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Thermal Curing Property of Silicone Encapsulant Containing Quantum Dot Surrounded by Various Types of Ligands

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In this study, the silicone thermal curing degree of the silicone-encapsulated quantum dot light emission diode was measured using the various types of chemical ligands around quantum dot. It was confirmed that the tri-octyl phosphin oxide (TOPO) ligand around the quantum dot was responsible for dispersion of the quantum dot in silicone encapsulant and decline of the thermal curing degree of the silicone encapsulant. Also, it was confirmed that the thermal curing degree of silicone encapsulants containing the steric acid (SA) and the dodecanoic acid (DA) ligands were higher than the one of TOPO ligand.

Key Words : Quantum dot, Silicone encapsulant, Ligand, Thermal curing degree, TOPO

Introduction

Quantum dot is a luminous substance which can emit visible light due to quantum size effects. Its luminous wavelength is varied according to the size of nanoparticles. Unlike the existing light emission diode (LED) phosphor, the quantum dot can emit light of wavelengths such as red, green and blue by controlling the size of quantum dot and it comes into the spotlight as a new luminous material.[1-6] When the quantum dot is used as a LED phosphor, the high color purity and the high photoluminescence (PL) are obtained, because the full width at half-maximum (FWHM) of emission is very narrow as 15-25 nm.[7-9] In general, it has known that the quantum dot is composed of a core inside, the shell surrounding the core, and the organic ligand around the shell for a high performance quantum dot LED package.[10-14] In particular, the organic ligand compound should have a binding group with the surface of quantum dot and a spacer group such as alkyl or aryl chain for dispersion within encapsulant resin, because the organic ligands outside the quantum dot are responsible for the affinity with the surface of the quantum dot and the dispersion with encapsulant resin for LED packaging. However, so far, there are few reports about the relationship between the encapsulant thermal curing properties and the chemical structures of organic ligand in the quantum dot LED package.

In this study, the thermal curing degree of a silicone encapsulant containing a quantum dot surrounded by various types of ligands was evaluated to know the relationship between the thermal curing degree of silicone encapsulant and the chemical structure of organic ligands around the quantum dot.

Experimental

Figure 1 shows chemical structures of a quantum dot (Nano square Co. Ltd.) composed of a core, shell, and organic ligands. The core of the quantum dot was CdSe which had an emission wavelength of 570 nm. The shell surrounding the core was ZnSe for passivation of surface defect of the quantum dot and the outermost organic ligands surrounding the shell was tri-octyl phosphin oxide (TOPO). Also, additional two kinds of organic ligands such as steric acid (SA) and dodecanoic acid (DA) were used to investigate the thermal curing properties of encapsulant depending on the chemical structures of the ligands

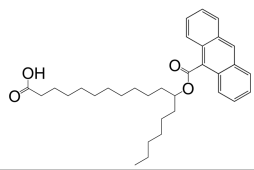
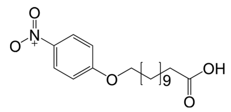
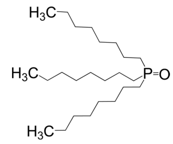
	Material	Molecular Structure
Core	CdSe	
Shell	ZnS	
Ligands	Steric acid (SA)	
	Dodecanoic acid (DA)	
	Tri-Octyl Phosphin Oxide (TOPO)	

Figure 1. Chemical structures of core, shell and ligands of quantum dot.

We prepared the pure quantum dot to investigate the dispersion property of quantum dot without TOPO among the encapsulant. To prepare the pure quantum dot to remove TOPO ligand, the purification process was carried out. For the quantum dot purification process, the quantum dot was dispersed into the mixed solvent of methanol and toluene mixed at 1:1 in a weight ratio and then the quantum dot-dispersed solution was centrifuged at 12000 rpm for 10 min. The purification number was defined as repeated number of purification process regarding the quantum dot. The quantum dot LED package was fabricated by thermal curing of an encapsulant of a liquid type silicone monomer which was composed of the Pt catalyst and the reactive silicone monomer having a vinyl group as a reactive group (KER-2500, Shinets Co. Ltd.). In the quantum dot packing process, the liquid type silicone 0.5 g and quantum dot 6 mg were mixed and then cured at 150 °C during 8 h for polymerization. Also, three types of organic ligands such as SA, DA, and TOPO were added into the silicone encapsulant in order to evaluate the silicone curing degree containing the various types of the organic ligand species, respectively. In addition, in the case of the TOPO ligand, three concentration samples such as, 0.03, 0.05 and 0.07 wt % were prepared to evaluate the thermal curing degree of the silicone encapsulant depending on the concentration of the TOPO ligand.

