section. The SiO₂ nanoparticles were cocoon-shaped, with an average particle diameter of 15 nm, and PL-1SL-non with an unmodified surface and a 12 wt% dispersion in isopropyl alcohol was used. The weight ratio of

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the monodisperse PMMA specimen and SiO₂ nanoparticles was set to 100/5. Figures 7a–c show the effects of heating time on the film transmittance when heating transparent hybrid films prepared using

transmittance when heating transparent hybrid films prepared using monodisperse PMMA specimens with different molecular weights to 140 °C, above the $T_{\rm g}$ of PMMA. For PMMA specimens $(M_{\rm w}=2.1\times10^4, M_{\rm w}/M_{\rm n}=1.1)$ with a molecular weight below $M_{\rm c}$, the film sustained high transmittance over the entire wavelength range without any decline, even after heating to 140 °C for 48 h, as shown in Figure 7a, despite some fluctuations. This tendency corresponded to the time dependence (Figure 6b) for the case in which polydisperse PMMA was used.

On the other hand, for hybrid films featuring a PMMA specimen, comprising polymer chains with a molecular weight of M_c or above shown in Figure 7b ($M_w = 29.8 \times 10^4$, $M_w/M_n = 1.1$) and Figure 7c $(M_w = 6.8 \times 10^4, M_w/M_n = 1.1)$, the transmittance decreased over the entire range when heated to 140 °C for many hours. In particular, cloudiness was observed in the former film after heating to 140 °C for 120 h (Figure 7b), similar to the hybrid films formed using polydisperse PMMA ($M_w = 9.6 \times 10^4$) shown in Figure 6a. Figure 8 shows a TEM image of the hybrid film after heating to 140 °C for 120 h. As the figure clearly shows, the secondary agglomeration of SiO₂ nanoparticles progressed by heating. Figure 9 shows the heating time dependence of transmittance for 400 nm shown in Figures 7a-c. As the figure shows, the transmittance hardly changed even after heating to 140 °C for many hours, and the agglomeration of SiO₂ nanoparticles did not occur for the monodisperse PMMA transparent hybrid film with a molecular weight of M_c or below (Figure 7a). On the other hand, when monodisperse PMMA specimens with a molecular weight of $M_{\rm c}$ or above were used, the rate at which the transmittance decreased accelerated with an increase in the molecular weight, and the time required for the decline in the reduction rate to stabilize became longer. These results are believed to indicate the molecular weight dependence of the process in which entanglements are formed owing to mutual intrusions caused by heating the PMMA chains, which hardly have any entanglements, to temperatures above T_{g} . The molecular weight between entanglement points is 1.5×10^4 based on the definition $M_c/2^{19}$, where $M_c = 3 \times 10^4$. The number of entanglement points in each specimen decreases with a decline in molecular weight by factors of 20 $(M_w = 29.8 \times 10^4)$ and 4.5 $(M_w = 6.8 \times 10^4)$. An entanglement equilibrium state (thermal equilibrium state) should be attained at an infinite heating time as the process of forming and disentangling entanglements is repeated. When the number of entanglement points (molecular weight) increases, the rate of selfdiffusion significantly decreases.²³ On the other hand, because the



Figure 7 Effect of heating time on the UV-vis spectra (transmittance) of the monodisperse PMMA/PL-1SL-non SiO₂ hybrid films. ((a): $M_{\rm w} = 2.1 \times 10^4$; (b): $M_{\rm w} = 29.8 \times 10^4$; (c): $M_{\rm w} = 6.8 \times 10^4$).



Figure 8 TEM image of the monodisperse PMMA/PL-1SL-non SiO₂ hybrid film (M_w = 29.8 × 10⁴) after heating to 140 °C for 120 h in Figure 7b.

equilibrium of entanglement formation and disentanglement is skewed toward the formation side, the increase in the rate at which the transmittance decreases and the extension of time required to achieve entanglement equilibrium are assumed to depend on the number of entanglement points. The study of the formation and disentanglement of polymer chain entanglements in the molten state is a topic of future research. Transparent hybrid films containing a PMMA specimen with a molecular weight of M_c or higher have SiO₂ nanoparticles dispersed in single-molecular PMMA chain aggregates. However, SiO₂ nanoparticles rapidly aggregate once PMMA chain entanglements are formed upon heating the PMMA specimen to T_g or above. It is suggested that the rate at which the transmittance decreases due to such entanglement agglomerations and the time required to stabilize the rate of decrease depend on the number of entanglement points, which increases with the molecular weight. On the other hand, it became clear that SiO₂ nanoparticles do not agglomerate and continue to remain in a dispersed state even when heated to a temperature of T_g or above for a PMMA specimen with a molecular weight of M_c or below because no effective entanglements of PMMA chains occur.

