



Investigation of metal xanthates as latent curing catalysts for epoxy resin via formation of in-situ metal sulfides



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ABSTRACT

Cu(I), Pb(II), Sb(III), Zn(II), Cd(II), In(III), Ga(III) xanthates were synthesized and characterized by ^1H NMR, ^{13}C NMR, infrared spectroscopy and elemental analysis. The final product of decomposition of metal xanthates at 200 °C subjected to XRD and EDS analysis, confirmed generation of metal sulfides. The curing behavior was analyzed by performing curing time investigation of epoxy composite as a function of temperature employing 5% metal xanthates as catalysts. None of the metal xanthates demonstrated any significant curing of epoxy composite prior to 150 °C proving their latent curing potency. Ga(III) xanthate exhibited comparatively the most effective catalytic property. Thermogravimetric analysis utilized to examine the thermal behavior of metal xanthates indicated, metal xanthates which are air-stable at ambient temperatures undergo latent decomposition upon thermal annealing. The order of curing time at a given temperature and the trend of decomposition temperature of metal xanthate under consideration was observed to be similar. XRD and EDS study of epoxy composite consisting of metal xanthates cured by thermal annealing illustrated generation of metal sulfide in-situ in the matrix. It was presumed that the phenomena of metal xanthates under investigation yielding corresponding in-situ metal sulfides in the epoxy composite upon thermal annealing in a latent fashion is responsible for exhibiting latent curing catalytic activity.

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1. Introduction

Metal xanthates as single source precursors for metal sulfides [1,2] is exploited in plethora of applications such as fabrication of polymer-nanocrystal hybrid solar cells [3], chemical vapor deposition [4], photochromic devices [5], hybrid optical sensors [6] and electroluminescent devices [7]. Employing metal xanthates as ideal precursors for metal sulfides is very attractive owing to their flexibility as a wide variety of alkyl substituents [8] and metal centers can be readily incorporated into xanthate species. Thus the properties of the materials such as solubility, decomposition temperature and room temperature air-stability can be tuned in according to the target application requirement [9]. Its well established [10,11] that metal xanthates stable under ambient conditions upon thermal annealing at certain threshold temperature decompose to yield metal sulfides in a latent fashion.

Cured epoxy composites are of high industrial relevance [12] pertaining to its unique properties such as high tensile strength [13], low weight [14], high stiffness [15], excellent thermal

properties [16] and chemical resistance [17]. They are extensively employed in various technological applications such as semiconductor encapsulation [18] aerospace industry [19], flame-retardant additives [20] and coating industries [21]. Curing is defined as transformation of low molecular epoxy oligomer into a highly cross-linked polymeric network achieved by utilizing curing agents [22]. Due to high commercial significance, cure processing conditions and curing agents have been receiving tremendous scientific pursuit [23]. Conventional curing agents consisting of Lewis acids [24,25] and bases [26] are reported to have restricted application potential due to instigation of curing even at ambient conditions [27] thereby reducing the shelf-life [28] of the formulated composite mixture. In addition, the uncertainty of the required conditions for curing makes it very difficult to have precise control over cure processing [29].

To circumvent these limitations latent curing agents [30] were explored as possible alternative solution, where in, curing is initiated only when desired upon trigger by external stimuli [31]. This facilitates enhanced shelf-life due to passivation of catalytic activity due to absence of external stimuli along with feasibility of precise control over curing. Thus preventing premature curing of the formulated composite mixture [32]. Utilization of these catalysts further endeavors several advantages such as easing of

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production line by elimination of requirement of control over mixing [33], homogenization of multiple components [34], stable storable one pot mixture making processing more economical and prior knowledge about the optimum conditions necessary for curing [35]. Thus the challenge for latent catalysts possessing ability to catalyze the curing process only upon instigation by threshold external stimuli are of huge demand.

