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RSC Advances

Communication

Electronic Supplementary Information

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

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1. General information:

Anhydrous gallium (III) chloride purchased from Tokyo Chemical Corporation, Japan. Potassium *tert* butoxide and carbon disulphide purchased from Wako Japan and 2, 2 - dimethyl-3-pentanol was purchased from Sigma Aldrich, Japan. Commercially available UCAT3512T supplied by Kyocera Company, Japan. ^{1}H NMR spectrum was recorded at 26 ^{0}C on JEOL JNM-A500 Nuclear Magnetic Resonance Spectrometer operated at 500 MHz. ^{13}C NMR spectrum was also recorded at 24 ^{0}C on JEOL Nuclear Magnetic Resonance Spectrometer at 125 MHz. NMR spectra were measured in $CDCl_3$ solution with internal reference TMS. All ^{1}H shifts are given in parts per millions (s = singlet; d = doublet; t = triplet; m = multiplet). High performance liquid chromatography (HPLC) was performed using JASCO Corporation system. The IR spectrum was recorded on a JASCO FT/IR 4100. Elemental analysis performed using Yanaco MT-5. Curing time of the epoxy resin at various temperatures was studied using Panasonic KT4 temperature controller. Electronic absorption spectra were recorded using JASCO V-670 spectrophotometer. Differential thermal analysis studied using DSC-60 Differential scanning calorimeter, Shimadzu. Thermogravimetric analysis studied using DTG-60 simultaneous DTA-TG apparatus, Shimadzu. JEOL JXA-8530F Field Emission Electron Probe Microanalyser for electron probe microanalysis.

