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COMMUNICATION

Gallium (III) xanthate as a novel thermal latent curing agent for epoxy resin composite

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Latent thermal curing catalyst “Ga (III) xanthate” for epoxy resin/phenol composite, and its curing behaviour are reported. Ga (III) xanthate swiftly cures the epoxy composite within 38.2 s at 200 °C. However curing time of epoxy composite with Gallium (III) xanthate did not change after storage for six months unlike commercially used catalyst.

Cured epoxy resins are one of the versatile industrial materials employed in high-performance thermosetting plastics, microelectronics, automobiles and other industries.¹⁻⁵ Traditionally acids⁶ and bases⁷ are employed as catalysts for curing of epoxy composites. In spite of high activity they have serious drawback of reduced shelf life even under ambient conditions.⁸ Utilization of latent catalytic activity therefore is highly desired to extend the working life of a formulated mixture by passivation of the catalyst activity until triggered by the external stimulus.⁹ This demands search for latent curing agents having controllable and optimum curing conditions along with enhanced shelf-life. In this present work, we would like to report the application of Gallium (III) xanthate as a novel latent curing agent and its curing behaviour for the epoxy resin. To the best of our knowledge, there is no report towards the application of metal xanthates as epoxy curing agent. Ga(III)-O-2,2-dimethylpentan-3-yl dithiocarbonate (Ga(III) xanthate) (Figure 1) was synthesized by adding an aqueous solution of anhydrous gallium (III) chloride (3 g, 17 mmol, 1 equivalent) to an aqueous solution of Potassium-diemthylpentanyl-3-yl dithiocarbonate¹⁰ (12.6 g, 55 mmol, 3.2 equivalents) drop wise and the solution was stirred for 2 h.

Notes:

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† Electronic Supplementary Information (ESI) available: ¹H NMR, ¹³C NMR, IR, HPLC of Ga (III) xanthate, DSC analysis, EPMA.

The precipitate obtained was filtered and washed with methanol, dissolved in CHCl₃ and recrystallized in methanol to obtain the desired product as yellow solid (yield: 2.8 g, 77%). HPLC, *t_R* 19.2 min. ¹H NMR (500 MHz, 26 °C, CDCl₃, δ): 4.78-4.74 (dd, 1H, CH), 1.78-1.71 (m, 2H, CH₂), 1.02-0.89 (m, 12H, 4 × CH₃) ppm. ¹³C NMR (125 MHz, 24 °C, CDCl₃, δ): 228.42 (CS₂O), 101.17 (CH), 35.94 (C (CH₃)), 25.94 (C (CH₃)), 23.28 (CH₂), 10.97 (CH₂-CH₃) ppm. IR (KBr pellet, cm⁻¹): 2965, 2873, 1462, 1364, 1252, 1129, 1058, 1027, 907. Elemental analysis: Ga (III) C₂₄H₄₅O₃S₆ Calculated: C 44.77%, H 7.0%, Found: C 44.75%, H 6.9%. (See Fig. S1 and S2 for NMR chart, S3 for HPLC and S4 for FTIR in the supporting information)

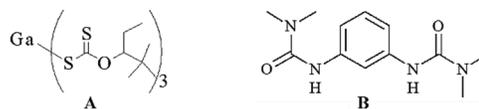


Figure 1: Structure of (A) Gallium (III) xanthate and (B) UCAT3512T

Variation of curing time with temperature was studied using Panasonic temperature controller (KT4). Commercially available UCAT3512T (supplied by Kyocera Company, Japan) was employed as the standard latent catalyst (Figure 1). A 1:1 molar ratio of epoxy resin (CNE200ELB65) and phenol (BRG556) supplied by Kyocera Company, Japan, was grinded homogenously with 2.5% catalyst and curing time at various temperatures was recorded (Figure 2). At 200 °C, 2.5% Ga (III) xanthate cured the epoxy resin composite within 39 s. With increase in temperature, decrease in curing time was observed for both of the catalysts. Nevertheless curing by UCAT3512T occurs at lower temperature and over the broad temperature range while in the case of Gallium (III) xanthate, significant curing was observed only after an optimum temperature of 170 °C.

