# Super Photo-base initiated organic-inorganic hybrid coatings by plural-cure mechanism

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**Abstract:**

Free Radical polymerisation forms the core chemistry of a majority of UV curable coatings produced today. Rapid curing at ambient temperatures using stable, single pack coating systems form the key value proposition that such coatings offer. However, owing to their limitations such as oxygen inhibition, shrinkage, toxicity profiles of reactive diluents (RD), and the limited chemistry available, efforts are being made to counter these challenges by innovating and exploring new systems that have the potential to replace the existing chemistries. Anionic polymerisation is one such promising area that has the potential to introduce a wide variety of chemistries in the field of UV curable coatings. A significant stride in this field has been the innovation of photo-labile bases in the UV industry and the diverse chemistries that these bases have brought to fore.

The primary focus of this study is to employ a super photo-base generator (PBG) in catalysing concomitant but independent reactions to develop organic-inorganic hybrid (OIH) coating networks by leveraging plural-cure chemistry. The super PBG has been used to initiate both Michael-addition (MA) reaction and sol-gel reaction concurrently, upon exposure to the UV source. Coatings have been formulated using uniquely designed acrylic oligomers (MA-acceptor), acetoacetate functional reactive diluents (MA-donors) and organo-silanes (sol-gel precursors), besides super PBG. The study highlights many technical and environmental benefits of these OIH coatings with potential for applications in advanced coatings and additive manufacturing.

**Introduction:**

The drive to make VOC-free coatings has paved the way for new coating technologies such as waterborne, powder coatings, UV-cure coatings etc. UV cure coatings present a striking balance of opportunities and challenges, with efforts being made each year to come up with innovative solutions to offset the latter while at the same time maintaining or improving the former. While rapid curing at ambient temperature forms the single-most important advantage these coatings offer, the phenomenon of oxygen inhibition, shrinkage, poor adhesion and the inherent inability to cure thicker films limit the out-reach of UV–curable coatings as compared to other coating systems. While several approaches are being developed to deal with these issues, a satisfactory approach eliminating all these challenges is yet to be found [1-3].

A novel approach to offset these limitations has been found by exploiting chemistries that form cross-linked networks using photo-triggered base catalysed reactions instead of photo-induced free-radical polymerisation. The mechanism of base-catalysed polymerisation eliminates the usage of free-radicals by using anions and therefore, the problem of oxygen inhibition is directly solved [2-5]. Efforts are being made to use such chemistries and contain problems such as high shrinkage and poor adhesion to metals. The photo-latent base (PLB) catalysts that have lately been developed for use in the UV curing industry use tertiary amines that are modified with alkyl or benzyl groups. Sufficient literature on photo-latent primary amines is available too, however, they find limited usage in catalysing addition/condensation reactions. Crosslinking reactions requiring amines of higher basicity than tertiary amines use amidines such as DBU (1, 5-diazabicyclo [4.3.0] undec-5-ene) and DBN (1, 5-diazabicyclo [4.3.0] non-5-ene). These bases are known to have basicity of a magnitude of 12-13 [4, 5]. The use of these bases as photolatent precursors was initially made possible through the use of their corresponding ketoprofen salts. But owing to their insufficient stability, the research is now underway to come up with non-ionic photo-base generators that release DBN or DBU upon UV exposure [2-6].
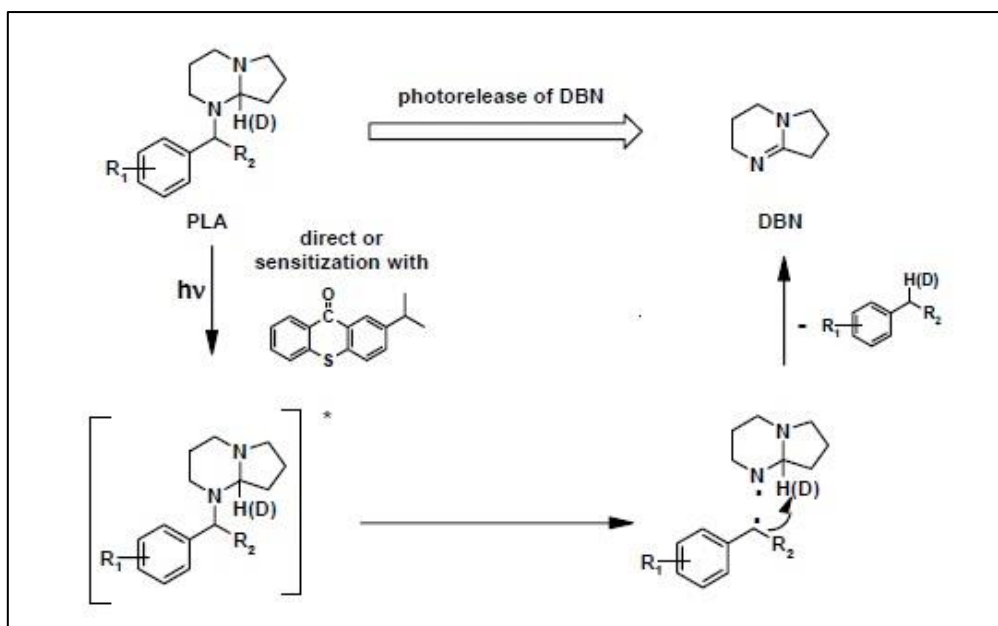
*Fig. 1: Photo-release of DBN from N-benzylated precursors [3].*

