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学位論文題目	SYNTHESIS OF HOLLOW SILICA NANOPARTICLES AND THEIR STRUCTURE CONTROL FOR OPTICAL PROPERTIES（中空シリカナノ粒子の合成および光学特性付与に向けた構造制御）
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論文内容の要旨

Silica nanoparticles have many interesting properties; for example, a high surface area, high mechanical strength, thermal and chemical stability, permeability, and a low refractive index and especially optical properties. Therefore, these particles are effectively applied for fillers in light diffuser film as type of volumetric diffuser. The light diffuser film is an important part of backlight unit of the liquid crystal display (LCD). The film generally employs fillers as a function of distributing the incident light and contributing the brightness. Therefore, structure of fillers is one of the main roles for improving performance of light diffuser films. For this reason, hollow structures of silica nanoparticles have shown a great promise to reduce light absorption of them in the diffuser films. Meanwhile, morphologies and surface properties of hollow silica nanoparticles probably affect the formation of good light diffuser film, which requires for LCDs. According to the assumptions, this work only used different structures of silica nanoparticles to fabricate, investigate, develop and innovative approach in producing films with high optical properties which are applied for light diffuser film.

All films in the study are fabricated by a bar coating machine and cured by a UV-photo surface processor. The study is mainly organized as follows

Chapter 1 introduces general background of silica especially silica nanoparticles and hollow silica nanoparticles. It mainly focuses on optical properties of the particles to apply for fabricating light diffuser films. Meanwhile, the important of a light diffuser film in backlight unit of LCDs is briefly introduced. Moreover, light scattering involving optical properties of particles in the films is described. Based on the attempt to fabricate light diffuser films with varying morphologies of silica in nanoscale and simplify the coating process, the goal of this study is conceptualized.

Chapter 2 describes a facile method to prepare the highly loaded silica dispersions. The method was the matching refractive indices of the silica nanoparticles and a UV-curable acrylate monomer. The obtained dispersions exhibit a long-term stability of silica dispersions during dark storage. This is due to the reduction of particle-particle attraction forces. Such dispersions were further coated on cleaned glass substrates for fabricating the thin solid silica UV-cured films. The amount of silica nanoparticles in the films was varied from 1 to 30 vol %. The coated films were investigated their optical properties by a UV-Vis-NIR spectrophotometer. The total transmittances of the films are close to the bare glass which indicates the films transparency. The increment of silica nanoparticles in the films does not significantly affect their transmittances but it improves the diffuse transmittance. The reasonable explanation is an enhancement of the multiple scattering in the films through the particles. The increased amount of silica nanoparticles also leads to the formation of the aggregated particles with a larger size and homogeneous dispersion as evidenced from the FE-SEM images. Remarkably, the thin solid silica film containing 30 vol% silica nanoparticles exhibits the highest diffuse transmittance in this experiment, which is about 20%. These indicated that the amount and distribution of the silica nanoparticles strongly affect the improved optical properties of the thin solid silica UV-cured film.

Chapter 3 applies spherical silica nanoparticles containing dense structures to modify UV-cured acrylate films. The films were prepared by coating suspension of silica-acrylate on cleaned glass substrates. The effect of the particle content on the optical properties of the modified films was investigated. The light diffusing ability of the films was also studied using an apparatus equipped with a laser lamp. Based on the visible absorption data, the transmittance of all the modified film coated substrates is lower than that of the unmodified film. The transmittance of the modified films decreases with the increasing silica content. The increasing silica content also improves the haze and light diffusing ability of the modified films. The highest haze of about 0.26 and the largest range of scattered light were achieved from the film modified with 30 vol% particles. These nanoparticles show a good potential to improve the optical properties of the UV-cured acrylate film, especially the light diffusing property that may be utilized in electronic display technologies.

Chapter 4 uses silica nanoparticles containing hollow structures to improve optical properties and light diffusing ability of UV-cured acrylate film. The hollow particles calcined at temperature of 400 °C were dispersed in a UV-curable acrylate monomer solution. The obtained dispersion was then coated on a cleaned glass substrate. The amount of the particles in the coated films was varied from 5 to 20 vol%. The optical properties and the light diffusing ability of the films were studied and then compared to those of the cleaned glass. As a result, the films become opaque when the amount of the particles increases. Although the opacity of the films was observed, the total transmittance of those was still high and close to that of cleaned glass substrate. Interestingly, a film based on 20 vol% hollow silica nanoparticles gives the highest total transmittance (93%) and diffuse transmittance (40%) when comparing to other films in this experiment. Meanwhile, the increased amount of the particles leads to the formation of aggregated particles with a larger size and homogenous dispersion as evidenced from the FE-SEM images. It also improves the optical properties of the films; for instance, diffuse transmittance and light diffusing ability. According to these results in the study, it can be concluded that the films based on the hollow silica nanoparticles as fillers have potentially in application as light diffuser films in the LCD industry.