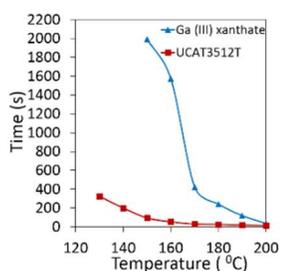


Figure 2: Curing time versus temperature with 2.5% catalyst content

Thermal behaviour of Ga (III) xanthate was investigated using thermogravimetric analysis (TGA) under N_2 atmosphere (Figure 3). Ga (III) xanthate thermally decomposes with weight loss corresponding to the formation of gallium sulphide around $170^\circ C$. Analysis of the weight loss pattern from the TGA curve clearly reveals the final formation of GaS via Ga_2S_3 . The fact that the minimum temperature required for initiation of curing matches well with the temperature corresponding to the beginning of the gallium sulphide formation suggests pivotal role played by gallium sulphide in curing of epoxy resin.

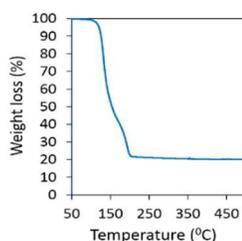


Figure 3: Thermogravimetric analysis curve of Ga (III) xanthate

1:1 molar ratio of Epoxy resin/phenol composite films were made on glass substrate and electronic absorption spectroscopic measurement was performed for two different temperatures viz., below the curing temperature ($120^\circ C$) and above the optimum curing temperature ($200^\circ C$). In the case of films without xanthate catalyst no absorption peak was observed in either of the cases.

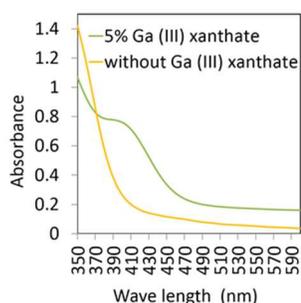
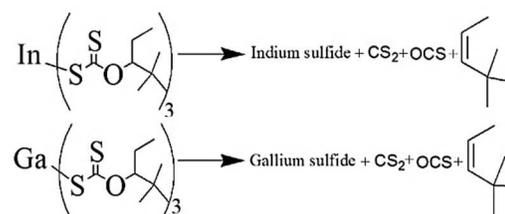


Figure 4: Electronic absorption spectra of epoxy composite in the presence and absence of Ga (III) xanthate baked at $200^\circ C$.

Absorption in the range from 380 to 420 nm was observed for the film containing Ga (III) xanthate baked at $200^\circ C$ (Figure 4) while the film

baked at $120^\circ C$ showed no such absorption (Figure S5 in supporting information). It has been reported that gallium sulphide and indium sulphide belong to the class of wide band gap semiconductor having the band gap in the region about 3.4 eV and 2.2 eV respectively¹¹. Based on the electronic absorption spectrum for 5 % gallium sulphide in the epoxy resin film shown in the Figure. 4, optical band gap was calculated by most commonly utilized Tauc plot and was found to be about 3.2 eV (Fig. S6 in supporting information). This indicates the formation of gallium sulphide after thermolysis of gallium (III) xanthate at $200^\circ C$ in the epoxy resin composite. In addition indium (III) xanthate has been reported to form indium sulphide^{10, 12} in situ after baking according to the reaction scheme 1. Therefore, it is expected that Ga (III) xanthate also decomposes in situ in the polymer matrix to form gallium sulphide in the similar fashion.



Scheme 1: Thermal decomposition of Indium (III) and Gallium (III) xanthates

In order to verify the superiority of Ga (III) xanthate over the conventional commercial catalyst for the curing of the epoxy resin, shelf-life study was conducted by storing 1:1 mixture of the epoxy resin/phenol including 2.5% catalyst at room temperature for six months. After the definite time intervals, the curing time at $200^\circ C$ was monitored for UCAT3512T and was compared with that of Ga (III) xanthate (see Figure S7 and table 1 in the supporting information). Curing time of epoxy resin/phenol composite including Gallium (III) xanthate remained unchanged but with UCAT3512T, it decreased from 14.5 to 12 s demonstrating that the former possesses better latent catalyst properties.

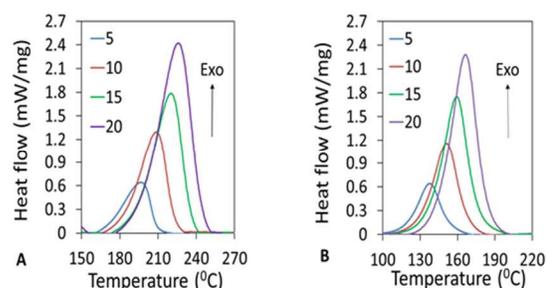


Figure 5: Differential scanning calorimetric analysis curves for curing of epoxy composite consisting of A) 5% Ga (III) xanthate and B) 5% UCAT3512T, at different heating rates ($^\circ C/min$).