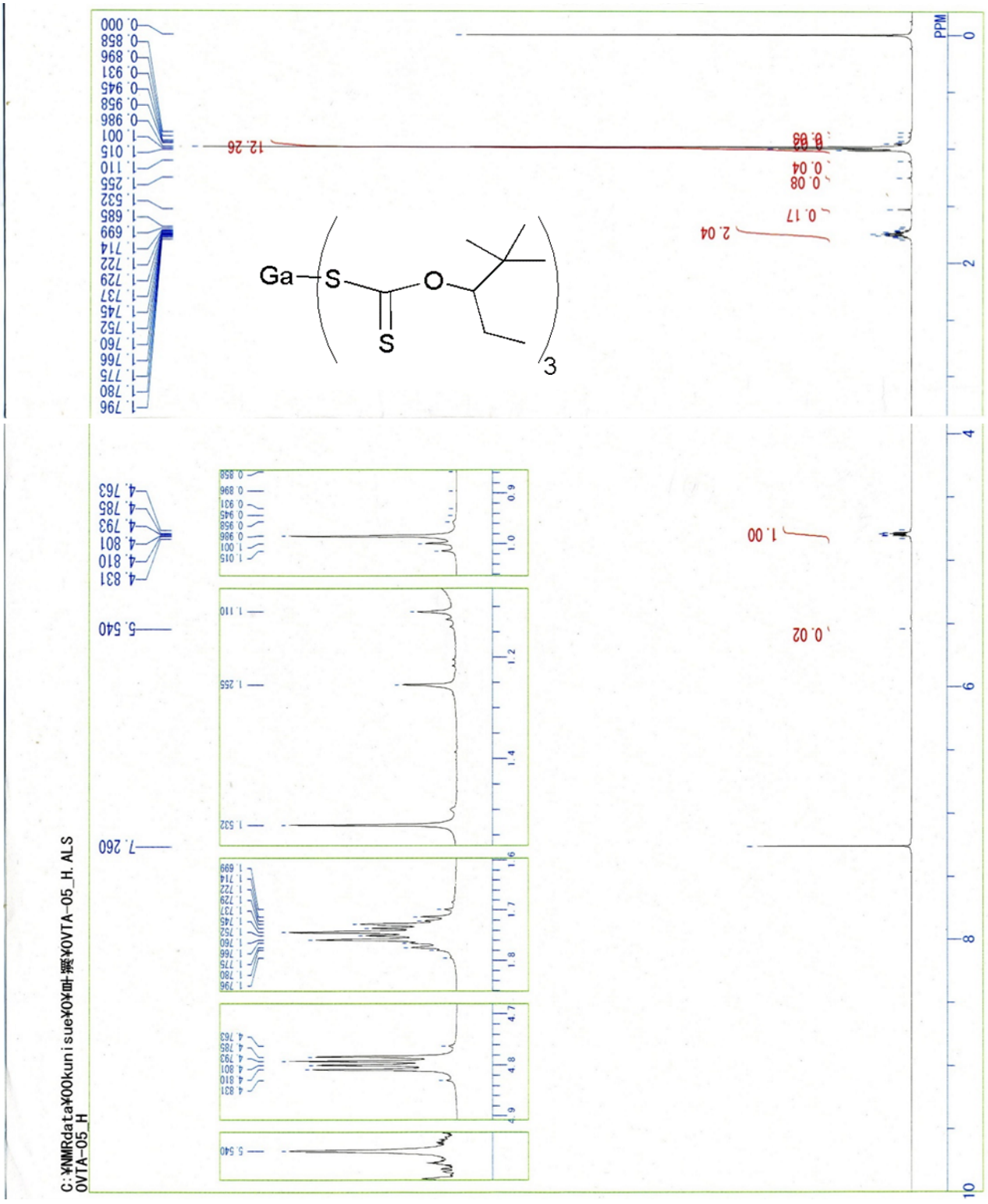

Figure S1: ^{1}H NMR Gallium (III) xanthate, $CDCl_3$, 26 ^{0}C, 500 MHz.

