# Study on “Core-Shell Particle” as new resin technology for UV curable formulation.

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## Introduction:

In order to achieve optimum performance in a UV cured formulation choices of raw materials are critical to the impact on crosslink density, glass transition temperature (Tg) and modulus. For thermoplastic polymer materials a common approach is to blend Core-Shell polymer particles (CSP) to obtain the desired properties. The addition of Core-Shell particles has been a common commercial practice for many years. The same approach has been considered for thermoset polymer materials with very limited success in UV curable resins. The primary difficulty with incorporating these particles into a thermoset system is in controlling the phase structure (dispersion of CSP) which is critical to achieve the desired results. In this paper, Core-Shell polymer particles (CSP) are studied as a potential new raw material for UV curable formulations. The characterization of UV cured formulations associated with CSP’s, such as physical properties are also discussed.

## Core-Shell Polymer Particles (CSP):

CSP particles have been commonly known in thermoplastic polymeric system over 40 years. A Schematic structure of a CSP particle is shown as Figure 1. The particle consists of a spherical core particle surrounded by a thin shell layer with both the core and the shell layers produced with a polymeric material. Typically, the core layer is a cross-linked rubber or flexible type polymer which is grafted to a hard polymer shell material at the surface. This type of structure allows the CSP to be blended and dispersed into thermoplastic resin systems without any change to its primary physical structure (size and geometry). The rubbery core layer provides the toughening mechanism while the glassy shell layer secures compatibility with the thermoplastic system of which the CSP is being dispersed into. Historically, many different CSP structures in terms of various core compositions, shell chemistry, size and geometry have been proposed for improvement of performance in each type of polymeric system. Over 1 million metric tons (2.2 billion LBS) of CSP in a powder form has been used in industry for thermoplastic polymeric systems such as PVC, ABS.

CSP are generally furnished as a dried solid powder comprising of millions of agglomerated CSP particles. Past attempts to incorporate CSP’s into UV curable formulations using such powdered

CSP results in a poor mixture characterized by rapid settling, high viscosity and an overall poor appearance of the cured UV coatings due to agglomeration of CSP. Agglomeration can be confirmed through microscopic (TEM) observation. In order to address this challenge a different approach to incorporate CSP is developed to continue this study.

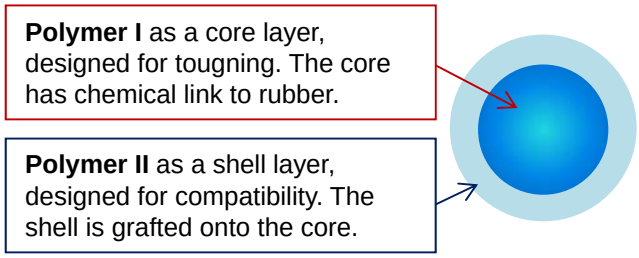


**Figure 1. Schematic Structure of CSP**

***INSERT KANE ACE MX OVERVIEW***

## CSP preparation to study in UV formulation:

All CSP used in this paper are prepared as 25wt% concentration in a number of standard acrylate monomers. These monomers were then used as starting materials for a variety of UV curable formulations.

An Example of a CSP concentrate is shown in Figure 2, which is 25wt% CSP in IBOA (Isobornyl acrylate). Attempts to obtain similar concentration using other common acrylate monomers resulted in success. These include TMPTA (Trimethylolpropane Triacrylate), TPGDA (Trypropyleneglycol diacrylate) and EO3TMPTA (Ethoxylated (3mol) TMPTA). All of these acrylate concentrations were prepared using Kaneka' proprietary MX manufacturing process. The resulting CSP concentrates exhibit excellent stability as there is no settling/agglomeration of the CSP out of the mixture observed over many months.

In order to obtain a UV curable formulation that contains CSP, the MX-acrylate 25wt% CSP concentrates are incorporated with other standard UV resins by a method of simple stirring. No shearing or strong mixing was employed to incorporate the CSP into the UV curable formulations. To confirm how well the CSP are dispersed in the UV formulations, microscopic observations (TEM) were carried out using a variety of UV cured formulations with the MX modification. A Typical example of aTEM picture is shown in Figure 3. As can be observed from the picture, the CSP are dispersed individually as discrete particles and no agglomerations are present.

