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

BACKGROUND

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 α,β – unsaturated compound.

iii) ***Sol-Gel Process :***

- Formation of a network of Si-O-Si chemical linkages using base catalyst.

BACKGROUND

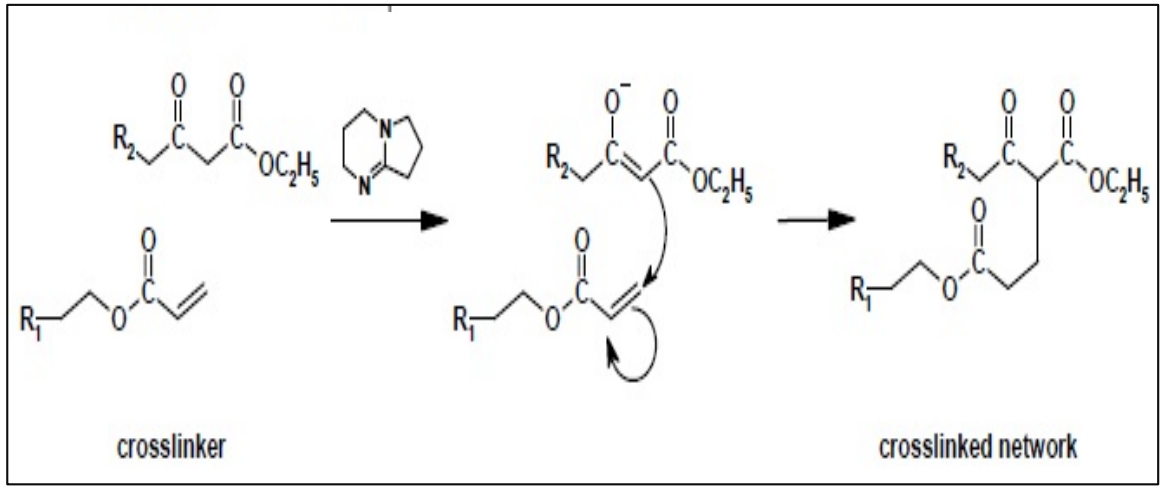

Fig. 1 : Michael Addition Reaction Mechanism

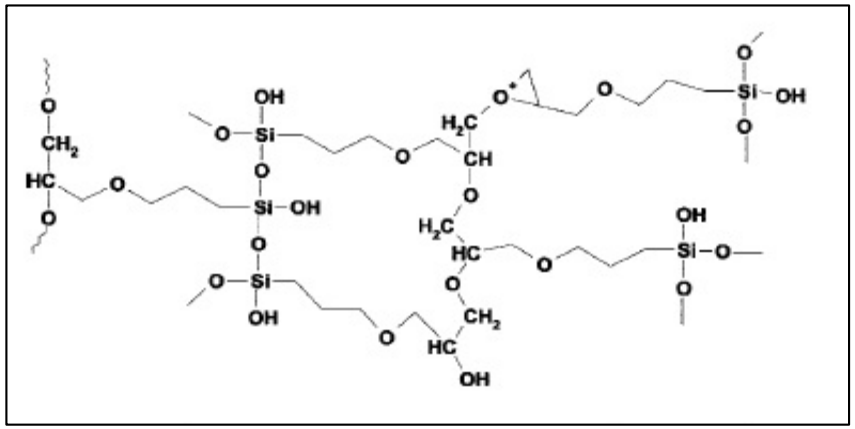

Fig. 2 : A typical hybrid Organic-Inorganic network

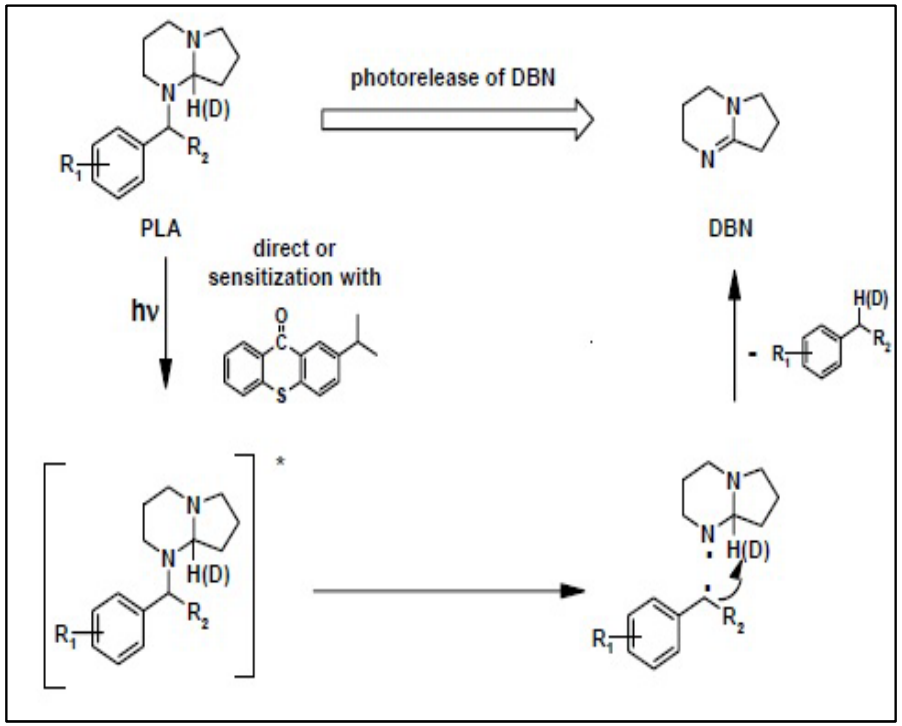

Fig. 3 : Photo-release of DBN from N-benzylated precursors