The research in the field of PBGs has brought to light the chemistry of Michael Addition reaction (MA). MA is the reaction between a nucleophile and an active double bond group [7]. There are many variations to this chemistry but the reaction between a β-keto ester and an acrylate double bond catalysed by a strong base is of particular interest as the crosslinked network formed is built on carbon-carbon bonds and therefore, the cured material has outstanding stability [4]. A general reaction scheme for the MA reaction mechanism is shown in Figure 2. MA has been extensively used to produce crosslinked networks in very short times. However, this advantage of producing networks in short times also frequently limits their applications due to very short pot life. The use of PLBs for photo-catalysing MA can help fix this problem and single-component formulations with acceptable shelf-life can be developed [2].
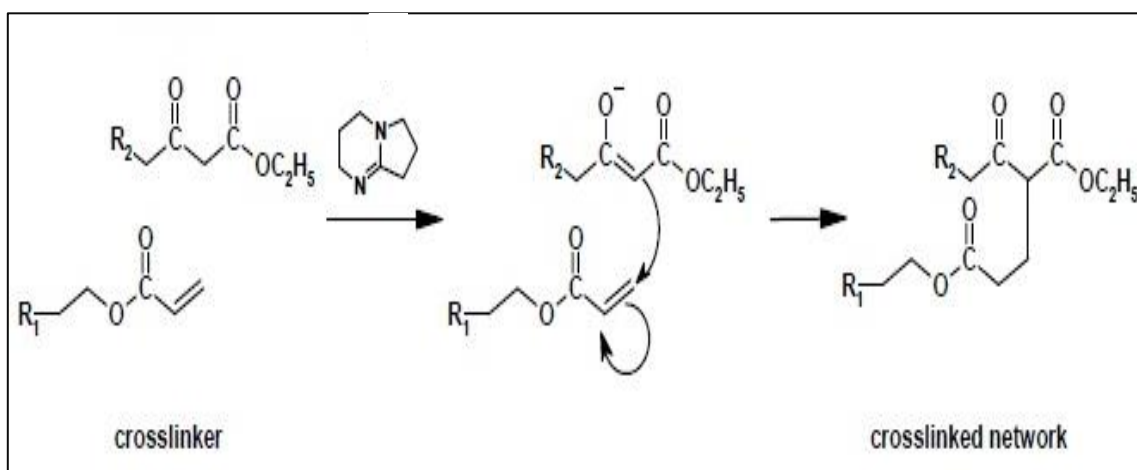


*Fig. 2: Michael Addition (MA) Reaction Mechanism [2].*

In the recent years, development of organic-inorganic hybrid (OIH) materials for improving thermo-mechanical properties has been established as a promising route. By controlling organic and inorganic domains at molecular level, it is possible to effectively manipulate properties of OIH materials. The mechanical properties of the coatings formed using MA can be further enhanced by incorporating suitable inorganic domains into the network such that a hybrid interconnected network can be formed. Previously, there have been attempts to do the same [5]. However, the toughness of the cured coating can be improved if the organic-inorganic components are joined by covalent bonds.

Base catalysed sol-gel chemistry presents a viable scheme that can be put to use where the photo-triggered base would also catalyse addition and condensation reactions of the silane groups. The choice of resins can be used to tailor the properties the cured coating exhibits based on the type and proportion of organic/inorganic components.

In this work, we have investigated a system that can undergo MA and sol-gel reactions upon UV exposure. The initial part of our research focused on determining the validity of MA and sol-gel chemistry in different, independent setups in presence of a suitable PLB. We observed very high extent of these reactions, when MA and sol-gel components were used alone as well as in combination. Building on to these encouraging results, we designed innovative coatings that combined both MA and sol-gel chemistry, while completely eliminating conventional acrylate type RDs. Furthermore, such compositions required only single UV-trigger for complete cross-linking. A series of coatings with increasing inorganic content were cured and tested for any improvement in mechanical properties. The results so obtained highlight many technical benefits of these coating systems with a potential for commercial exploitation in advanced coatings, adhesives, inks and additive manufacturing. Additionally, as an extension of this concept for eliminating conventional acrylate type RDs, the effectiveness of the newly synthesised resins in reducing viscosity was compared with the reduction in viscosity observed with the conventional acrylate type RDs.
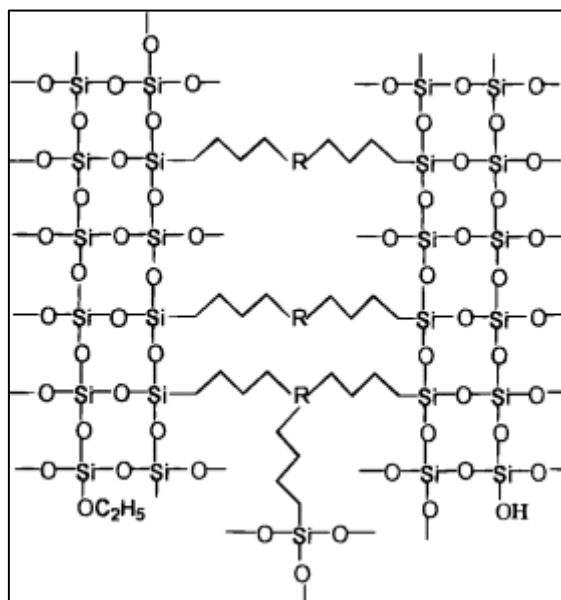


*Fig. 3: A typical Organic-Inorganic Hybrid (OIH) network [8].*

**Materials and Methods:**

**A. Materials:**

T-butyl acetoacetate (t-BAA) (CAS Number: 1694-31-1) was obtained from Eastman Chemical Company. This compound was used to synthesise acetoacetate based resins. Trimethylolpropane Triacrylate (TMPTA), 1, 6 – Hexanediol Diacrylate (HDDA), Dipropylene Glycol Diacrylate (DPGDA) and Pentaerythritol Triacrylate (PETIA) were obtained from Allnex Inc. Ebecryl 8402 (aliphatic urethane acrylate) and Ebecryl 854 (polyester acrylate) were obtained from Allnex Inc. and these acrylates were used for viscosity measurements. 1, 1, 1 – Tris (hydroxymethyl) propane (TMP) (CAS Number – 77-99-6), 1, 6-Hexane Diol (HD) (CAS Number – 629-11-8), Pentaerythritol (PET) (CAS Number – 115-77-5) and Dipropylene Glycol (DPG) (CAS Number – 25265-71-8) were obtained from Sigma Aldrich and these alcohols were used to synthesise acetoacetate based resins. Gelest 6487, obtained from Gelest, USA, is the trade-name for methacryloxypropyltriethoxysilane (CAS Number: 21142-29-0) and was used as a source of silane functional groups. Desmodur N3800 (obtained from Covestro) is an aliphatic polyisocyanate and it was used in the synthesis of urethane acrylate. 2-Hydroxyethyl acrylate (CAS Number: 818-61-1) was obtained from Sigma Aldrich and was used in the

synthesis of urethane acrylate. Dibutyltin Dilaurate (DBTDL) (CAS Number: 77-58-7) was the catalyst used for urethane acrylate synthesis and was obtained from Sigma Aldrich. CGI – 90® is a PBG provided by BASF. 2-isopropylthioxanthone (ITX) (CAS Number: 5495-84-1) is photo-synergist used in conjunction with CGI - 90®. Acetone was obtained from Sigma Aldrich. Thin Cold-Rolled steel panels (3 x 6 x 0.020 ") were obtained from ACS. All commercial products were used as received without further purification.