**Figure 2. Example of 25wt% CSP dispersed in acrylate monomer (IBOA)**

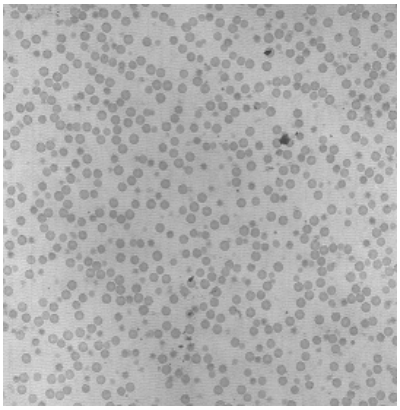

**Figure 3. TEM observation on UV cured "TMPTA/Ebe5129/10wt%CSP"**

A schematic summary of this section is shown in Figure 4. We have confirmed that the CSP prepared for this study can be dispersed in individual (discrete) particles, remain in uniform suspension, and are stable without agglomeration throughout the curing process to achieve consistent phase structure of the cured materials generated through the UV curing process.

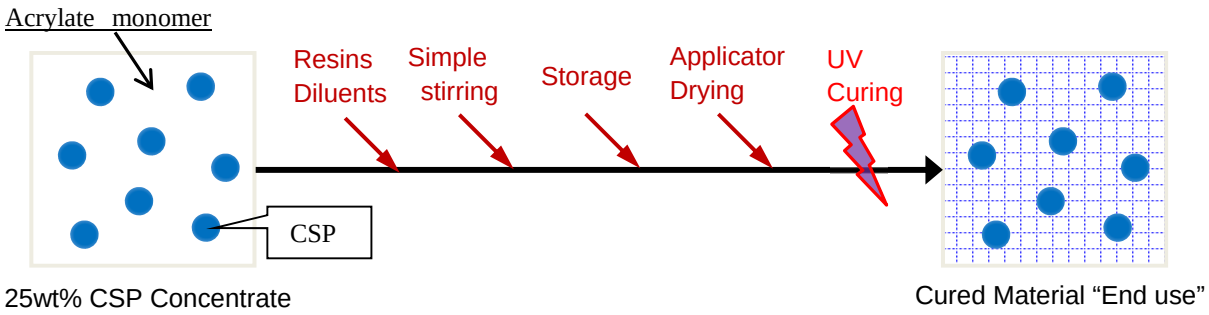


**Figure 4. Schematic summary on resin phase structure of CSP incorporated UV formulation**

## Formulation to incorporate CSP :

The CSP prepared as a 25wt% concentrate in acrylate monomer as described earlier, was incorporated into each testing formulation by simple stirring with other UV resins. Example formulations are shown in Table 1. To understand the impact of the addition of CSP, characterization was carried out through comparison between CSP incorporated formulation and its corresponding control formulation that has identical components aside from the CSP.

**Table 1. Examples of formulation for testing (Control and CSP incorporated).**

| Control | | With 10parts of CSP added to Control | |
|---|---|---|---|
| Resin A | 30 parts | Resin A | 30 parts |
| Monomer B | 40 parts | Monomer B | 40 parts |
| Monomer C | 30 parts | Monomer C | 0 parts |
| | | 25wt% CSP in Monomer C | 40 parts |
| Photoinitiator | 5 parts | Photoinitiator | 5 parts |
| Solvent | 45 parts | Solvent | 45 parts |

Monomer C: 30 parts
CSP: 10 parts

This concept of comparison can be further explained graphically as shown in Figure 5. All components listed in Figure 5 are the same as Table 1 above.

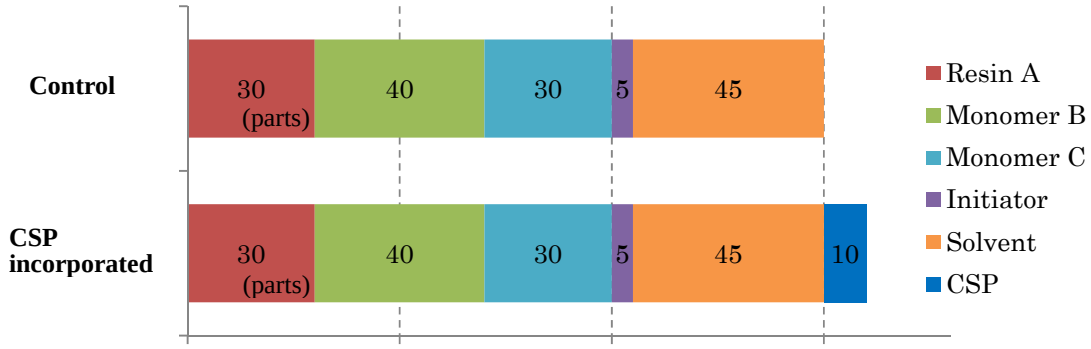


**Figure 5. Comparison of each components between formulations shown in Table 1.**

## Characteristics of UV cured formulation that contains Core-Shell polymer particle;

Since CSP's are well known to work as a "toughening agent", impact properties in UV coating formulations were investigated. Formulations and test results are shown in Table 2. Du Pont type falling weight impact test (JIS K5600 / ISO 6272) was carried out on UV cured coated films (1 mil), which were prepared on steel panels using 4 different coating formulations. Improved impact toughness was observed by incorporating CSP into the UV formulation along with an increase in surface hardness. However, some drawbacks in surface hardness were also observed when compared to the control formulation.

