Synthesis and Spectroscopic Properties ofMolybdenum-Cadmium Metal clusters and Their Glyptal Metal Polymer

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Abstract

Molybdenum-Cadmium metal clusters and their units were synthesizedin dehydratedconc. nitric acid condition. Glyptal Metal Polymer of these clusters were obtained by condensation of phthalic-anhydrates and glycerol in hydrogen peroxide environment. Metal-clustersreactswith glyptal to yields polymeric $Cd(iOBut)_2.Mo_nO_x(iOBut)_4$. Glyptalis multi-dimensional structures having charge-balancing positive ions and its hydrated in the cluster framework cavities. A statistical study of the effect on the polymerization process, the molar ratio of the component oxides and the water content of the mixture reveals that both the metal clusters specifically follows the studied parameters. The polymerization mechanism and structures of the products were investigated using conductivity, TGA, DCA analysisXRD and SEM spectroscopy.

Keywords: Co-polymer, Molybdenum-Cadmium metal clusters, $Cd(iOBut)_2.Mo_nO_x(iOBut)_4$- Glyptal, Thermostable, Hydrated fluxional cavities.

Introduction

The strategy for incorporating metal-nanocomposites into polymers and macromolecular systems has often led to new properties and capabilities that would otherwise be challenging for purely-organic analogues to achieve. The increasing research activity in metal-nanocomposites and organometallic polymers is a testament to the opportunity for advancing our fundamental understanding of polymer science and for triggering innovation in various technologies (1,2).This trend can be linked to$Cd(iOBut)_2$.MonOx$(iOBut)_4$-Glyptal polymer, the toughening of the legislation in terms of fire hazards combined with the growing use of flame retardants.The flammability behavior of polymers is defined on the basis of several processes and parameters, such as burning rates (solid degradation rate and heat release rate), spread rates (flame, pyrolysis, burn-out, smolder), ignition characteristics (delay time, ignition temperature, critical heat flux for ignition), product distribution (in particular, toxic species emissions)(23), smoke production, etc (7,8). Our goal is then to inhibit or even suppress the combustion process acting chemically and physically in the solid, liquid or gas phase. We can interfere with combustion during a particular stage of this process, e.g. during heating, decomposition, ignition or flame spread. Three approaches can then be considered to reduce the flammability of polymers (9-11).

In organic synthesis, fire retardants and conducting material industry play a vital role in a growth of our nation; thus, its improvement can help economic growth by increasing the efficiency of organic reagents compounds, polymeric conducting materials and other product. In this researcharticle, nanocomposites metal glyptal polymers, a new class of polymers, having a fundamental role in improvement of polymer, because they have better thermal and conductivity properties and they also act as better organic reagents than the pure glyptal polymer(6).

Materials and Methods

Materials

Sodium Molybdate-(Na_2MoO_4. $2H_2O$)-M.wt, Assay 98-100%,Cadmium Sulphate-($CdSO_4$. $8H_2O$) M. wt. 769.52 Assay 98-100% , BurogyneBurbidge's& CO (India) Mumbai, Hydrogen peroxide-(H_2O_2)M. wt.34.01 g/mol, Isobutyl alcohol- ($C_4H_{10}O$) M. wt.74.122 g/mol, Phthalic-anhydride – $C_8H_4O_3$M. wt.142.12g/ml, Toluene- (C_7H_8 ,M. wt.92.14 g/mol, Glycerol – $C_3H_8O_3$,M. wt.92.09 g/mol was procured from Thomas Baker (chemicals) pvt. Ltd. Mumbai). All chemical and reagents has research grade.

Synthesis of Nanoparticles and Clusters

In this research, synthesis of organo-metallic Polymer is carried out via the oxidative addition reaction on central metal atom by approaching the organic monomers in inert condition. In this synthesis, thevacant d orbital's configurations of Mo-Cd metal atom are used and the synthesis of$Cd(iOBut)_2.MonOx(iOBut)_4$ is done in excess amount of iso-butanol. The mixture was refluxed for 5 hours in round bottom flask with water condenser. After refluxing, the mixture was decanted in china dish and dried in hot oven at 80^o C.