## B. Methods:

The uncured coating compositions were subjected to infrared spectroscopy using Bruker-Tensor 27 FTIR spectrometer using NaCl pellets. The cured coating compositions were characterised using Bruker Hyperion ATR analyser. All coating compositions were applied on thin cold-rolled steel panels using a draw-down applicator at a wet-film thickness of 1 mill (25 microns). All coated panels were passed through UV–curing equipment (Fusion UV with a H-bulb) at a belt speed of 12 ft./minute for a total of 3 passes. The acrylate peak consumption was done by peak intensity ratio analysis where the analysis was made using the spectrums obtained through FTIR and ATR. The carbonyl peaks at 1725 cm$^{-1}$ (uncured composition) and 1715 cm$^{-1}$ (cured composition) were used as reference peaks for normalization of acrylate and acetoacetate peak results [9, 10].

$$[\% \text{ Acrylate Conversion}] = (1 – (A_t/A_o)) * 100 \tag{1}$$

$$[\% \text{ Acetoacetate Conversion}] = (1 – (A'_t/A'_o)) * 100 \tag{2}$$

Where A and A' represent the normalized intensity of the acrylate and the acetoacetate peaks respectively and the subscripts $t$ and $o$ indicate the curing time and the beginning of the curing, respectively.

The acrylate consumption was tracked and calculated using the peak at 810 cm$^{-1}$ and the acetoacetate consumption (depletion of active methylene group in β-keto ester) was tracked and calculated using the peak at 1410 cm$^{-1}$ [10]. For validating the sol-gel chemistry (silane conversion to siloxane), the broadening of peak for Si-O-C linkage to Si-O-Si linkage (between 1050 cm$^{-1}$ to 1110 cm$^{-1}$) was analysed [9]. Coating compositions involving MA chemistry alone were stored at room temperature (25 ° C) for 24 hrs. after curing and were then subjected to ATR analysis. Coating compositions involving sol-gel chemistry were stored at room temperature for 72 hrs. after curing and were then subjected to ATR analysis. The mechanical properties of the coatings formed were characterised using ASTM standards such as Pendulum Hardness (ASTM- D-4366-16), Impact Resistance (ASTM D - 2794 – 99), MEK Double Rub Test (ASTM D – 4752-98) and Cross-Cut Adhesion Test (ASTM D3359-07). The measurement of viscosity was done using Brookfield's CAP 2000+ viscometer at 25 ° C and at an RPM of 50 using Spindle No. 1. (ASTM D4287).


**Experimental:**

**A. Synthesis of Acetoacetate Functional compounds:**

Four acetoacetate functional compounds were synthesised separately by condensation of multi-functional alcohols TMP (f = 3), HD (f = 2), DPG (f=2) and PET (f=4) and the acetoacetate functionality was introduced using t-BAA. Stoichiometric amounts of the multi-functional alcohols and t-BAA were added in separate 3-neck round bottom flasks and the reactions were carried at a temperature of 130 ° C for 3 hrs. under constant stirring. T-butanol was obtained as a by-product and no catalysts were required. The products obtained were then subjected to vacuum distillation to remove the leftover t-butanol and the percentage yield was calculated. The four acetoacetate-functional compounds were named as TMP-AA, HD-AA, DPG-AA and PET-AA for alcohols TMP, HD, DPG and PET respectively [11, 12].

*Table 1: Brief summary of the composition of the reactants and products used for synthesising acetoacetate based compounds*

|  | Alcohol (in g) | t-BAA (in g) | Weight of Product (in g) | Equivalent weight* of product formed (in g) |
|---|---|---|---|---|
| TMP – AA | TMP – 30.54 | 120.00 | 100.62 | 131.65 |
| HD – AA | HD – 36.62 | 108.96 | 102.71 | 144.70 |
| DPG-AA | DPG – 39.82 | 104.20 | 105.56 | 151.96 |
| PET-AA | PET – 25.07 | 129.52 | 100.98 | 122.19 |

*Active hydrogen equivalent weight for MA reaction.*

## B. Synthesis of Urethane Acrylate:

In a 3-neck round bottom flask, 21.64 g (0.186 equivalents) of 2-HEA was placed along with 0.03 g of DBTDL. The flask was then connected to a mechanical stirrer, thermocouple and nitrogen purging inlet. In a dropping funnel, 78.36 g (0.205 equivalents) of Desmodur N-3800 and 50 g of THF was added. The temperature of the flask was maintained between 60 – 70 ° C and the isocyanate solution was added gradually over a time of 2 hours such that the temperature remained between 60 – 70 ° C. After all isocyanate was added, the reactive mixture was stirred at 60 ° C for half-an hour after which a sample from the reactive mixture was tested for %NCO content using ASTM D2572 – 97. The reactive mixture was then kept at 25 ° C overnight for the residual NCO groups to react with OH groups. A sample of the resin formed was procured again and tested for %NCO content. The equivalent weight of the resin (pure) formed was determined to be 498 g [13].

## C. Preparation of Coatings:

Following is a brief summary of the coating compositions that were prepared and characterized: -

*Table 2: Summary of the coating compositions.*

| Part – 1 | | | | | | |
|---|---|---|---|---|---|---|
|  | TMPTA (in g) | TMP – AA (in g) | Gelest 6487 (in g) | CGI – 90 (in g) | ITX (in g) | Acetone (in g) |
| C–1 | 3.89 | 5.45 | - | 0.37 | 0.09 | 1.49 |
| C–2 | - | - | 4.14 | 0.16 | 0.04 | 0.66 |
| C–3 | 1.58 | 4.41 | 4.00 | 0.40 | 0.10 | 1.60 |
| Part – 2 | | | | | | |
|  | UA (in g) | TMP – AA (in g) | Gelest 6487 (in g) | CGI – 90 (in g) | ITX (in g) | Acetone (in g) |
| OIH-0 | 3.97 | 1.02 | - | 0.15 | 0.037 | 0.60 |
| OIH-5 | 3.77 | 0.97 | 0.25 | 0.15 | 0.037 | 0.60 |
| OIH-10 | 3.57 | 0.92 | 0.50 | 0.15 | 0.037 | 0.60 |
| OIH-15 | 3.37 | 0.87 | 0.75 | 0.15 | 0.037 | 0.60 |
| Part – 3 | | | | | | |
|  | UA (in g) | TMPTA (in g) | Gelest 6487 (in g) | CGI – 90 (in g) | ITX (in g) | Acetone (in g) |
| C-4 | 3.97 | 1.02 | - | 0.15 | 0.037 | 0.60 |