**Table 2. Mechanical properties of cured formulation**

| ID | #110 | #110C | #111 | #111C |
|---|---|---|---|---|
| Formulation | With 25 parts CSP | Control | With 20 parts CSP | Control |
| Resins (parts) | PETA (60), TPGDA (15), NVP (15), CD9053 (10) | | PETA (60), Ebe8402 (15), NVP (15), CD9053 (10) | |
| DuPont Impact (Falling height) | 20.3kgcm (45cm) | 15.8kgcm (35cm) | 18kgcm (40cm) | 15.8kgcm (35cm) |
| Pencil Hardness | 3H | 4H | 2H | 4H |

DuPont Impact (@r.t.): Falling weight= 450g, Steel Panel (SPCC-SB, t=1/4"), DFT=1mil
Pencil Hardness: On acrylic panel
PETA: Pentaerythrytol triacrylate, CD9053: Adhesion enhancing monomer (Sartomer)
NVP : N-vinyl pyrrolidone, Ebe8402: Ebecryl 8402 (Urethane acrylate, Cytec)
30 parts of MEK and 5 parts of photoinitiator were also added to all formulations before applying it onto steel panels

Resin shrinkage was also studied as shown in Table 3 using pure TMPTA and TPGDA, respectively. When 15wt% of CSP was existing in pure TMPTA (i.e. TMPTA/CSP=85/15wt%), shrinkage was down to 10.9%, whereas 12.5% shrinkage observed without CSP (TMPTA=100wt%) An improvement in shrinakage of 12.8%. In case of TPGDA with 25wt% CSP (TPGDA/CSP=75/25wt%), the shrinkage was down to 8.7%, whereas it was 11% without the CSP(TPGDA=100wt%) an improvement of 20.1%. Since CSP can be considered as a "filler" and no additional polymerization will be expected by incorporating CSP, CSP is also working as a shrinkage control additive.

**Table 3. Low shringkage properties observed at CSP containing acrylate monomers**

| | Shrinkage after curing | |
|---|---|---|
| | With CSP | Neat Monomer |
| Trimethylolpropane Triacrylate | **10.9%** (with 15wt% CSP) | **12.5%** |
| Tripropyleneglycol Diacrylate | **8.7%** (with 25wt% CSP) | **11%** |

Because of the reduced shrinkage properties observed and discussed above, the impact to adhesion was also studied utilizing the standard cross-cut adhesion test (ASTM D3359). Details on the formulation and results are shown in Table 4. These formulations were applied then UV cured to form a film on an acrylic test panel. Though the level of improvement varied by formulation, it was observed that small amounst of CSP are very effective in helping to improve the adhesion property of a UV curable coating.

**Table 4. Cross-cut adhesion test in model UV formulation - effect of CSP content in formulations**

| Control | #1 | #2 |
|---|---|---|
| | Ebe8402 (30), TMPTA (10), THFA (60) | Ebe8402 (30), TMPTA (15), THFA(55) |
| Test result: # of Area Removed / # of Area Tested. | | |
| No CSP | **19** /121 | **112** /121 |
| With 2 parts CSP | **0** /121 | - |
| With 5.3 parts CSP | **0** /121 | **18** /121 |

Ebe8402: Ebecryl 8402 (Urethane acrylate, Cytec)
THFA: Tetrahydrofurfulryl acrylate

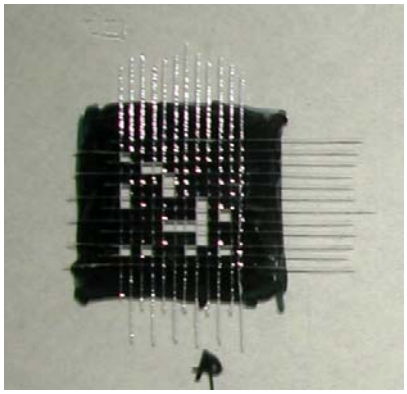

**Fig.6 Cross-cut adhesion test specimen for control formulation #1 (no CSP included)**

## Summary;

In this paper, CSP (Core-Shell polymer particle) are discussed as a potential new resins for UV curable formulations. Consistent phase structure in UV cured materials can be obtained by using a properly designed CSP dispersed in acrylate monomers. UV cured coatings obtained in this study were characterized with a smooth and glossy surface, most likely due to the consistent phase structure in the cured coated films. It is also observed that CSP provide an effective method for improving properties of UV curable materials in terms of impact toughness, shrinkage and adhesion. Further investigation will be published in the near future.