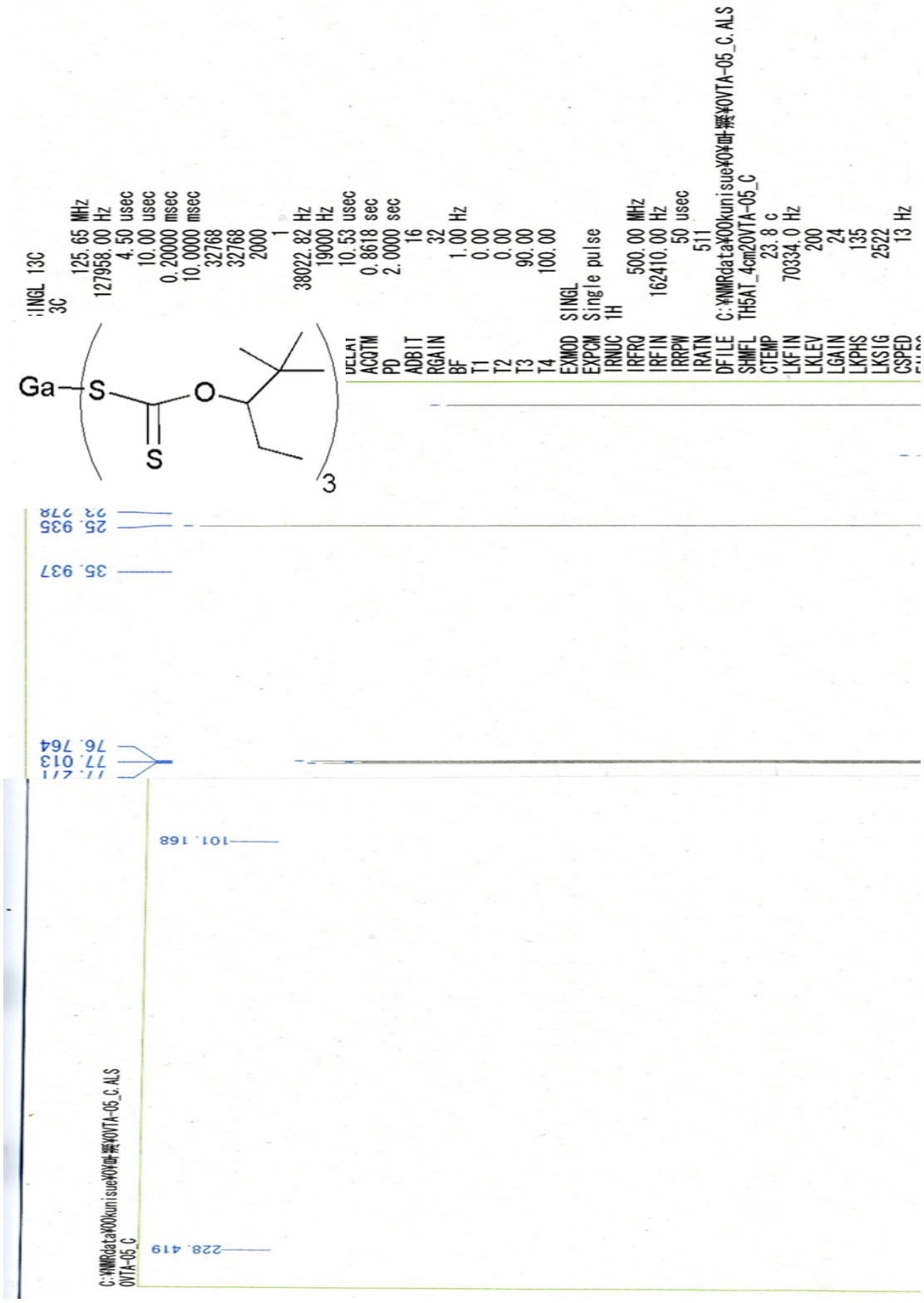

Figure S2: ^{13}C NMR Gallium (III) xanthate, $CDCl_3$, 24 ^0C, 125 MHz.

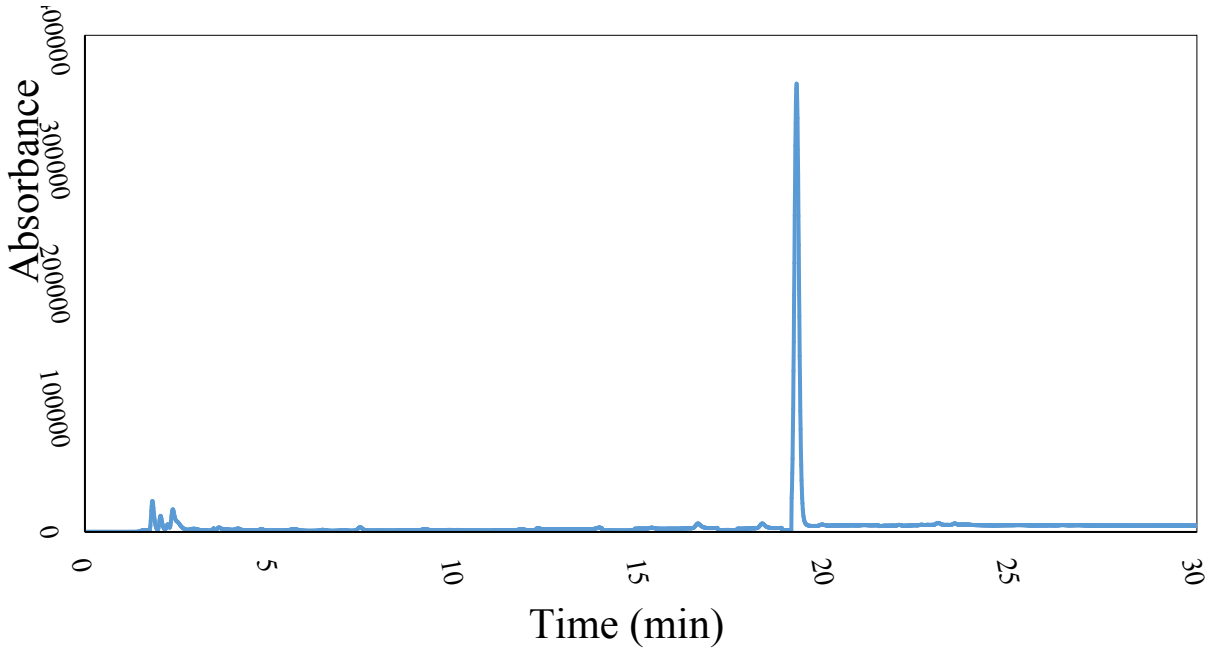

Figure S3: HPLC of Gallium (III) xanthate. Gradient System: A= 70% to 100%, A - Methanol, B - Distilled Water, Flow rate: 1 ml / min, Elution time: 30 min.