**D. Resin Systems – Viscosity Reduction:**

For each urethane and polyester acrylate, varying amounts of acetoacetate based and acrylate based RDs were added to 2 g of resin (Ebecryl 8402 and Ebecryl 854). The samples so prepared were then subjected to viscosity measurement using the cone and plate viscometer (CAP 2000+). Following is a brief summary of the resin systems prepared for the measurement:

*Table 3: Summary of the compositions of resin systems used for viscosity reduction analysis.*

| | Resin : Ebecryl 8402 (Urethane Acrylate) (2 g) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | HDDA (in g) | HD-AA (in g) | DPGDA (in g) | DPG-AA (in g) | TMPTA (in g) | TMP-AA (in g) | PETIA (in g) | PET-AA (in g) |
| 15% | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 |
| 20% | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| 25% | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 |
| 30% | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 |
| 35% | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 |
| 40% | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 |
| | Resin : Ebecryl 854 (Polyester Acrylate) (2 g) | | | | | | | |
| | HDDA (in g) | HD-AA (in g) | DPGDA (in g) | DPG-AA (in g) | TMPTA (in g) | TMP-AA (in g) | PETIA (in g) | PET-AA (in g) |
| 15% | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 |
| 20% | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| 25% | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 | 0.67 |
| 30% | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 |
| 35% | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 | 1.08 |
| 40% | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 |

**Results and Discussion:**

**A. Plural – Cure System Design:**

In order to establish the feasibility and appreciable extent of UV- triggered MA as well as sol-gel reactions, some experimental work was carried out wherein these reactions were studied separately. Part–1 of the Table-2 contains three coating compositions. Sample C–1 has been prepared to investigate the feasibility of MA between acetoacetate groups and acrylate groups in the presence of CGI – 90 (after UV curing). Therefore, sample C–1 doesn't contain any silane functional groups. C–2 has been prepared to investigate the feasibility of sol-gel reaction in the presence of CGI – 90 (after UV curing). Sample C–3 contains functional groups for both MA as well as sol-gel chemistry. This composition was prepared, cured and characterized to investigate whether MA and Sol-Gel can occur concomitantly but independently with each other in the presence of CGI – 90 (after curing). Thus, sample C–3 cures by dual cure mechanism where the super base released by CGI – 90 upon its UV induced photolysis initiates MA and catalyses the hydrolysis and condensation of the silane groups to form siloxane linkages. For all compositions in part-1, TMPTA has been used a source for acrylate groups and TMP- AA, synthesised in our laboratory, has been used as the source for acetoacetate groups. It is also worthwhile to note that the Gelest 6487 also contributes to the methacrylate group and the stoichiometry of all these compositions has been calculated keeping that into consideration. The percentage dose of CGI – 90 for these compositions has been chosen to be 3% of the resin weight. The number has been decided based on preliminary tests for different concentrations along with some literature articles backing the same. ITX has been added as a photo-sensitizer to enhance the efficiency of CGI – 90. The ratio of CGI – 90 to ITX has been fixed at 4 : 1 for maximum efficiency [2]. Acetone has been used in minimal amounts to dissolve CGI – 90 and ITX and form a solution.

Part – 2 of the Table-2 contains four coating compositions. For all compositions in Part-2, the urethane acrylate (UA) synthesised in our laboratory has been used. After validation of MA and Sol-Gel chemistries using model reactants and CGI-90, a UA comparable in molecular weight to those used in commercial UV cure application was synthesised. UA chemistry was chosen in keeping with their high viscosities so that the effect of acetoacetate type reactive diluents can be adequately assessed. OIH-0, OIH-5, OIH-10 and OIH-15 have been formulated such that the silane content varies as 0%, 5%, 10% and 15% (by mass), respectively. Therefore, OIH-0 would only have MA chemistry and OIH-5, OIH-10 and OIH-15 would have both MA and Sol-Gel chemistries during or after UV-exposure. These OIH films have been studied to measure the changes in film properties as a function of silane content.

Part-3 of Table-2 contains a coating composition that has only acrylate groups and has been designed to assess the extent of acrylate conversion using CGI–90. The percentage of TMPTA in C-4 is the same as the percentage of TMP-AA in OIH-0. Since the conventional UV–curable coatings contain a low-molecular weight acrylate as a reactive diluent (e.g. TMPTA ), it is important to compare cured films based on solely acrylate chemistry with those containing MA and sol-gel chemistries, in addition to acrylate chemistry. This would clearly provide insights into the role of each component and how these chemistries can be manipulated to optimize performance of their films. Another important rationale for studying sample C-4 is to demonstrate how a photo-base generator can be used to cure an acrylate composition. Most of the photo-initiators used today rely on free-radical mechanism, which brings its own set of disadvantages. CGI–90 releases a super base DBN upon UV irradiation which brings about curing of acrylate groups via anionic polymerisation. [16]

In a coatings containing acrylates and acetoacetate functional components, the super-base DBN released upon irradiation of UV will initiate or catalyse two competitive cure reactions. These are the MA reaction between acrylates and acetoacetate groups and anionic polymerization of acrylate groups. In order to investigate what reaction takes precedence over the other, the cure characterization has been studied by tracking both acrylate as well as the acetoacetate groups before and after UV-curing. It is important to note that while the depletion of acetoacetate groups directly points to the extent of MA reaction, the acrylate group depletion points to the extent of both MA as well as the acrylate polymerisation of acrylates. By subtracting the extent of MA from the % conversion of acrylate groups, the extent of anionic polymerisation of acrylate groups can be estimated.

The use of organo-silane compound Gelest 6487 adds a new dimension to the coating compositions. Gelest 6487 has two functional groups- (meth)acrylate group and the silane group. Both these groups are bound together with a chain of 3 carbon-carbon covalent bonds. Therefore, after UV curing, the (meth)acrylate group would become a part of the organic network and the silane groups would self-condense via siloxane linkages forming inorganic domains within cured coating network. Thus, the organic-inorganic sub-networks would be interwoven by carbon-carbon covalent bonds, adding greater toughness and resilience to the otherwise organic-inorganic networks that are bonded together by relatively weaker forces of attraction such as dispersion forces, dipole-dipole interactions etc.