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

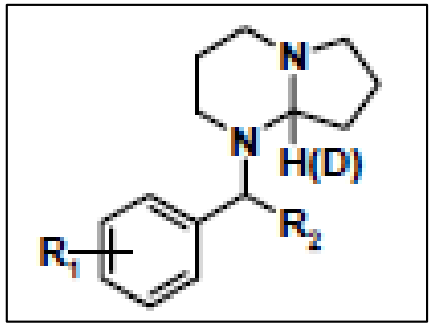

Fig. 4 : Generic Structure of CGI – 90 obtained from BASF

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

Table 1: Reaction Summary for the 3 reactions.

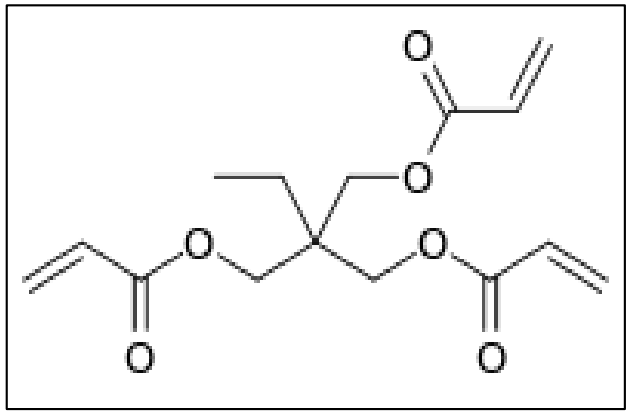

Fig. 5: TMPTA structure

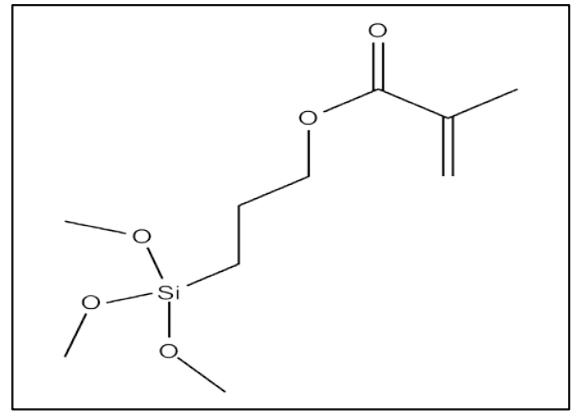

Fig. 6 : Gelest 6487 structure

METHODS

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

Raw Material	Composition 1	Composition 2	Composition 3
Ebecryl 860	100 %	75 %	65 %
Gelest 6487	0 %	25 %	35 %