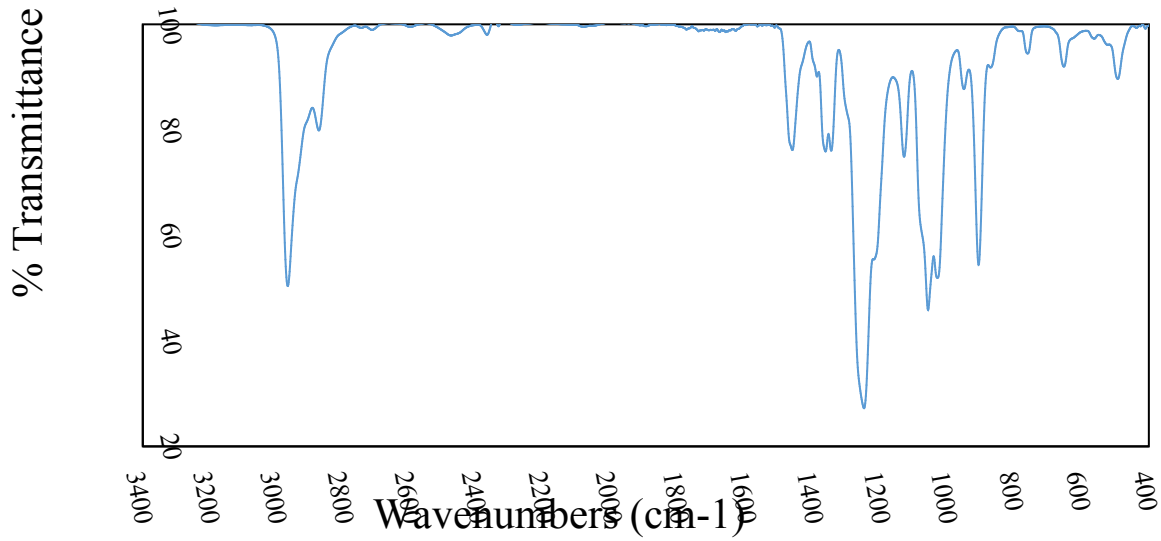

Figure S4: FTIR spectrum of Ga (III) xanthate.

Epoxy resin films consisting of 5% Gallium (III) xanthate.
To a 2 g mixture of 1:1 molar ratio of epoxy resin (CNE200ELB65) and phenol (BRG556) 5% Ga (III) xanthate (0.1 g) dissolved in 2.5 mL of chloroform was added. The mixture was heated at 80 ^{0}C for 5 min and mixed to form a homogenous mixture. The viscous substrate was spread on glass slides and cooled to room temperature to form a film. The films were baked at 120^0 C and 200 ^{0}C temperatures separately and the absorbance was recorded.

Epoxy resin films without Gallium (III) xanthate.
To a 2 g mixture of 1:1 molar ratio of epoxy resin (CNE200ELB65) and phenol (BRG556), 2.5 ml chloroform was added. The mixture was heated to 80 ^{0}C for 5 min and mixed to form a homogenous mixture. The viscous substrate was spread on glass slides and cooled to room temperature to form a film. The films were baked at 120 ^{0}C and 200 ^{0}C temperatures separately and the absorbance was recorded.

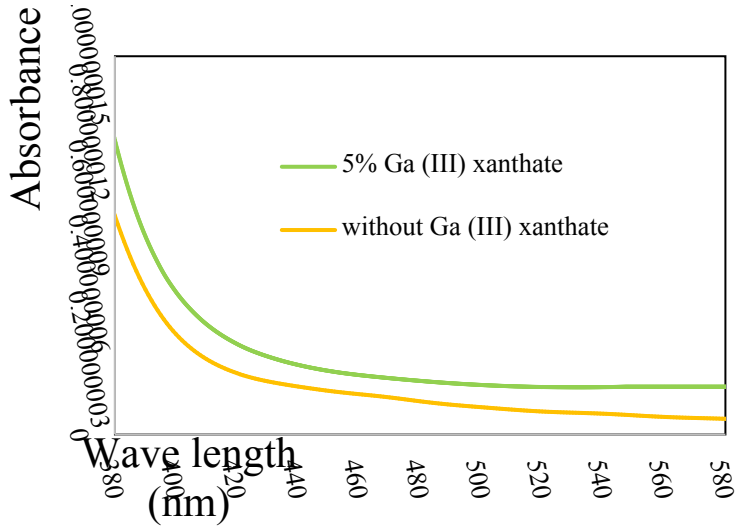

Figure S5: Electronic absorption spectra of epoxy composite consisting of Ga (III) xanthate baked at 120 ^{0}C (0% and 5% catalyst content)

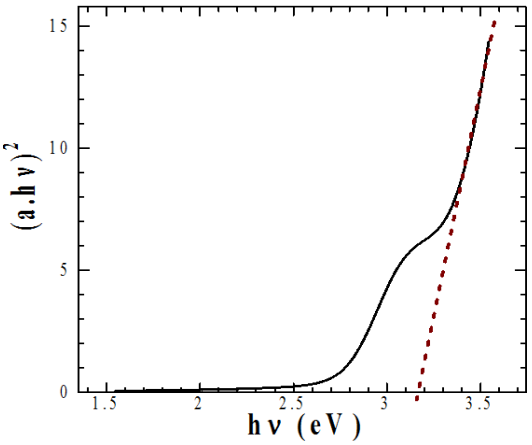

Figure S6: $(\alpha h\nu)^2$ vs. hv (Tauc plot) for the determination of optical band gap (Eg). Eg was estimated by linear extrapolation as shown by the dotted line. Since gallium sulphide formed was in homogenously distributed in the resin matrix, and lack of exact thickness of gallium sulphide, value of absorbance (A) was used in place of (α) as representative for the Eg calculation.