For synthesis of clusters, Sodium Molybdate-(Na_2MoO_4. $2H_2O$)and Cadmium Sulphate-($CdSO_4$. $8H_2O$) are merge together in china dish by heating on sand bath. After 10 min Con.$HNO_3$is added to convert its in liquid. This mixture is heated for aprox. half an hour when the yellow fumes get evaporated and the product is obtained in clusty form,which is then cooled and collected.

Fig:-01 Nano-composites of $Cd(^iOBut)_2.Mo_nO_x(^iOBut)_4$ Fig:-02 Clusters of $Cd_n.Mo_nO(NO_3)_{2n}$

Synthesis of $Cd(^iOBut)_2.Mo_nO_x(^iOBut)_4$-Glyptal polymer

In these syntheses, nanoparticles were fused in glyptal-polymer by condensation polymerization method. Very small amount of $Cd(iOBut)_2.Mo_nO_x(iOBut)_4$nanoparticles are induced in0.9209 g/mole glycerol treated with 1.4212 g/mole phthalic anhydride of themixture was first heated vigorously on direct flame in china dish at above 105^oC (6). After well mixing $Cd(^iOBut)_2.Mo_nO_x(^iOBut)_4$-Glyptal polymerbecome which is viscous, then dried over the sand bath at 125^oC to 135^oC. Depending on the ratio of nanoparticlesvarious proportions of $Cd(^iOBut)_2.MonOx(^iOBut)_4$-Glyptal polymer are obtained.

Fig:-03Cd(^{i}OBut)$_2$.MonOx(^{i}OBut)$_4$-Glyptal polymer Zr(^{i}OBut)$_2$Glyptal (0.0602 NCs)

Fig:-04 Cd(^{i}OBut)$_2$.MonOx(^{i}OBut)$_4$-Glyptal polymer (0.0337g NCs)

Table 1 XRD data

Sr.no.	Ti(^{i}OBut)$_4$	Phthalic-anhydride	Glycerol
1.	0.0602mg	8 g	3g
2.	0.0337mg	8 g	3g

Characterization and Data Analysis

XRD Analysis Cd(^{i}OBut)$_2$.Mo$_n$O$_x$(^{i}OBut)$_4$-Glyptal polymer

Calculation of Particle Size from XRD Data

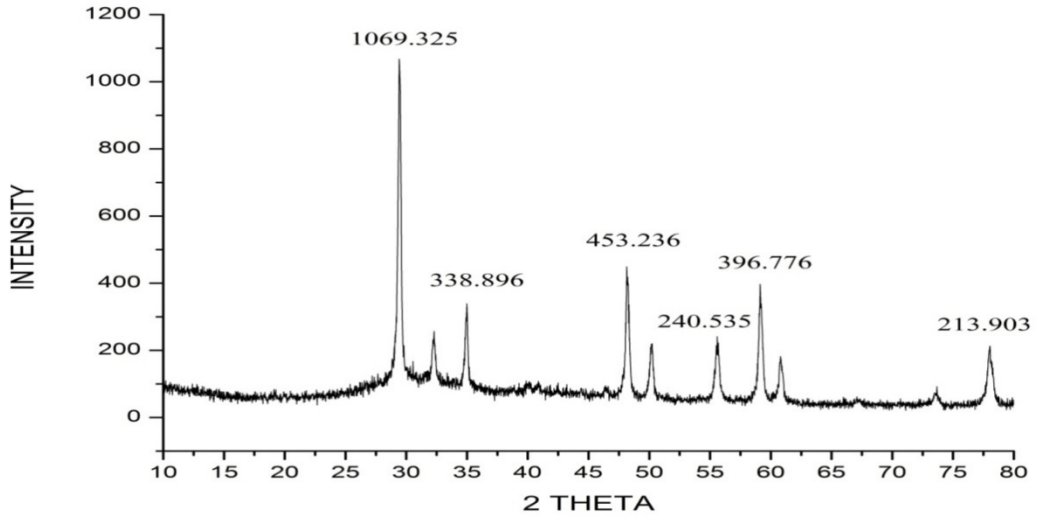
From the XRD data, considering the peak at degrees, average particle size has been estimated by using *Debye-Scherer formula (3)* is $D= 0.9 \lambda / \beta \cos\theta$. Inter-planar spacing between atoms (d-spacing) is calculated using *Bragg's Law (4)is* $2d\sin\theta = n\lambda$ and enumerated in Table 2.