The transmittance and haze property of the silicone-encapsulated quantum dot package were measured to evaluate the dispersion properties of the quantum dot in silicone encapsulant depending on the purification number throughout the light wavelength from 350 nm to 750 nm using a spectrophotometer (CM-3600d, Konica Minolta Co. Ltd.).

It is difficult for directly measure the curing degree of the sample on thermal curing. Therefore, the evaluation of thermal curing degree for silicone was indirectly measured for thermal change of logarithmic damping ratio of silicone resin using a rigid-body pendulum type physical properties testing instrument (RPT 3000W, A&D Co. Ltd.). Here the trace of the change logarithmic damping ratio is approximately connected to the change of the viscosity by the formation of polymer network under thermal curing of silicone encapsulant and also the thermal curing degree of silicone encapsulant on thermal curing.

Results and Discussion

Table 1 shows the average transmittance and haze from 350 nm to 750 nm of the silicone-encapsulated quantum dot package depending on the purification number. Furthermore, Figure 2 shows the transmittance of the silicone-encapsulated quantum dot package depending on the purification number of the quantum dot throughout all light wavelengths from 350 nm to 750 nm. Unfortunately, it was impossible to measure the transmittance and haze of the silicone encapsulant containing a non-purificated quantum dot surrounded by TOPO ligand, because the thermal curing of silicone monomer could not proceed.

Table 1. Average transmittance and haze of silicone encapsulant depending on the purification number of quantum dot

	Haze (%)	Average transmittance (%)
Pure silicone	0	92.64
1st purification	86.07	62.24
2nd purification	88.56	60.12
3rd purification	89.73	60.66
4th purification	94.27	56.51
5th purification	96.15	54.98

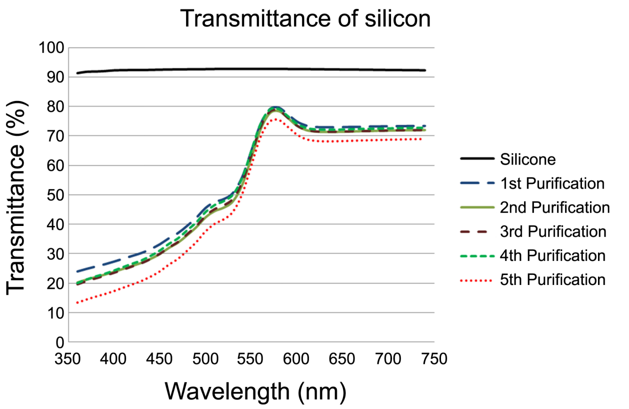


Figure 2. Transmittance depending on purification number of the silicone encapsulated quantum dot package having 570 nm emission wavelength.

The transmittance of the quantum dot package was decreased and the haze of the quantum dot package was increased along with the increase of the number of purifications of quantum dot as shown in Table 1 and Figure 2.

These results indicate that the removal of the TOPO ligand according to the repeat of the quantum dot purification process causes the decline of dispersion of the quantum dot in the silicone encapsulant, increase of haze of light due to the increase of light scattering by formation of quantum dot aggregation structure more than several hundreds of nanometers equivalent to the ultra-violet (UV) and visible light wavelength. Therefore, we know that the TOPO ligands have a role of increasing the dispersion property of the quantum dot among the silicone encapsulant.

Figure 3 shows the measurement result of logarithmic damping ratio depending on the temperature when the various concentrations of TOPO ligand, such as, 0.03, 0.05 and 0.07 wt % were added into the silicone-encapsulated