1:1 Epoxy resin/phenol composite consisting of 2.5% UCAT3512T.
To a 2 g mixture of 1:1 molar ratio of epoxy resin (CNE200ELB65) and phenol (BRG556) 0.5 g of UCAT3512T was added and grinded thoroughly and transferred into a glass bottle and stored under vacuum.

1:1 Epoxy resin/phenol composite consisting of 2.5% Ga (III) xanthate.
To a 2 g mixture of 1:1 molar ratio of epoxy resin (CNE200ELB65) and phenol (BRG556) 0.5 g of Ga (III) xanthate was added and grinded thoroughly and transferred into a glass bottle and stored under vacuum.

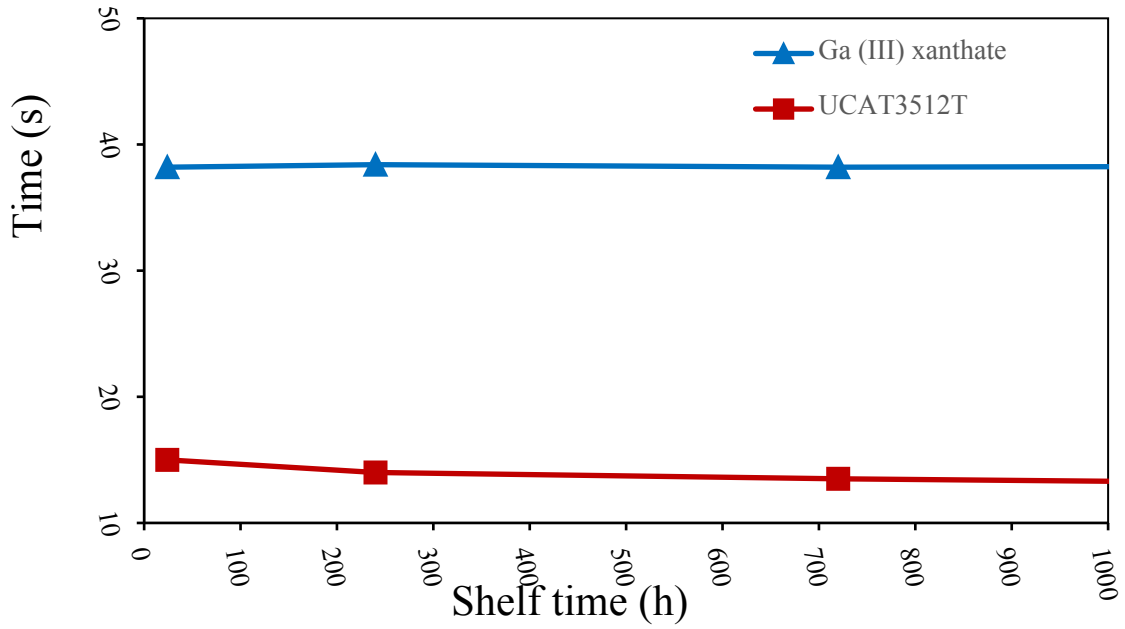

Figure S7: Curing time of epoxy resin composite conducted at 200 ^{0}C after storage at room temperature for different time intervals (2.5% catalyst content).

Table 1: Curing time at 200 ^{0}C after storage at room temperature

Shelf life time (h)	Curing time (s) with 2.5% standard catalyst at 200 ^{0}C	Curing time (s) with 2.5% Ga (III) xanthate at 200 ^{0}C
24	14.5	38.2
240	14.0	38.4
720	13.5	38.2
1440	13	38.3
2160	12.3	38.2
4320	12	38.3

Appendix 1. Differential scanning calorimetric (DSC) measurements and calculation of Energy of activation

