DEVELOPMENT OF A NOVEL COATING SYSTEM USING PHOTO-LATENT BASE TECHNOLOGY

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GOALS AND OBJECTIVES

- Development of a stable dual-cure system with a single trigger (UV)
- Replacement of Harmful acrylic monomers
i) **Photo-latent bases in UV Curing – click chemistry** :

- Photo-latent bases act as photo-initiators and initiate anionic polymerisation.

ii) **Michael Addition Reaction** :

- Conjugate 1,4 – addition of a resonance stabilized carbanion to an activated \( \alpha,\beta \) – unsaturated compound.

iii) **Sol-Gel Process** :

- Formation of a network of Si-O-Si chemical linkages using base catalyst.
**Fig. 1 : Michael Addition Reaction Mechanism**

**Fig. 2 : A typical hybrid Organic-Inorganic network**

**Fig. 3 : Photo-release of DBN from N-benzylated precursors**
BACKGROUND

- Development of a novel UV curable hybrid organic-inorganic bio-based nano-composite coating
- Chemistry of photo-latent base catalyst with Michael addition and Sol-Gel process
- Commercial Exploitation: Replacement of the present monomeric/small chain acrylates that have adverse health effects
METHODS

**i) Acetoacetate Resin Synthesis:**
- Di-functional (AA-2) and tri-functional resin (AA-3) synthesis

**ii) UV Curing:**
- Michael Addition and Sol-Gel Process chemistry was involved

<table>
<thead>
<tr>
<th>Process</th>
<th>Main Ingredients</th>
<th>Photo-initiator Dose</th>
<th>Curing Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Michael Addition</td>
<td>AA – 3 + TMPTA</td>
<td>CGI – 90 (4%) ITX (1%)</td>
<td>1 mill – CRS Panels</td>
</tr>
<tr>
<td>Sol-Gel</td>
<td>Gelest 6487</td>
<td>Acetone</td>
<td>12 ft./minute 3 cycles</td>
</tr>
<tr>
<td>Michael Addition + Sol-</td>
<td>Gelest 6487</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel</td>
<td>AA – 3 + TMPTA + Gelest</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Reaction Summary for the 3 reactions.

Fig. 4: Generic Structure of CGI – 90 obtained from BASF

Fig. 5: TMPTA structure

Fig. 6: Gelest 6487 structure
iii) Hybrid Organic – Inorganic Chemistry:

- Coatings with 3 different compositions of Ebecryl 860 and Gelest 6487 UV cured
- AA-3 addition varied with acrylate composition

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Composition 1</th>
<th>Composition 2</th>
<th>Composition 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ebecryl 860</td>
<td>100 %</td>
<td>75 %</td>
<td>65 %</td>
</tr>
<tr>
<td>Gelest 6487</td>
<td>0 %</td>
<td>25 %</td>
<td>35 %</td>
</tr>
</tbody>
</table>

Table 2: Compositions for preparing hybrid organic – inorganic bio-based coating

Fig. 7: Ebecryl 860 structure
RESULTS AND DISCUSSION

i) **UV Curing:**

- FTIR/ATR studies for the uncured and cured coating composition
- **Michael Addition:** Hard, tack-free film observed after curing

- Disappearance of the double bond peak for acrylate group at 1650 cm⁻¹
- Diminishing of the methylene peaks at 2950-3000 cm⁻¹
- The carbonyl peak at 1700 cm⁻¹ used as reference.

*Fig. 8: FTIR analysis (uncured)*

*Fig. 9: FTIR-ATR Analysis (cured)*
RESULTS AND DISCUSSION

- **Sol-Gel Process**: Semi-solid, tacky film observed 24 hours after curing
- Solid film formation 48 hours after curing
- Broadening of the silane peak between 1050-1110 cm\(^{-1}\) suggesting siloxane formation

Fig. 10: A comparative analysis of the uncured coating and cured coating.

Fig. 11: Sol-Gel process depicting growth and gelation.
RESULTS AND DISCUSSION

- For Michael + Sol-Gel, a tacky-semi solid was formed after curing.
- Tack-Free film observed after keeping at room temperature for 3 hours.
- Storage stability (in dark) for > 2 months.

Fig. 12: A comparative analysis of the FTIR of uncured coating and ATR of cured coating.
iii) Hybrid Organic – Inorganic Bio-based Coating

- 3 compositions of hybrid organic-inorganic bio-based coatings were prepared using Ebecryl 860
- Film application at 25 microns on CRS panels
- UV cured for 3 cycles at 12-13 ft./minute
- Cured films tested for hardness, flexibility, impact resistance
- Improved flexibility, increased hardness and greater impact resistance with increasing inorganic content

<table>
<thead>
<tr>
<th>Composition No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conical Mandrel</td>
<td>Failed</td>
<td>Passed</td>
<td>Passed</td>
</tr>
<tr>
<td>Pencil Hardness</td>
<td>3 H</td>
<td>6 H</td>
<td>6 H</td>
</tr>
<tr>
<td>Pendulum Hardness</td>
<td>23</td>
<td>27</td>
<td>35</td>
</tr>
<tr>
<td>Impact Resistance</td>
<td>40</td>
<td>100</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 3: Test Results performed for 3 coating compositions
RESULTS AND DISCUSSION

- DSC Analysis:

<table>
<thead>
<tr>
<th>Composition No.</th>
<th>Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>113.13 °C</td>
</tr>
<tr>
<td>2</td>
<td>160.52 °C</td>
</tr>
<tr>
<td>3</td>
<td>166.2 °C</td>
</tr>
</tbody>
</table>

Table 4: Glass Transition Temperatures (Tg) for the three cured compositions.

- TGA Analysis:

  Two decomposition peaks in the range of 270-280 °C and 430-450 °C, correspond to acrylate and acetoacetate functionality.

- Results consistent with increasing hardness seen in Pendulum Hardness and Pencil Hardness test.

<table>
<thead>
<tr>
<th>Composition No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition Peaks</td>
<td>T = 270.09 °C</td>
<td>T = 276.66 °C</td>
<td>T = 271.78 °C</td>
</tr>
<tr>
<td></td>
<td>T = 436.45 °C</td>
<td>T = 452.87 °C</td>
<td>T = 448.16 °C</td>
</tr>
<tr>
<td>Residue Percentage</td>
<td>8.46%</td>
<td>11.50%</td>
<td>13.37%</td>
</tr>
</tbody>
</table>

Table 5: Percentage Residues and decomposition peaks for the three cured compositions.
CONCLUSION

- Novel UV-cure coating system developed for deriving Organic-Inorganic hybrid with high bio-based content
- CGI-90 ® has been found to successfully trigger MA and Sol-gel reactions – concomitantly but independently.
- Validated MA and sol-gel reactions using FT_IR spectroscopy.
- This chemistry allows development of UV-cure coatings free of acrylic monomers
Authors would also like to acknowledge Dr. Eugene Sitzmann of BASF, Southfield, MI for providing CGI – 90®, as well as for technical discussion, support and encouragement. We are also thankful to Dr. John Texter for his guidance in running different characterization instruments used in this work.

Arnaud Gigot, M. S. (2015, May). In-situ synthesis of organic-inorganic coatings via a photolatent base. Torino, Italy: Polymer 68.