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

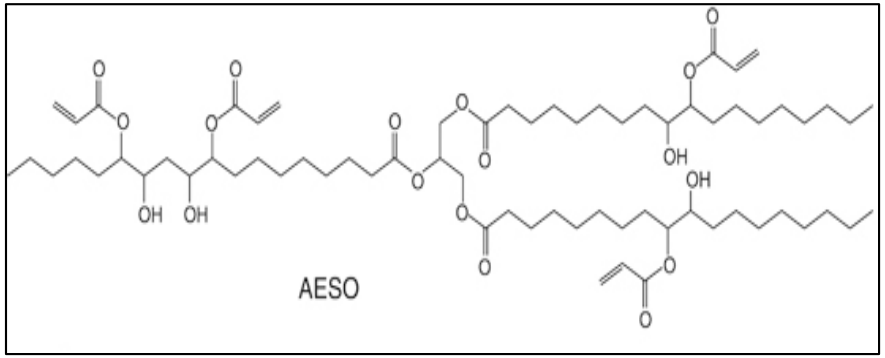

Fig. 7 : Ebecryl 860 structure

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

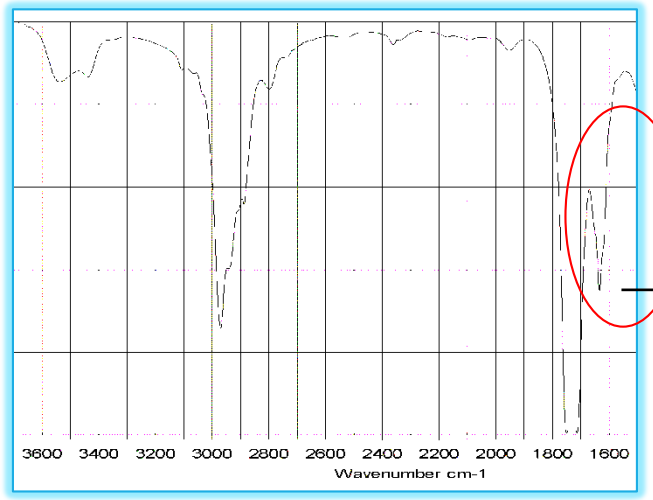

Fig. 8 : FTIR analysis (uncured)

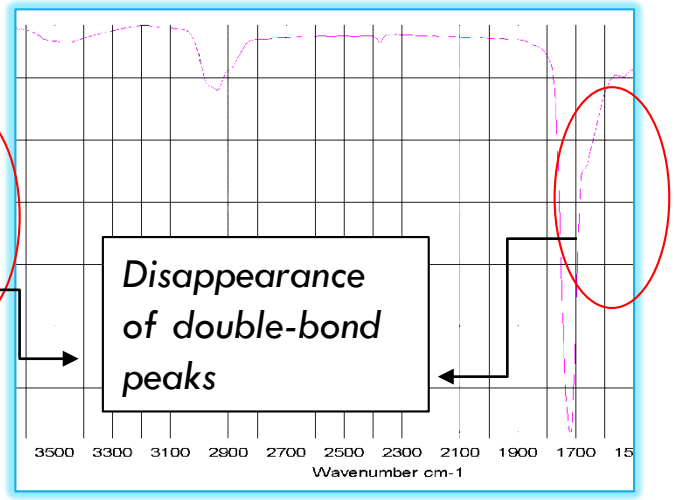

Fig. 9 : FTIR-ATR Analysis (cured)

- 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.