The curing thermal data were obtained by means of Shimadzu DSC-50 differential scanning Calorimeter. Pure Indium was taken as standard for calorimetric calibration. Runs were carried out using an empty cell as a reference. The non-isothermal DSC curves for 1:1 epoxy resin/phenol composite system including 5% catalyst were recorded at different heating rates ranging from 5-20 ^{0}C/min. The DSC cure of epoxy resin is characterized by a broad exothermic peak. The peak temperature, Tp, shifts to a higher temperature range with increasing heating rate. The non-isothermal isoconversional[1] Flynn–Wall[2]–Ozawa[3] method was applied to the dynamic heating experimental data obtained at different heating rates to derive activation energy.[4] The reaction rate equation utilized to study the resins curing kinetics can be expressed, in general, as[5]:

$$d\alpha/dt = kf(\alpha) \text{---------- (1)}$$

where α is degree of cure, t is time, k is the rate constant expressed by Arrhenius equation and is a function of temperature, and f(α) is the reaction model. Considering a dynamic curing situation equation (1) including Arrhenius equation can be written as[6]

$$q\, d\alpha/dT = A\, e^{(-E/RT)}\, f(\alpha) \text{----------(2)}$$

Where q is the heating rate, T is the temperature, A is pre-exponential factor, E is activation energy, R is gas constant. An integral form of the rate equation can be now expressed as[7]:

$$g(\alpha) = AE/qR\, p(x) \text{----------(3)}$$

$$p(x) = \int_{x}^{\alpha} \exp(-x)/x^2\, dx \text{ ----------(4)}$$

Where g (α) is $\int_0^{\alpha} d\alpha/f(\alpha)$ is the intigrated form of the conversion dependent function and p(x) defined by equation 4 where $\boldsymbol{x}$ is defined as E/RT. Using Doyle`s linear approximation[7] the Flynn-Wall-Ozawa method can be modified as

$$\log q = \log (AE/g(\alpha)R - 2.315 - 0.457E/RT \text{------(5)}$$

Based on assumption that the extent of reaction is constant and independent of the heating rate at exothermic peak temperature[9,10] the equation 5 can be rearranged as

$$\log q = A^* - 0.457E/RT_{peak} \text{---------- (6)}$$

where A* = log (AE/g(α)R and is a constant. [11]The slope value obtained by the plot of inverse of peak temperatures (1000 / K) of exotherms obtained at various heating rates as the horizontal axis and the common logarithm of the heating rate (K / min) as the vertical axis (Arrhenius`s plot) activation energy E can be determined since R (universal gas constant) is known.

Table 2: Peak temperatures obtained from differential scanning calorimetric analysis curves for curing of epoxy composite at different heating rates.

Curing agent (5% by mass)	Heating rate (^{0}C / min)	Peak temperature (^{0}C)
Ga (III) xanthate	5	196.51
	10	206.55
	15	210.51
	20	220.17
UCAT3512T	5	137.70
	10	151.17
	15	159.36
	20	166.49