Where, λ is wave length of X-Ray (0.1540 nm), β is FWHM (full width at half maximum), θ is diffraction angle, d is d-spacing and D is particle diameter size.

XRD analysis, Main Graphics view:

Nano-composite (Cd.Mo) : [iso-butyl alcohol (30ml) +H_2O (10ml) + Cd 2.56g + Mo 2.41g]

Measurement Date / Time	3/30/2015 3:01:23 PM	Scan Axis	Gonio
Start Position [°2Th.]	10.0142	End Position [°2Th.]	100.0062
Step Size [°2Th.]	0.0080	Scan Step Time [s]	14.5925
Scan Type	Continuous	PSD Mode	Scanning
PSD Length [°2Th.]	2.12	Offset [°2Th.]	0.0000
Divergence Slit Type	Fixed	Divergence Slit Size [°]	0.4785
Specimen Length [mm]	10.00	Measurement Temp.[°C]	25.00
Anode Material	Cu	K-Alpha1 [Å]	1.54060
Goniometer Radius [mm]	240.00	Dist. Focus-Diverg. Slit [mm]	91.00



XRD Graph:- 01Cd(iOBut)$_2$.Mo$_n$O$_x$(iOBut)$_4$-Glyptal

Table 2 Inter-planar spacing between atoms

Pos. [°2Th.] (θ)	2 θ	Cosθ	sin θ	FWHM [°2Th.] (β)	βcosθ	Size of particles (D)(nm)	Rel. Int. [%]
14.7134	29.4268	0.5458	0.8385	0.285	0.1552	0.2544	100
17.4971	34.9943	0.2166	0.9762	0.294	0.0636	0.6398	39.69
23.7259	47.4519	0.1632	0.9865	0.241	0.0393	0.8492	42.38
27.6429	55.2898	0.8071	0.5903	0.299	0.2413	0.1717	22.49
29.2144	58.4288	0.5897	0.8075	0.277	0.1633	0.2350	37.10
28.8291	77.6582	0.4266	0.9044	0.321	0.1369	0.3248	20.00