**B. Cure Study:**

FT-IR spectra of coatings before and after UV exposure have been acquired to determine type of cure reaction and using peak intensity ratio method, the extent of reactions have been calculated. A comparison of the IR spectrum (Fig. 4) of C–1 before and after curing clearly indicates that acrylate groups (810 cm$^{-1}$) and the acetoacetate groups (1410 cm$^{-1}$) have depleted. This validates that MA reaction does occur. A peak intensity ratio analysis of the two spectra indicated that while acetoacetate depletion was around 77%, the acrylate depletion was around 93.78%. This data clearly suggests that MA takes precedence over acrylate anionic polymerisation when the functional groups for both reactions are present. It is also worthwhile to note that cured films of sample C-1 were hard-to-touch with no signs of tackiness when examined immediately after UV-exposure. Comparison of the IR spectra of sample C–2 before and after curing showed broadening of the peak at 1080 cm$^{-1}$. The peak broadening validates that CGI – 90 is a suitable PBG that can also catalyse sol-gel reactions. Based on the spectrums obtained for samples C–1 and C–2, the comparison for C–3

details the changes observed in the IR spectra for both C–1 and C–2 combined. Therefore, it can be safely concluded that CGI – 90 is an effective PBG that can initiate and catalyse both MA and sol-gel reactions concomitantly but independently. An additional observation that can be of significance is the time the films take to reach the *Dry-to-Hard* stage. While sample C–1 cures to form a solid film instantly after UV irradiation curing, C–2 takes approximately 48 hours at room temperature to form a dry hard film. C–3, though curing by plural-cure mechanism, forms a dry hard film in about 3-4 hours.
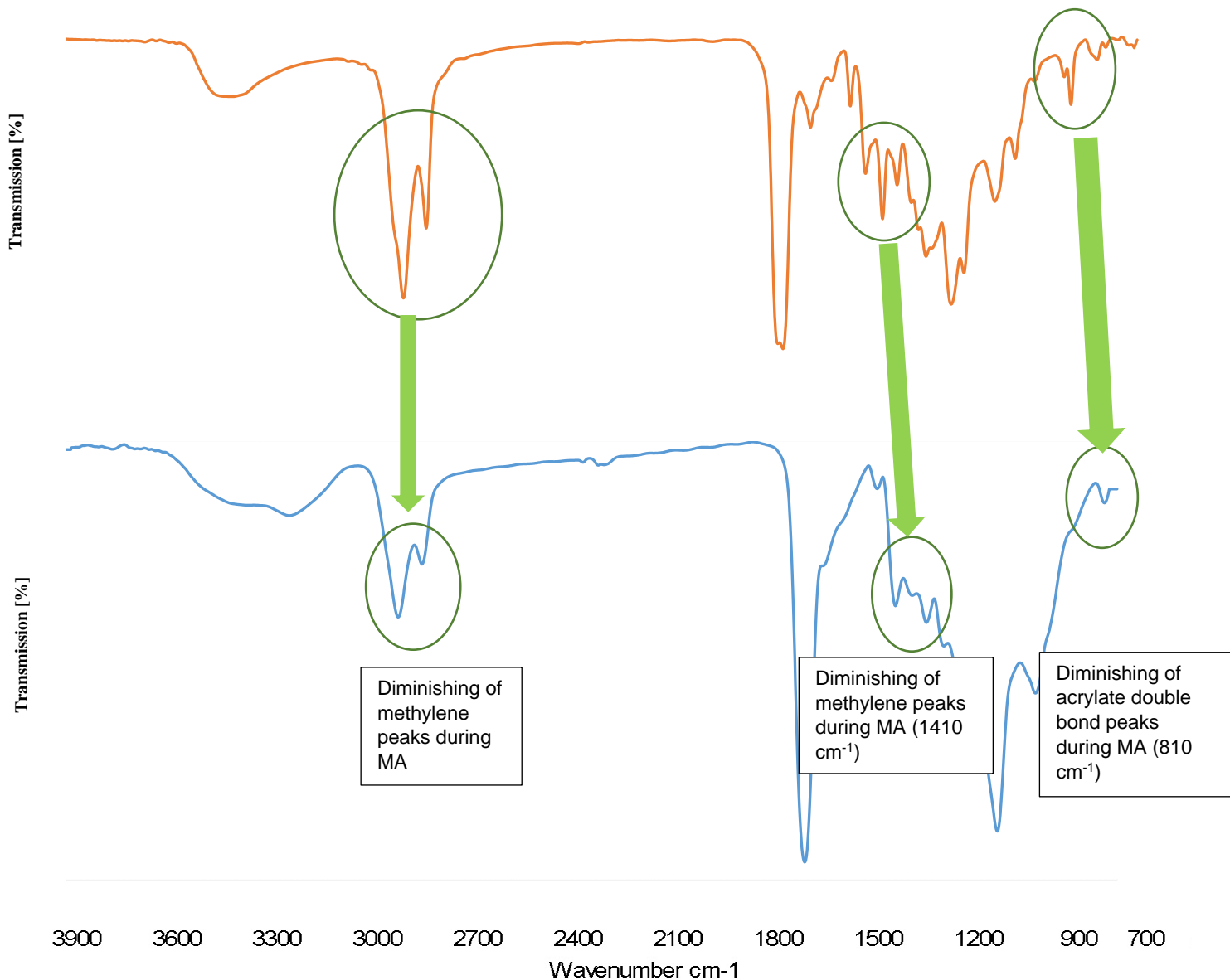


*Fig. 4: A comparison of the IR spectrums of C–1 before (above) and after (below) cure. The disappearance of methylene peaks suggest acetoacetate depletion and acrylate double bond peaks suggest acrylate depletion. The depletion has been observed and calculated with respect to the carbonyl peak between 1715-1725 cm$^{-1}$ (reference peak).*