New dispersion-agglomeration transition mechanism

Figure 10 shows a schematic diagram of the dispersion-agglomeration transition phenomenon in the hybrid suspension^{17,18} and hybrid film. First, when the PMMA molecular weight in the hybrid suspension is such that $M_c < M_{w_2}$ the molecular random coil chains come into contact and interpenetrate as the PMMA concentration increases and eventually form entanglements. Such formation of molecular chain entanglements is believed to act as a driving force for the agglomeration



Figure 9 Heating time dependence of transmittance at 400 nm for the monodisperse PMMA/PL-1SL-non SiO₂ hybrid films.

of SiO₂ particles and induce the rapid clouding of the suspension. On the other hand, in cases in which the PMMA molecular weight in the hybrid suspension is such that $M_w < M_c$, the molecular chains come into contact with one another as the PMMA concentration increases. However, because no effective entanglements are formed, there is no driving force for the agglomeration of the SiO₂ nanoparticles. As a result, the hybrid suspension remained transparent.

The PMMA molecular chains in the transparent hybrid films obtained from heat pressing the hybrid powders generated by reprecipitation in the suspension prepared at a concentration of C^* or below come into contact with one another as aggregates of singlemolecular chain particles without any entanglements, as indicated in the schematic diagram. When the PMMA molecular weight is such that $M_{\rm c} < M_{\rm w}$, heating PMMA to temperatures above $T_{\rm g}$ leads to gradual mutual intrusions, particularly among molecular chains, the formation of entanglements and an increase in the domain of the entangled PMMA chains. This process acts as a strong driving force for eliminating SiO₂ nanoparticles and causing the agglomeration of SiO₂ particles. In turn, the hybrid films become cloudy with an increase in the heating time. On the other hand, as PMMA chains come into contact and interpenetrate in hybrid films with $M_w < M_c$ when no clouding occurs, disentanglement of entanglements also occurs simultaneously and no effective entanglement effects appear. As a result, no agglomeration of SiO₂ nanoparticles emerges, which is assumed to be the reason why the hybrid films remained transparent.

CONCLUSION

We developed a method for preparing hybrid films that maintain the dispersion-agglomeration condition intact in the suspension by reprecipitating a PMMA/SiO₂ nanoparticle hybrid suspension to collect a hybrid powder, comprising SiO₂ nanoparticles in the disperse-agglomeration condition and using a heat press to process the powder. Furthermore, we discovered that SiO₂ nanoparticles in the hybrid films were agglomerated and the entire film became cloudy when the transparent hybrid films with SiO₂ nanoparticles (2.7 vol%) evenly dispersed in the PMMA matrix with a molecular weight equal to M_c ($M_w = 3 \times 10^4$) or above were heated at 140 °C for many hours. The clouding of the transparent hybrid films is believed to occur when the molecular PMMA chains gradually interpenetrated and formed entanglements owing to the thermal motion caused by heating to temperatures above Tg. It appears that rapid agglomeration occurred when the density of the entanglements of the molecular chains increased, which acted as a driving force for the formation of entanglements in the PMMA chain domain, eventually expelling



Figure 10 Schematic diagram of the dispersion-agglomeration transition phenomenon in the hybrid suspension and hybrid film.

SiO₂ nanoparticles from the domain. Moreover, this agglomeration of SiO₂ nanoparticles depended on the molecular weight of PMMA. The transmittance decline (agglomeration) rate increased as the molecular weight increased while the time required for stabilizing the transmittance decline also increased. This effect was likely due to the decline in the self-diffusion rate that occurred as the number of entanglement points increased with increasing molecular weight. On the other hand, we confirmed that no cloudiness (agglomeration of SiO₂ nanoparticles) appeared in the transparent hybrid films prepared using a PMMA specimen with a molecular weight equal to M_c or below even when heated to 140 °C. This effect can be attributed to the fact that no effective entanglement effects of PMMA chains emerged.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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- Derjaguin, B. & Landau, L. Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. *Prog. Surf. Sci.* 43, 30–59 (1993).
- 2 Verwey, E. J. W. Theory of the interaction of two electrochemical double layers in combination with the forces between particles in suspensions and lyophobic sols. *Chem. Weekbl.* **39**, 563–566 (1942).
- 3 Verwey E. J. W. & Overbeek J. Th. G. Theory of the Stability of Lyophobic Colloids (Elsevier, Amsterdam, 1948).
- 4 Krishnamoorti, R. & Vaia, R. A. ACS Symposium Series 804 Polymer Nanocomposites Synthesis, Characterization, and Modeling (American Chemical Society, Oxford University Press, 2001).
- 5 Winey, K. & Vaia, R. A. Polymer Nanocomposites (MRS Bulletin, Material Research Society, Pittsburgh, PA, USA, 2007).
- 6 Vaia, R. A. & Maguire, J. F. Polymer nanocomposites with prescribed morphology: going beyond nanoparticle-filled polymers. *Chem. Mater.* 19, 2736–2751 (2007).