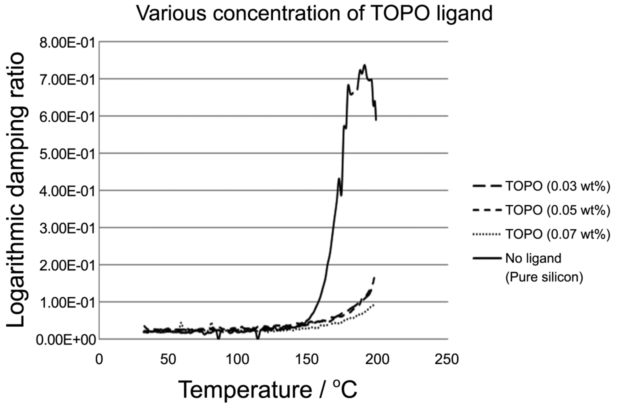


Figure 3. Logarithmic damping ratio of the silicone-encapsulated quantum dot package with various TOPO concentrations.

quantum dot package. The pure silicone resin without the TOPO ligand was observed to have an abrupt increase of logarithmic damping ratio at 150 °C. Here, the abrupt increase point of logarithmic damping ratio signifies the starting temperature of thermal curing for the silicone monomer. The TOPO concentration of 0.07 wt % shows the lowest logarithmic damping ratio compared to those of 0.03 and 0.05 wt % in the silicone encapsulated quantum dot package at the vicinity of 200 °C, furthermore there are no abrupt increase of logarithmic damping ratios in the three silicone monomers containing the TOPO ligand in comparison with the pure silicone monomer. Namely, the abrupt increase of viscosity following to thermal curing could not clearly be observed in all types of silicone monomer containing the TOPO ligand exchanged-quantum dot.

These results imply that the thermal curing degree of the silicone monomer is decreased along with an increase of concentration for TOPO added to the silicone encapsulant and also the thermal curing of the silicone was not easily proceed when TOPO ligand was used as quantum dot ligand. In general, the TOPO presented the high polarity due to the dipolar phosphorus-oxygen bond and allowed this compound to bind to metal ions.[15] Therefore, it is expected for the TOPO to make the complex with Pt catalyst among the silicone monomer including vinyl groups for thermal curing reactive group. As a result, the decline of reaction activity of the Pt was occurred and then prevented the curing of the vinyl group regarding the silicone monomer used as the encapsulant.

Figure 4 presents the measurement result of logarithmic damping ratio depending on the temperature when the 0.03 wt % of three types of ligands, TOPO, DA and SA were added into the silicone-encapsulated quantum dot package. The SA ligand-added silicone monomer shows the most abrupt increase of logarithmic damping ratio around 152 °C, the DA ligand-added silicone monomer shows a slight increase of logarithmic damping ratio around 170 °C, and the TOPO added-silicone monomer does not clearly show the increase of logarithmic damping ratio as shown in Figure 4. These results indicate that the SA and the DA ligand-added silicone monomer have the higher thermal curing degree compared to the TOPO ligand-added silicone monomer. Therefore we could know that the DA and SA had the small effect in the decline of curing of silicone because DA and SA were difficult to make the complex with Pt catalyst among the silicone monomer compared to TOPO. Consequently, we can say that the SA and the DA organic ligand are more suitable for the ligand of the quantum dot in comparison with the TOPO on the view of thermal curing for silicone encapsulant.

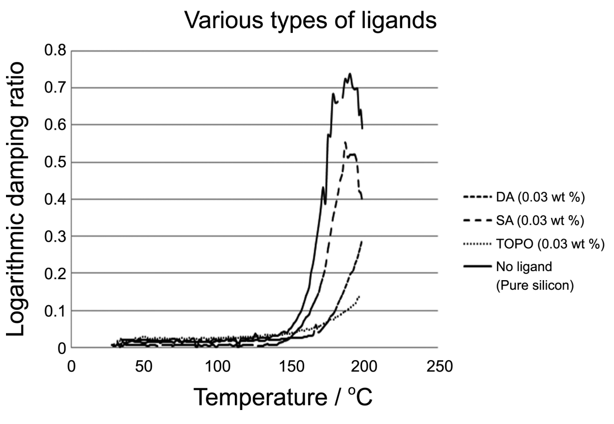


Figure 4. Logarithmic damping ratio of the silicone-encapsulated quantum dot package containing three kinds of ligands.

Conclusion

It was confirmed that the TOPO organic ligand around the quantum dot was responsible for dispersion of the quantum dot in silicone encapsulant and decline of the thermal curing degree for the silicone encapsulant. Moreover, it was confirmed that the SA and the DA organic ligand were more suitable for thermal curing of the silicone encapsulant of the quantum dot in comparison with the TOPO ligand.

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