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

Peak Broadening Confirms silane-to siloxane formation (sol-gel reaction)

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

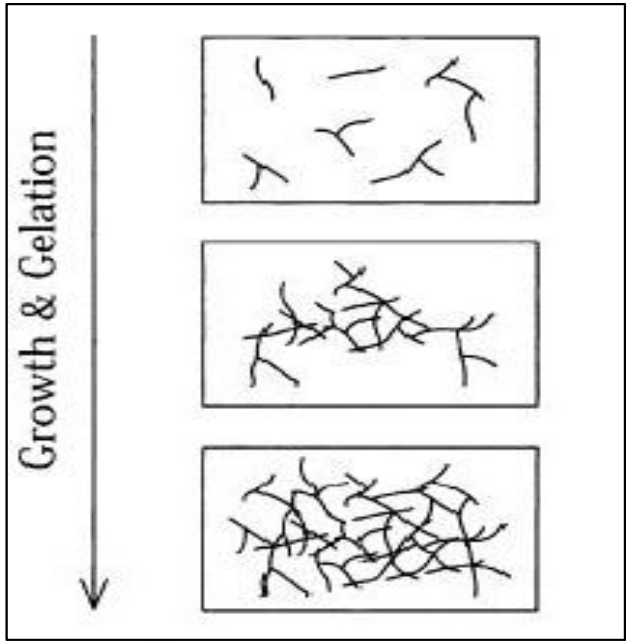

Fig. 11 : Sol-Gel process depicting growth and gelation

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

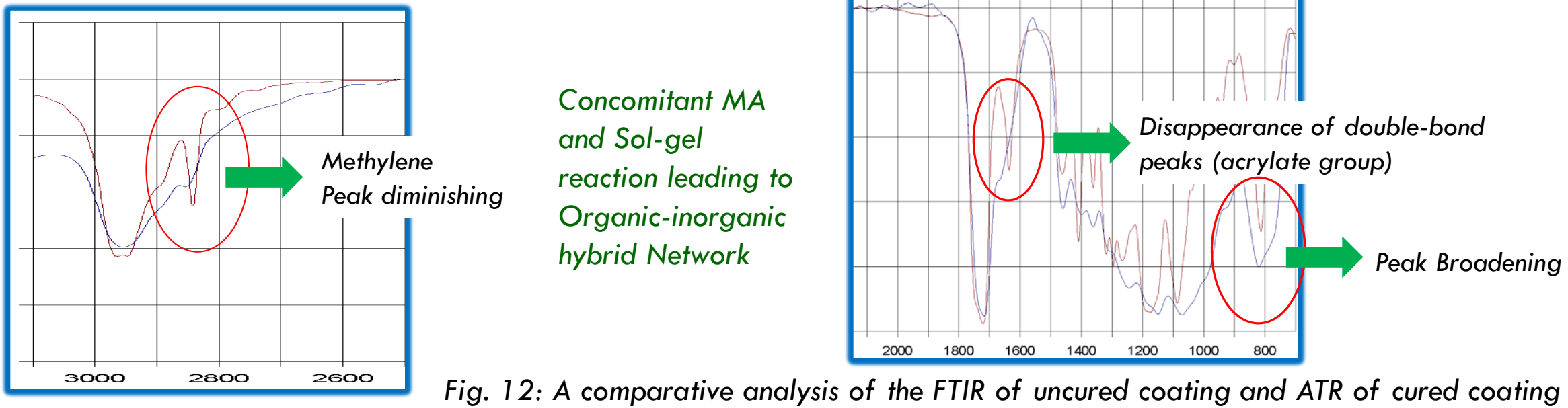

Fig. 12: A comparative analysis of the FTIR of uncured coating and ATR of cured coating

RESULTS AND DISCUSSION

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

Composition No.	1	2	3
Conical Mandrel	Failed	Passed	Passed
Pencil Hardness	3 H	6 H	6 H
Pendulum Hardness	23	27	35
Impact Resistance	40	100	80

Table 3 : Test Results performed for 3 coating compositions

RESULTS AND DISCUSSION

- **DSC Analysis :**

Composition No.	Tg
1	113.13 ° C
2	160.52 ° C
3	166.2 ° C

Increasing

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

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

- **TGA Analysis :**

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

Composition No.	1	2	3
Decomposition Peaks	T = 270.09 ° C T = 436.45 ° C	T = 276.66 ° C T = 452.87 ° C	T = 271.78 ° C T = 448.16 ° C
Residue Percentage	8.46%	11.50%	13.37%

Increasing

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

ACKNOWLEDGEMENTS

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