UV-Waterborne Nanocomposite Coatings: Curing Kinetics Study

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Introduction

- Paint and coatings industries
  - Use important quantities of finishing products (solvent based)
- Importance of environmental protection interest
  - Review of regulations (VOCs emission)
- Development of more eco-friendly products
  - UV-cured coatings
- Wood products industry
  - Shift from solvent-based to waterborne coatings
- UV-waterborne coatings
  - Meet requirements of the industry (mechanical properties)

Investigation of nanocomposite approach
UV-Waterborne Coatings

- **Advantages**
  - Fast
  - No emission of VOCs
  - Excellent mechanical properties (abrasion and scratch resistance)
  - Good optical properties (gloss, yellowing)

- **Disadvantages**
  - High water surface tension → difficulties of wetting
  - Sensitive to oxygen → polymerization inhibition
  - Lower properties
  - Higher price

{vs high solid content coatings}
### Some current nanoparticles and their properties

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Alumina</th>
<th>Zinc oxide</th>
<th>Silica</th>
<th>Clays</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrasion resistance</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Hardness</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>UV Protection</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antimicrobial</td>
<td>✓</td>
<td>✓</td>
<td></td>
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</tr>
<tr>
<td>Scratch resistance</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Fire barrier</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>
Material

- **Formulation**
  - PUA resin
  - Photoinitiator

- **Nanoalumina and modified nanosilica**
  - High specific surface area + Hydroxyl group
    - difficult dispersion in aqueous media
  - Surface modification by trialkoxysilanes
    - dispersibility improvement in acrylate media

- **3 loading rates: 1, 3 and 5 wt%**
  - Suitable mechanical properties → less quantities of nanoparticles
    - high efficiency
- Measure of the gloss retention at 60°
- Nanoparticle addition → scratch resistance
- Coatings based on nanosilica → important of scratch resistance
- Grafting trialkoxysilanes → acrylate functions and acrylate double bonds
Polymerization process

- Understanding is essential
- Fast and efficient polymerization

Optimize the curing process

- Temperature
- Resin type and concentration
- Photoinitiator type and concentration
- UV-light intensity

Photo-DSC

- Simple and efficient way
- Evaluate the curing kinetics
Experimental

- Nanoparticles dispersion
  - Ultrasound

- Photo-DSC experiments
  - Differential scanning calorimeter
  - Light source = mercury-xenon lamp

- Process
  - Previous drying
  - $I = 47 \text{ mW/cm}^2$
  - $T = 30^\circ\text{C}$, air flow

- Exothermic curves
  - Heat flow as a function of reaction time

1 wt% nanoAl$_2$O$_3$ - 10 min (750 W à 50 %)
- Exotherms under nitrogen conditions → observed by 2 authors
- Drying before UV-curing → free-radical polymerization in solid state
- Humidity in air atmosphere = plasticizer effect → chain mobility in dried films → UV-curing efficiency
Nanoalumina Effect

- Nanoalumina addition $\rightarrow$ exotherms
- High specific surface area and $-OH$ groups $\rightarrow$ aggregates presence
- Effect at 1, 3 et 5 wt% fairly equivalent $\rightarrow$ aggregates effect more important that loading effect
Nanosilica Effect

- Nanosilica addition → exotherms
- Aggregates presence
- Effect at 3 et 5 wt% fairly equivalent → aggregates effect is predominant
Nanoparticle Type Effect

- Exotherms FAnU1 < FSnU5
- Surface modification of nanosilica $\rightarrow$ aggregates size and amount
- Number of acrylates functions and reactive groups $\rightarrow$ UV-curing efficiency
Interesting Advantages for All Coatings Industries

- Mechanical properties
  - Excellent scratch resistance
- UV-curing process
  - Presence of aggregates $\rightarrow$ lower of efficiency
  - Fast
  - No effect of air atmosphere
- Surface modification
  - Improve mechanical and kinetics properties

Excellent properties with 1 wt% of nanosilica


Hajas J.; Lenz P.; Schulte K.; **Enhancing mechanical properties of UV-curing wood varnishes by synergistic combinations of silicones and nano-alumina particles**, *RadTech Europe Conf*, 2005


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Thank you

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