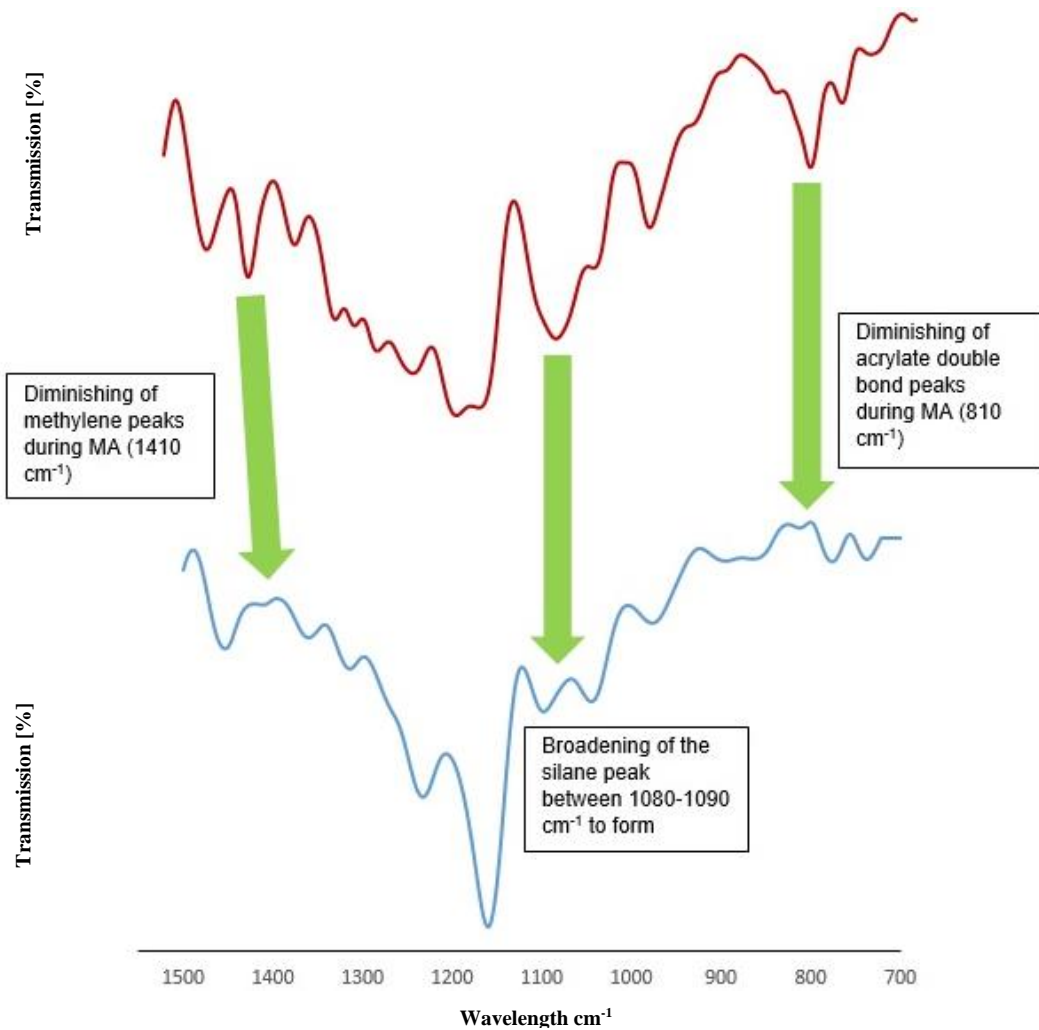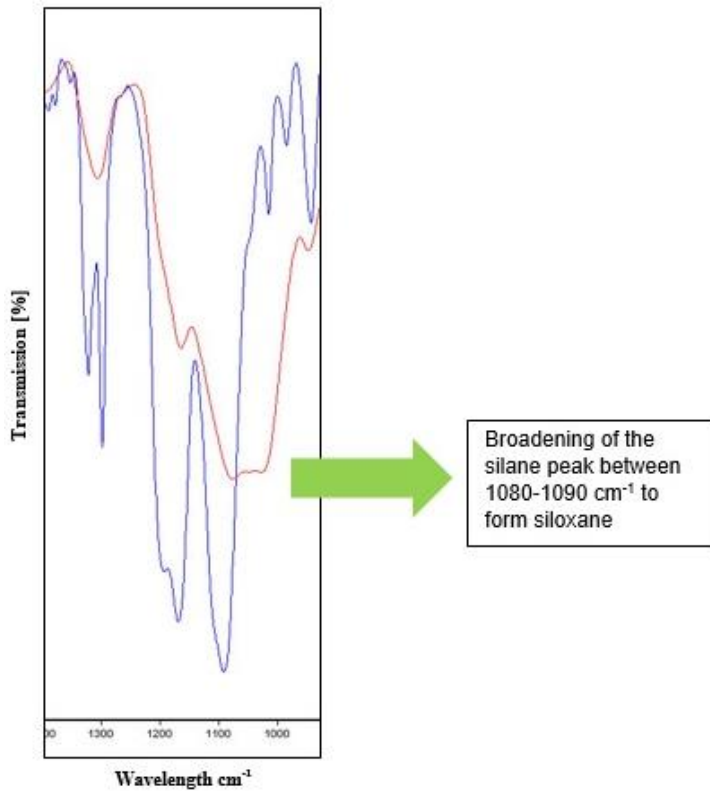*(Right) Fig. 5: A comparison of the IR spectrums obtained for C–2 before (blue) and after (red) cure.*

Broadening of the silane peak between 1080-1090 cm⁻¹ to form siloxane

Diminishing of methylene peaks during MA (1410 cm⁻¹)

Diminishing of acrylate double bond peaks during MA (810 cm⁻¹)

Broadening of the silane peak between 1080-1090 cm⁻¹ to form

*Fig. 6: A comparative analysis of the IR spectrums for C–3 before (red) and after (blue) cure.*

Table-4 shows an analysis of the peak-intensity ratios for OIH-0, OIH-5, OIH-10 and OIH-15.

*Table 4: Percentage conversion of acetoacetate and acrylate groups after UV curing for coating compositions OIH-0, OIH-5, OIH-10, OIH-15 and C-4. (UV-Dose: Belt Speed-12 ft./min., H-Lamp 1-mil Wet Film Thickness, 3 passes)*

|  | OIH-0 | OIH-10 | OIH-10 | OIH-15 | C-4 |
|---|---|---|---|---|---|
| % acetoacetate conversion | 79.45 % | 87.7% | 88.5 % | 87.13 % | - |
| % acrylate conversion | 83.3 % | 100 % | 94.17 % | 87.45 % | 65.36 % |

The analysis of the above results clearly reinforces our previous assertion that MA takes precedence over acrylate polymerization and the overall extent of reaction shows that both acetoacetate and acrylate group depletion is fairly high with little residual groups in the film. This is an important observation as residual functional groups may have serious repercussions on the long-term durability of the film. Table-5 shows some primary film properties of OIH coatings as a function of silane content.