It has been widely accepted that curing of the epoxy resins by conventional catalysts is activated process and this activation energy for curing was determined using the differential scanning calorimetric (DSC) analysis.¹³ Figure 5 exhibits the DSC thermograms recorded at different heating rates for epoxy composite containing 5% of Ga (III)

xanthate as well as UCAT3512T. The exotherms indicate that curing process in the case of standard catalyst has an overall onset of 100 °C and with Ga (III) xanthate an overall higher onset of 170 °C. This clearly indicates that with Ga (III) xanthate no curing occurs at lower temperature unlike conventional catalyst. To verify curing completeness using Ga (III) xanthate a second DSC run was conducted after the completion of first DSC cycle from 30-300 °C. The absence of the exothermic peak in the second DSC run cycle confirms that curing of the resin was complete (see figure S8 in the supporting information).

Using the peak temperatures obtained at different heating rates activation energy can be determined by Flynn-Wall-Ozawa^{14, 15} method utilizing the general expression represented by

$$\text{Log } q = A^* - 0.457E/RT_{\text{peak}} \quad \text{-----1}$$

Where q , A^* , E , R and T represents the heating rate, pre-exponential factor, activation energy, ideal gas constant and temperature respectively (see appendix 1 of supporting information for detailed analysis).¹⁶ Activation energy was thus calculated by plotting $\ln q$ vs $1000/T_{\text{peak}}$ where, T_{peak} is the exothermic peak temperature at different heating rates¹⁷ (table 2 in supporting information) as shown in the Figure 6. The slope of this graph was used to calculate the value of the activation energy as per equation 1.

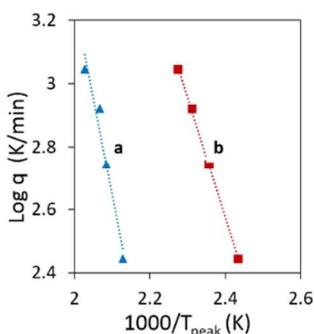


Figure 6: Ozawa Plot ($\ln q$ versus $1000/T_{\text{peak}}$) for curing of epoxy resin utilizing 5% of the catalyst content of (a) Ga(III) xanthate (b) UCAT3512T

The energy of activation was estimated to be 109.99 kJ mol⁻¹ and 69.27 kJ mol⁻¹ for Ga (III) xanthate and standard catalyst respectively. Since the activation energy of Ga (III) xanthate mixture is higher, it can be concluded to have better latent properties than conventional catalyst owing to attainment of the triggering temperature associated with its decomposition temperature.

Electron probe micro analysis (EPMA) was conducted for the product obtained after annealing Ga (III) xanthate at 200°C. The EPMA image with elemental mapping (Figure S9 in supporting information) shows that gallium and sulphur both are present at the same place indicating the formation of gallium sulphide. It is interesting to note that in figure S9 (in supporting information) relative abundance of elemental Ga and S contents at the same place shows the ratio of approximately 2 : 1 indicating the formation of GaS as the final

product of thermolysis of gallium (III) xanthate precursor heated at 200 °C. To determine the nature of the final product after curing of the epoxy resin using the gallium (III) xanthate precursor the cured resin after the DSC analysis using this xanthate precursor was subjected to the investigation using FE-SEM equipped with energy dispersive X-ray (EDAX) analysis. In the EDAX, it can be observed that both Ga and S are present at the binding energy of 9.2 KeV (Ga K α) and 2.3 KeV (S K α), respectively (see Figure S10 in the supporting information). The relative signal counts for Ga and S in the EDAX spectra were found to be 2:1. This further confirms that the final product of the thermolysis of gallium (III) xanthate precursor in the epoxy resin composite after the completion of curing is GaS.

In summary, we are able to successfully employ Ga (III) xanthate as catalyst in the curing of epoxy resin/phenol system. The composite consisting of Ga (III) xanthate had very long shelf life-time since the curing time remained unchanged even after storage for six months at room temperature. The activation energy for curing with Ga (III) xanthate was higher than that of conventional catalyst. It's concluded that this catalyst has better latent catalyst properties than standard catalyst UCAT3512T.

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