Since metal xanthates as potential precursors forming metal sulfides in-situ in a latent fashion is illustrated. In this report the latent capability of metal xanthates to yield metal sulfides is explored for the possibility of this phenomena in catalyzing the curing reaction of epoxy resin composite. Metal xanthates by incorporating different metals on the xanthate species were synthesized and characterized. Subsequently the influence of metal ion on metal xanthates thermal behavior, curing catalytic property and ultimately the mode of mechanism of curing was investigated.

2. Experimental

2.1. Materials

Potassium tert-butoxide, carbon disulfide, zinc(II) chloride, cadmium(II) chloride, lead(II) nitrate, copper(II) chloride anhydrous were purchased from Wako Japan. Antimony potassium tartrate hydrate was purchased from Alfa Aesar. 2,2-dimethyl-3-pentanol and indium(III) chloride tetrahydrate were purchased from Sigma Aldrich, Japan. Anhydrous gallium(III) chloride was purchased from Tokyo Chemical Corporation, Japan. Ortho-cresol novolac epoxy resin (CNE200ELB65) melting point 65 °C and Novolac phenolic resin (BRG556) melting point 80 °C used in the current work were supplied by Kyocera Company, Japan.

2.2. Instrumentation

¹H NMR was recorded at 26 °C on JEOL JNM-A500 nuclear magnetic resonance spectrometer operated at 500 MHz. ¹³C NMR spectrum was also recorded at 24 °C on JEOL nuclear magnetic resonance spectrometer at 125 MHz. NMR spectra were measured in CDCl₃ solution using tetramethylsilane as internal reference. Infra-red (IR) spectrum was recorded on a JASCO FT/IR 4100 spectrometer and performed using the KBr form. Elemental analysis was performed using Yanaco MT-5 elemental analyzer. Powder X-ray diffraction (XRD) was measured utilizing Rigaku RINT-2000/PC X-ray diffraction apparatus. Curing time of the epoxy resin at various temperatures was studied using Panasonic KT4 reaction hot plate with temperature controller. Electronic absorption spectra were recorded using JASCO V-670 spectrophotometer. Differential thermal analysis studies were carried out employing DSC-60 differential scanning calorimeter, Shimadzu. Thermogravimetric analysis studied using DTG-60 simultaneous DTA-TG apparatus, Shimadzu. Hitachi S-5200 Scanning Electron Microscope (SEM) – Energy-dispersive X-ray spectroscopy (EDS) was utilized for elemental analysis and mapping.

2.3. Synthesis

Potassium xanthate (K-O-2,2-dimethyl pentan-3-yl-dithiocarbonate) was synthesized following the literature report [36]. Scheme 1 represents a general synthetic protocol for the synthesis and Fig. 1 portrays different metal xanthates employed in the current study.

2.3.1. Zinc(II) xanthate (4)

2.3.1.1. (Zinc(II)-O-2,2-dimethylpentan-3-yl-dithiocarbonate). To an aqueous solution of zinc(II) chloride (1 g, 7 mmol), potassium-O-2,

2-dimethyl pentan-3-yl dithiocarbonate (3.71 g, 16 mmol) dissolved in water was added drop wise while stirring at room temperature. A white precipitate formed was collected by suction filtration and washed with methanol. The solid obtained was extracted into chloroform and recrystallized from methanol to obtain white powder (yield: 2.9 g, 89%).

¹H NMR (500 MHz, 26 °C, CDCl₃, δ): 4.92–4.98 (dd, 1H, CH), 1.79–1.72 (m, 2H, CH₂), 0.96–0.98 (m, 12H, 4 × CH₃) ppm.

¹³C NMR (125 MHz, 24 °C, CDCl₃, δ): 230.79 (CS₂O), 100.56 (CH), 35.88 (C (CH₃)), 25.95 (C (CH₃)), 23.20 (CH₂), 10.96 (CH₂–CH₃) ppm.

IR (KBr pellet, cm⁻¹): 2965, 2875, 1468, 1367, 1236, 1129, 1056, 1033, 902.