*Table 5: Characterization results for the mechanical properties of cured films for OIH-0, OIH–5, OIH-10, OIH-15 and C-4. (UV-Dose: Belt Speed-12 ft./min., H-Lamp, 1-mil Wet Film Thickness, 3 passes)*

|  | OIH-0 | OIH-5 | OIH-10 | OIH-15 | C–4 |
|---|---|---|---|---|---|
| MEK Double Rubs | 20 | 107 | 172 | 200 | 32 |
| Pendulum Hardness | 17 | 19 | 25 | 28 | 114 |
| Impact Resistance ( lbs. x inch ) | 140 | 140 | 140 | 140 | 140 |
| Cross-Cut Adhesion | 0 B | 0 B | 0 B | 0 B | 0 B |

As can be seen, increasing silane content increases hardness and solvent resistance (MEK-double rub test) of the films, suggesting that increasing inorganic content leads to the films with improved hardness and crosslinking density. The overall improvement in mechanical and solvent resistance properties can be attributed to the formation of organic-inorganic network. This OIH network can be viewed as nano-composite film wherein dense silica domains (inorganic) are covalently bonded and uniformly distributed into a relatively flexible polyurethane matrix (organic). Increase in hardness in samples OIH-0 through OIH-15 can be attributed to increase in hard silica domains, as a result of increasing silane content from 0% to 15%. Furthermore, increase in solvent-resistance of these samples, which is a measure of cross-link density, is clearly due to increase in silica domains (highly cross-lined network). Very poor solvent resistance for sample C-4 is due to absence of silica domains.

A comparison of the solvent resistance for C-4 and OIH-0 indicates that both the acetoacetate and acrylate groups lead to nearly similar cross-link density. However, significantly higher pendulum hardness of sample C-4 compared to OIH-0, can be attributed to the absence of acetoacetate moiety in C-4. Acetoacetate moiety, connected to the coating matrix from one point with two dangling ends is expected to provide increased flexibility and lower hardness. Relatively lower hardness of all OIH samples compared to sample C-4, can be attributed to this structural feature of coatings.

Results for impact resistance test provide very interesting information. All the OIH samples, despite of significant increase in their crosslink densities and moderate increase in hardness, show almost identical and high impact resistance. This might be due to the reinforcing effect of silica domains to the urethane matrix providing high toughness. Higher toughness all the films studied, in general, is also due to the presence of urethane structure that is known for high toughness.

**C. Viscosity Study- Efficiency of Reactive Diluents:**

In order to assess the effectiveness of acetoacetate type reactive diluents for their viscosity reduction efficiency, viscosity profiles of compositions containing four different acetoacetate type RDs were compared relative to their conventional acrylate type RD counterparts. Furthermore such study was done using two different oligomer types – aliphatic urethane acrylate (Ebecryl 8402) and polyester acrylate (Ebecryl 854). Figure 7 and 8 highlight the changes in viscosity of these systems with different RDs in varying percentages, ranging from 15% to 40%. The curves with solid colored markers represent acrylate-based RDs and the those with white markers represent acetoacetate-based RDs.
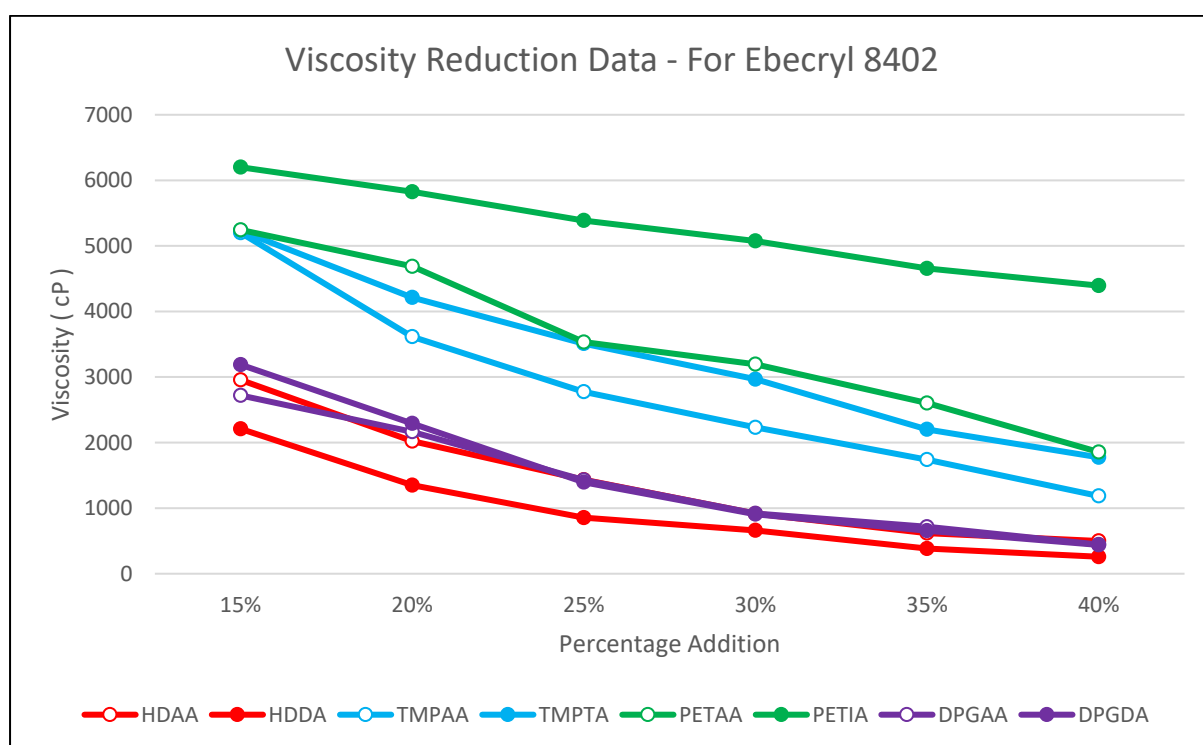