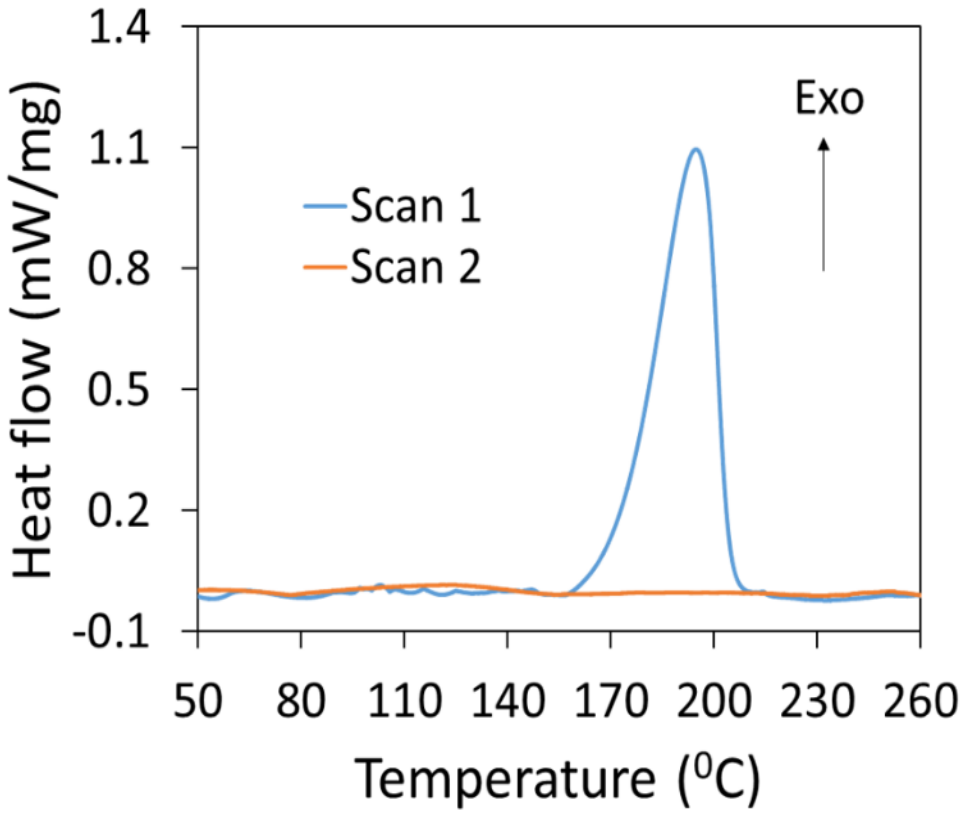

Figure S8: Differential scanning calorimetric analysis curves for curing of epoxy composite consisting of 5% Ga (III) xanthate at 10 ^{0}C/min heating rate. **Scan 1**: First scan from 30^{0}C to 300 ^{0}C. **Scan 2**: A repeated scan from 30 to 300^{0}C for the same sample used for first scan.

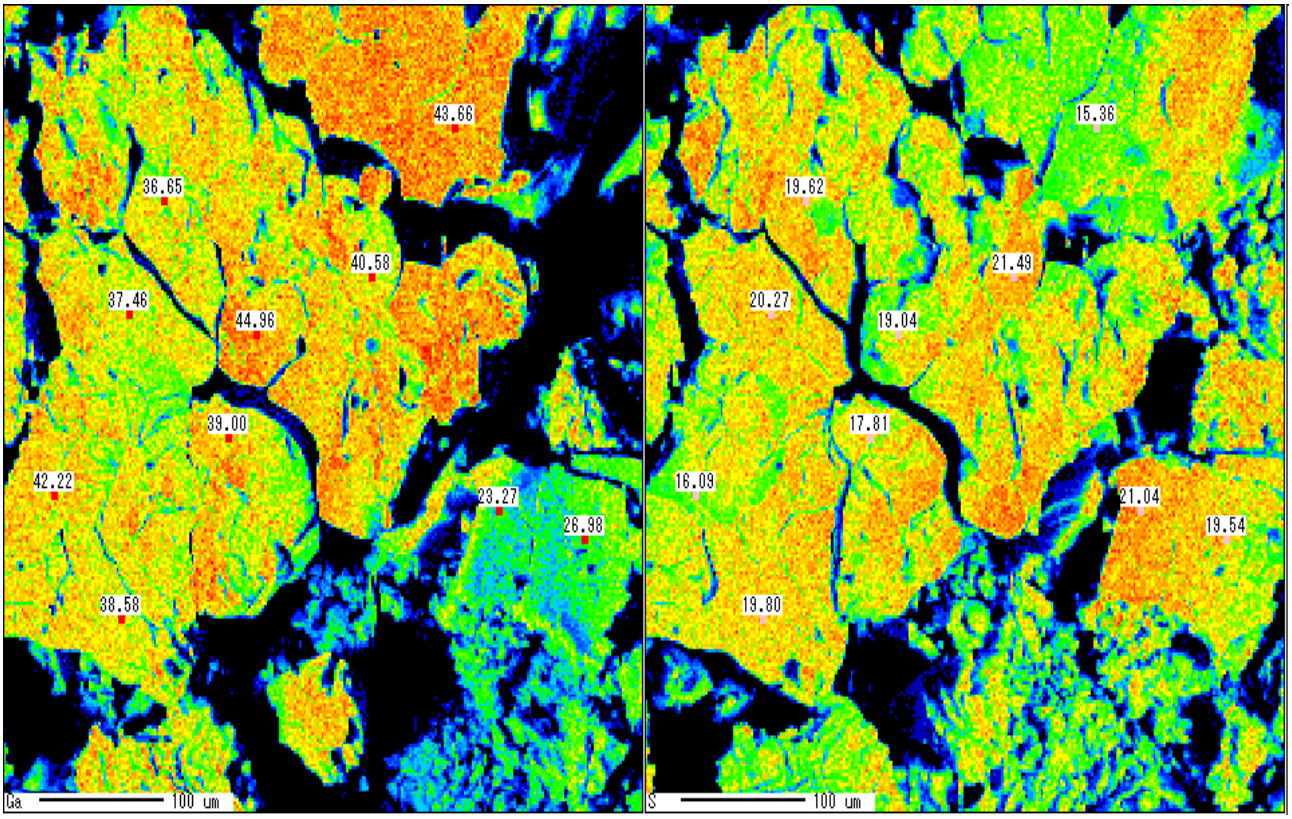

Figure S9: EPMA micrograph with elemental distribution mapping for Ga (III) xanthate after annealing at 200 ^{0}C. Left mapping for Ga while right mapping for S.