Chapter 5 controls the morphologies and surface properties of hollow silica nanoparticles with varying pH of HCl in the core-template removal process. The obtained particles were then dispersed in a UV-curable acrylate monomer. The dispersions containing different hollow particles were employed to fabricate silica/UV-cured polymer composite films. The high pH of HCl produces the thinner shell and larger window cavities of the hollow silica nanoparticles. Moreover, it provides the higher specific surface area of those. Meanwhile, the film embedded with hollow silica nanoparticles, which contain larger size of hollow interiors, thinner shells, larger window cavities and high specific surface area exhibits higher total transmittance (~80%), higher diffuse transmittance (~80%) and better light diffusing ability when comparing to other composite films. Its properties still maintain at longer wavelength. Therefore, the distinct morphologies and surface properties of the hollow silica nanoparticles significantly affect the optical properties and the morphologies of the resulting films. In addition, the hollow silica nanoparticles with hierarchical structures are one of the effective inorganic fillers for light diffuser films which probably reduce the number of backlight unit in the LCD industry leading to energy saving and subsequently light-weight LCD screens.

Finally, Chapter 6 presents the overall concluding remarks of the present work and the directions for the future research. The techniques presented in all studies of this dissertation provide an informative foundation for the structures of silica nanoparticles, which affect optical properties of silica films. It is a template and a saving energy approach for the various future applications in the field of optical materials, especially light diffuser films for backlight unit in the LCD industry.

論文審査結果の要旨

液晶ディスプレイが広く使われている中、液晶ディスプレイバックライト用光拡散ユニットはなくてはならない物である。光拡散ユニット内の拡散粒子には光の減衰が少なく、光拡散が多い特性を持った粒子が理想であり現在それに関する研究が盛んに行われている。そのような背景の中で当研究グループは、中空粒子と呼ばれる内部の空洞と外部のシェルから構成される粒子に注目し研究を行っている。本研究では、中身の詰まった中実粒子、中身が空洞の中空粒子、中空粒子の側面に窓のような穴の空いた中空窓穴粒子を拡散粒子に用いることで、光学特性にどのような違いがみられるかを調査し、光拡散に最適な粒子構造の解明を目的としている。

本実験では、紫外硬化樹脂に拡散粒子を含有させ拡散膜とし評価した。アクリル系紫外硬化樹脂に拡散粒子を分散させ、バーコーターを用いてスライドガラスに製膜した。その後紫外線を照射し樹脂を硬化させ拡散膜とした。用いた拡散粒子は中実粒子、中空粒子、中空窓穴粒子の3種類を選択し、中実粒子/中空粒子含有薄膜の評価を行うことで、中空構造を持つことによる光拡散の違いの調査、中空粒子/中空窓穴粒子を用いることで粒子形状の最適化を目的とした。今回使用した中空粒子は無機粒子テンプレート法により作製しているが、この方法はコアとなる無機粒子にゾルゲル法を用いてシリカのシェルをコーティングし、酸処理を施すことによりコアを除去することで中空構造の粒子を得るという方法である。中空粒子におけるシェル厚、内径、シェル密度などの微構造は、例えばシリカ源の添加量により調整可能である。今回はシェル厚、内径、シェル密度、比表面積を変えることによって、光拡散に最適な中空粒子微構造の調査を行った。

中実粒子を紫外線硬化樹脂に含有させることにより光の拡散性能は向上したが、依然拡散透過率は低かった。それに対して、中空粒子含有薄膜における光拡散透過率は、中実粒子含有薄膜よりも高い値を示し、拡散透過率の向上に成功した。中空構造を有することで光拡散性が向上したことが示唆される。さらに紫外線硬化樹脂中の中空粒子の濃度をあげることで、拡散率が劇的に向上した。粒子濃度をあげることにより、懸濁液の粘度が増加し粒子同士が凝集しやすくなる。薄膜内での粒子の凝集が光拡散には重要な要因の一つで、凝集径の制御はシリカ微構造や、溶液粘度に依存する。シリカのシェル密度を変え樹脂に含有し薄膜の評価を行ったところ、光透過性が減少した。これはシェルの密度が高い粒子はシェルでの光の吸収が起きるためであると考えられる。本研究で様々条件を変え作製した拡散膜においては中空粒子の空洞部の直径が大きく、シェルが厚く、シェル側面に穴が開き、比表面積の大きな構造を有した中空粒子を用いることで高い光拡散性を示すことが分かり、その時得られた粒子の凝集が光拡散に適していることが示唆された。

以上の結果より中空粒子を光拡散粒子として使用することで拡散膜の光拡散性が向上することが分かった。中空粒子を液晶ディスプレイバックライト用光拡散ユニットに応用すれば高拡散のユニットとなるため省エネが期待できる。この粒子の発明は材料科学における工学的意義が非常に大きい。以上により、本論文は、博士(工学)の学位授与に相当する内容であると認められる。