*Fig. 7: Viscosity Reduction Data recorded for Ebecryl 8402 and the RDs based on acetoacetate and acrylate moieties. The measurements were done using CAP 2000+ at 25 ° C.*

For Ebecryl 8402 (Fig.7), the acetoacetate-based RDs (TMP-AA and PET-AA) perform better in reducing viscosity than their corresponding acrylate-based RDs, with the PET-AA being a far better RD than PETIA. A closer look at the curve for DPG-AA and DPGDA shows that both RDs have nearly the same viscosity reduction for almost entire range studied, For HDDA and HD-AA, HDDA appears to be a slightly better contender than HD-AA for viscosity reduction. However, the difference in the measured viscosities is not so great to rule out its usage for commercial purposes. Additionally, at higher percentage additions (greater than 30%), the curves for both these RDs converge to even smaller differences in viscosities.
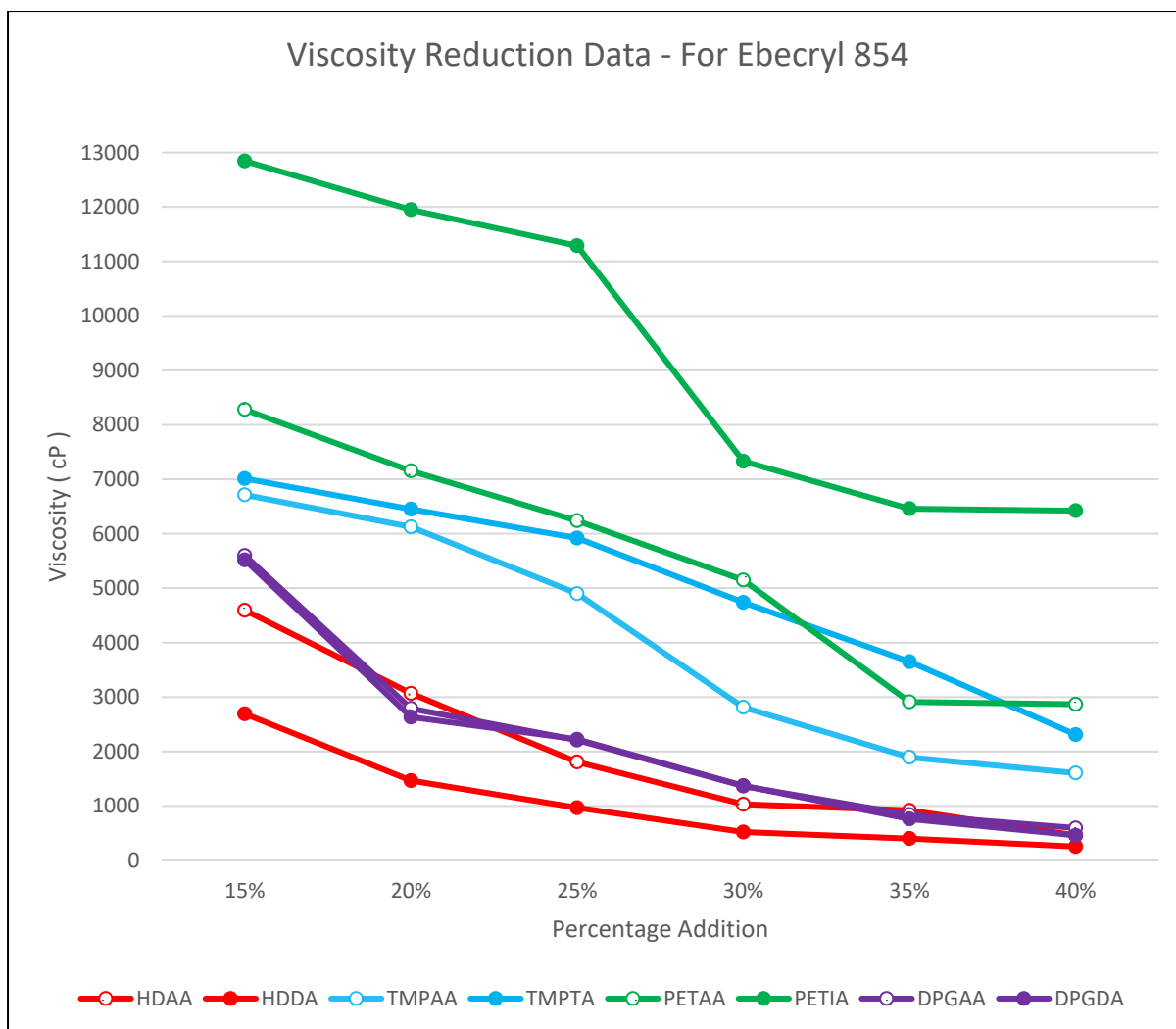
*Fig. 8: Viscosity Reduction Data recorded for Ebecryl 854 and the RDs based on acetoacetate and acrylate moieties. The measurements were done using CAP 2000+ at 25 ° C.*

For Ebecryl 854 (Fig.8), results similar to those obtained for Ebecryl 8402 have been observed. While the difference between the measured viscosities for PET-AA and PETIA, and TMP-AA and TMPTA are higher than in the case of Ebecryl 8402, the trend observed for HD-based and DPG-based RDs is almost the same. Thus, the viscosity study clearly indicates that acetoacetate type RDs are effective in viscosity reduction of oligomers and hence can replace corresponding acrylate type ones in coating formulations.

**Conclusion:**

Super Photo-base (CGI-90) can successfully be used to trigger Michael-addition, anionic polymerization of acrylates, and sol-gel reaction of organosilanes concomitantly upon irradiation of UV light. Coating compositions containing Michael donor/acceptor, acrylate compounds and organosilanes have been successfully cured using a single UV-trigger. The study shows that it is possible to develop UV-curable coating with tuneable properties by leveraging different cure reactions using a single UV trigger. Such coatings can be formulated without the use of conventional acrylate RDs or free-radical initiator, providing significant technical and environmental and health related benefits. The studies also highlight the ability of the synthesised acetoacetate type reactive diluents can effectively reduce viscosity when compared with the conventional RDs used in the industry today. Owing to our ability to manipulate multiple cure reactions and coating micro/nano-structures, such

systems may have many promising applications in coatings, adhesives and in additive manufacturing space.

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