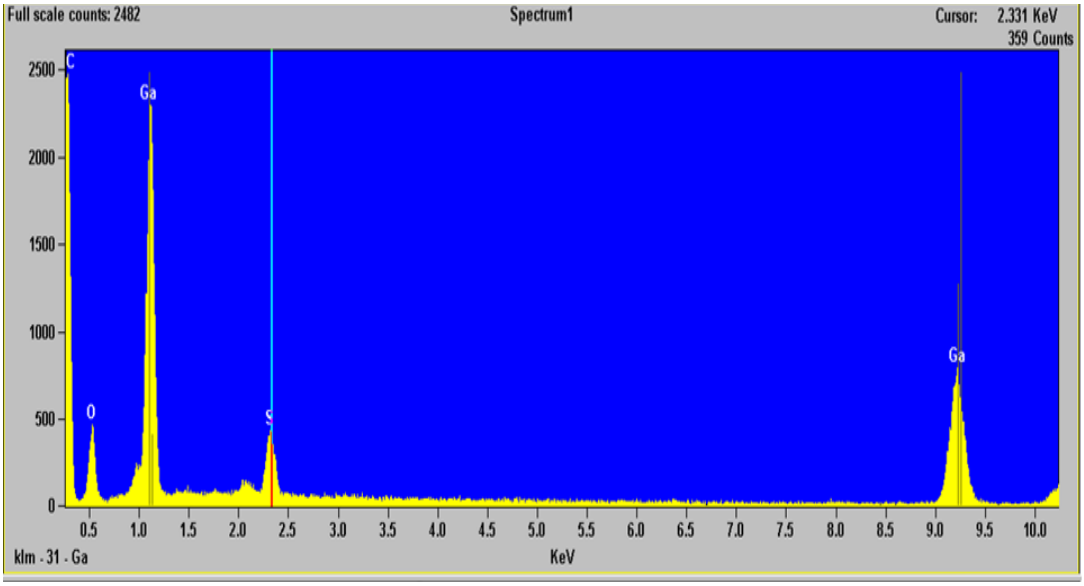

Figure S10: EDAX analysis for epoxy resin containing 5 % Ga (III) xanthate precursor after conducting the differential scanning calorimetric analysis indicating the presence of Ga and S after curing.

11. References

[1] J. Zhang, Y. Wang, X. Wang, G. Ding, Y. Pan, H. Xie, Q. Chen and R. Cheng, *Journal Applied polymer science*, 2014, **131**, 40472.
[2] J.H. Flynn and Leo A. Wall, *Journal of research of the national bureau of standards – A,* 1966, **70A(6)**, 1.
[3] T. Ozawa, *Journal of Thermal Analysis*, 1970, **2**, 301.
[4] J.C. Domíngueza, J.C. Grivela and B. Madsena, *Thermochemical Acta*, 2012, **529**, 29.
[5] M.V. Alonso, M. Oliet, J. Garc´ıa, F. Rodr´ıguez and J. Echeverr´ıa, *Chemical Engineering Journal,* 2006, **122**, 159.
[6] G. Francucci, F. Cardona and N. W. Manthey, *Journal Applied polymer science,* 2013, **128(3)**, 2030.
[7] Z. Zhang, G. Liang, P. Ren, J. Wang and *Polymer Composites*, 2008, **29**, 77.
[8] L. Barral, J. Cano, J. Lo´Pez, I. Lo´Pez-Bueno, P. Nogueira, M. J. Abad and C. Rami´Rez, *Journal of Polymer Science: Part B: Polymer Physics*, 2000, **38**, 351.
[9] F. Mustata, N. Tudorachi and I. Bicu, Composites*: Part B,* 2013, **55**, 470.
[10] T. Yang, C. Zhang, J. Zhanga and J. Cheng, *Thermochemical Acta,* 2014, **577**, 11.
[11] I. Hamerton, W. Tang, J.V. Anguita, S. Ravia and P. Silva, *Reactive & Functional Polymers*, 2014, 74, 1.