- 7 Bhattachaya, S. N., Gupta, R. K. & Kamal, R. M. Polymeric Nanoconposites (Hanser, Cincinanati, OH, USA, 2008).
- 8 Jancar, J., Douglas, J. F., Starr, F. W., Kumar, S. K., Cassagnau, P., Lesser, A. J., Sternstein, S. S. & Buehler, M. J. Current issues in research on structure-property relationships in polymer nanocomposites. *Polymer* **51**, 3321–3343 (2010).
- 9 Sugimoto, H., Daimatsu, K., Nakanishi, E., Ogasawara, Y., Yasumura, T. & Inomata, K. Preparation and properties of poly(methylmethacrylate)-silica hybrid materials incorporating reactive silica nanoparticles. *Polymer* 47, 3754–3759 (2006).
- 10 Meth, J. S., Zane, S. G., Chi, C., Londono, J. D., Wood, B. A., Cotts, P., Keating, M., Guise, W. & Weigand, S. Development of filler structure in colloidal silica-polymer nanocomposites. *Macromolecules* 44, 8301–8313 (2011).
- 11 Asakura, S. & Oosawa, F. On interaction between two bodies immersed in a solution of macromolecules. J. Chem. Phys. 22, 1255–1256 (1954).
- 12 Asakura, S. & Oosawa, F. Interaction between particles suspended in solutions of macromolecules. J. Polym. Sci. 33, 183–192 (1958).
- 13 De Hek, H. & Vrij, A. Phase separation in non-aqueous dispersions containing polymer molecules and colloidal spheres. J. Colloid Interface Sci. 70, 592–594 (1979).
- 14 De Hek, H. & Vrij, A. Interractions in mixtures of colloidal silica spheres and polystyrene molecules in cyclohexane. J. Colloid Interface Sci. 84, 409–422 (1981).
- 15 Fleer G. J., Scheutjens J. H. M. H. & Vincent B. in: The Stability of Dispersions of Hard spherical Particles in the Presence of Nonadsorbing Polymer. 'Polymer Adsorption and Dispersion Stability ACS Symposium series' 245 (ACS, Washington, 1984).
- 16 Vincent, B., Edwards, J., Emmett, S. & Jones, A. Depletion flocculation in dispersions of sterically-stabilised particles ('SOFT SPHERES'). *Colloid Surf.* 18, 261–281 (1986).
- 17 Tadano, T., Zhu, R., Muroga, Y., Hoshi, T., Sasaki, D., Yano, S. & Sawaguchi, T. A new mechanism of silica nanoparticle dispersion-agglomeration transition in Poly(methyl methacrylate)/Silica hybrid suspension. *Polym. J.* 46, 342–348 (2014).
- 18 Tadano, T., Zhu, R., Muroga, Y., Hoshi, T., Sasaki, D., Yano, S. & Sawaguchi, T. Molecular weight dependence of SiO₂ nanoparticle agglomeration behavior in monodisperse PMMA/SiO₂ hybrid suspension. *Chem. Lett.* **43**, 705–707 (2014).
- 19 Ferry, J. D. Viscoelastic Properties of Polymers 377–378 (John Wiley & Sons, New York, NY, USA, 1980).
- 20 Zhu, R., Hoshi, T., Chishima, Y., Muroga, Y., Hagiwara, T., Yano, S. & Sawaguchi, T. Microstructure and mechanical properties of polypropylene/poly(methyl methacrylate) nanocomposite prepared using supercritical carbon dioxide. *Macromolecules* 44, 6103–6112 (2011).
- 21 Hsu, J. C., Wang, P. W., Lin, Y. H., Chen, H. L., Chen, Y. Y., Yao, Y. D. & Yu, J. C. Anti-reflective effect of transparent polymer by plasma treatment with end-hall ion source and optical coating. *Opt. Rev.* **17**, 553–556 (2010).
- 22 Thuzyo, K. & Harada, Y. On the distance between particles in synthetic polymer emulsion. *Kolloid-Z. and Z. Polym.* 201, 66–68 (1965).
- 23 De Gennes, P. G. Scaling Concept in Polymer Physics 76–77 (Cornell University Press, Ithaca, New York, NY, USA, 1979).