Elemental analysis: *Anal.* Calc. for Zn(II) C₁₆H₃₀O₂S₄: C, 42.9; H, 6.76. Found: C, 42.02; H, 6.55%.

2.3.2. Cadmium(II) xanthate (5)

2.3.2.1. (Cadmium(II)-O-2,2-dimethylpentan-3-yl dithiocarbonate). An aqueous solution of potassium-O-2,2-dimethylpentan-3-yl dithiocarbonate **1** (2.8 g, 15 mmol) was added drop wise to a solution of cadmium(II) chloride anhydrous (1 g, 6 mmol), while stirring at room temperature. A white precipitate resulted was collected by suction filtration and washed with methanol. The solid was recrystallized from methanol after extracting into chloroform (Yield: 2.4 g, 5 mmol, 87%).

¹H NMR (500 MHz, 26 °C, CDCl₃, δ): 4.98–5 (dd, 1H, CH), 1.79–1.79 (m, 2H, CH₂), 1–1.02 (m, 12H, 4 × CH₃) ppm.

¹³C NMR (125 MHz, 24 °C, CDCl₃, δ): 230.71 (CS₂O), 101.03 (CH), 35.90 (C (CH₃)), 25.12 (C (CH₃)), 23.37 (CH₂), 11.14 (CH₂–CH₃) ppm.

IR (KBr pellet, cm⁻¹): 2965, 2874, 1468, 1365, 1230, 1130, 1029, 947, 902.

Elemental analysis: *Anal.* Calc. for Cd(III) C₁₆H₃₀O₂S₄: C, 38.81; H, 6.11. Found: C, 38.48; H, 5.93%.

2.3.3. Lead(II) xanthate (2)

2.3.3.1. (Lead(II)-O-2,2-dimethylpentan-3-yl dithiocarbonate). Lead chloride was not clearly soluble in water therefore no formation of lead xanthate precipitate was observed. However lead(II) nitrate was highly soluble in water therefore was preferred for reaction with potassium xanthate [37]. An aqueous solution of Lead(II) nitrate (1 g, 3.02 mmol) was added to an aqueous solution of Potassium-dimethylpentan-3-yl dithiocarbonate (1.53 g, 6.64 mmol) drop wise and the solution was stirred for 2 h. The precipitate obtained was filtered and washed with methanol, dissolved in CHCl₃ and recrystallized in methanol to obtain the desired product as grey solid (yield: 1.3 g, 71%).

¹H NMR (500 MHz, 26 °C, CDCl₃, δ): 5.45–5.47 (dd, 1H, CH), 1.78–1.87 (m, 2H, CH₂), 1.04–1.01 (m, 12H, 4 × CH₃) ppm.

¹³C NMR (125 MHz, 24 °C, CDCl₃, δ): 229.51 (CS₂O), 94.11 (CH), 35.76 (C (CH₃)), 26.19 (C (CH₃)), 23.08 (CH₂), 11.13 (CH₂–CH₃) ppm.

IR (KBr pellet, cm⁻¹): 2965, 2874, 1464, 1370, 1212, 1125, 1056, 1017, 904.

Elemental analysis: *Anal.* Calc. for Pb(II) C₁₆H₃₀O₂S₄: C, 32.58; H, 5.13. Found: C, 32.47; H, 5.05%.

2.3.4. Antimony(III) xanthate (3)

2.3.4.1. (Antimony(IV)-O-2,2-dimethylpentan-3-yl dithiocarbonate). Antimony potassium xanthate clearly dissolves in water and therefore reaction with potassium xanthate was feasible. In contrast, antimony chloride was insoluble in water and therefore no reaction was observed with potassium xanthate aqueous solution. To an aqueous solution of antimony potassium tartrate hydrate (1 g, 1.63 mmol), potassium-O-2,2-dimethylpentan-3-yl dithiocarbonate (1.20 g, 5.216 mmol) dissolved in water was added drop wise while stirring at room temperature. The mixture was centrifuged and washed with methanol. The solid obtained was

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