SEM Analysis of Cd(^{i}OBut)$_2$.Mo$_n$O$_x$(^{i}OBut)$_4$-Glyptal polymer

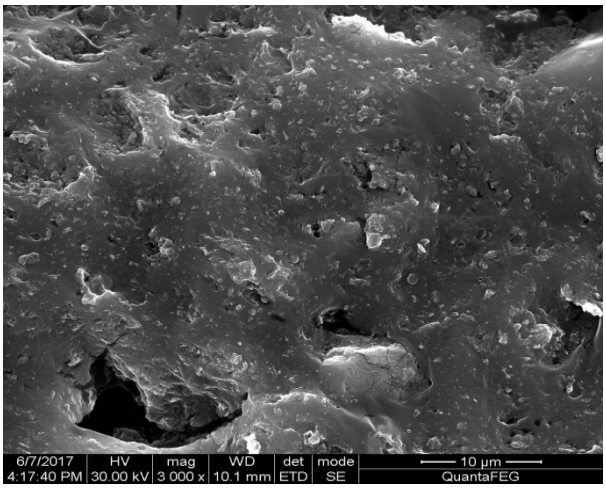


Fig.05

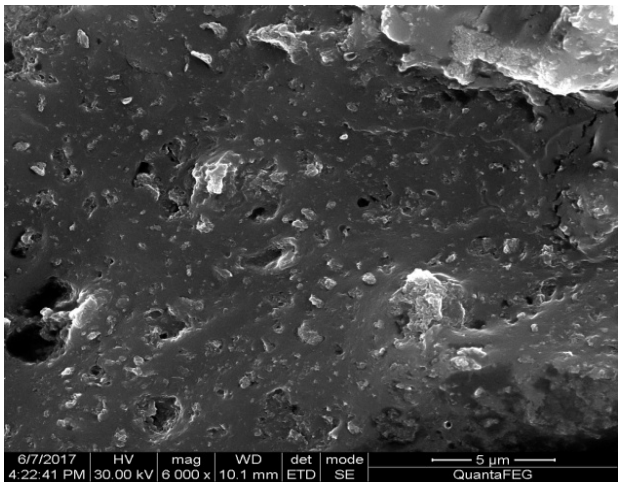
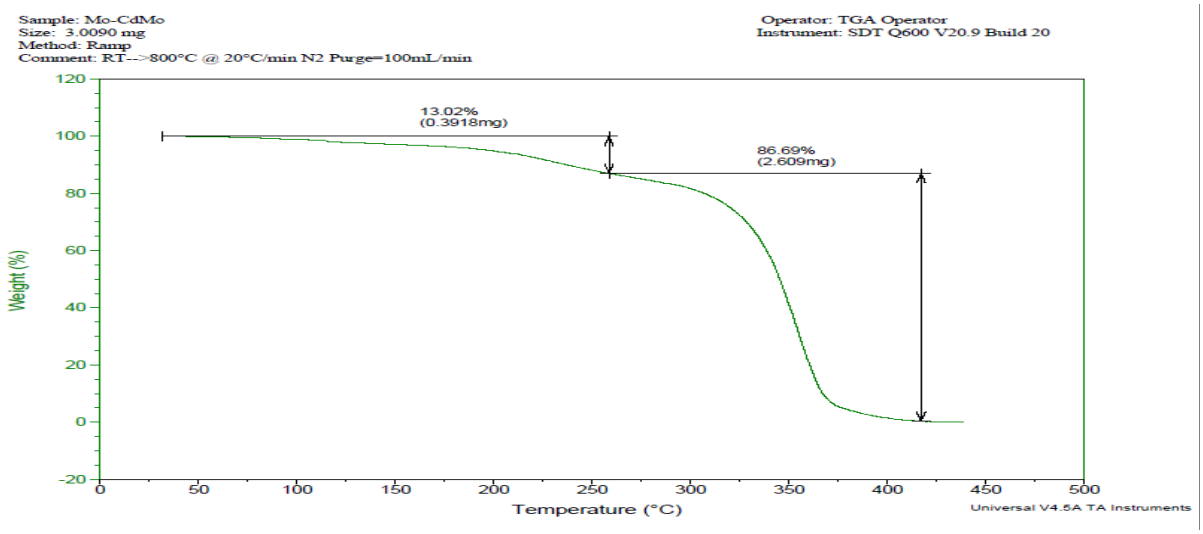


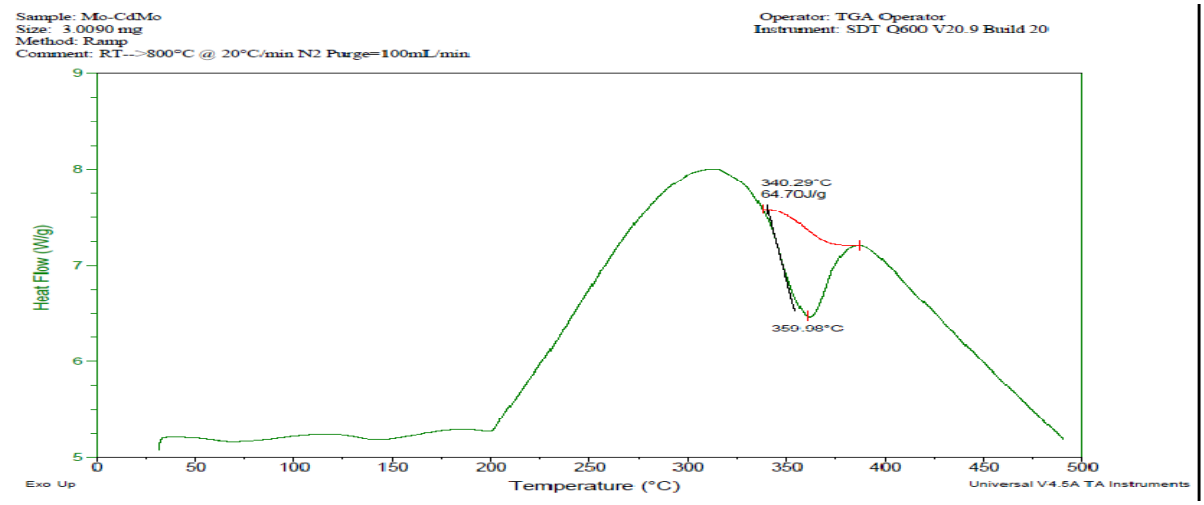
Fig.06

TGA and DSC Analysis of Cd(^{i}OBut)$_2$.Mo$_n$O$_x$(^{i}OBut)$_4$-Glyptal polymer



TGA Graph:- 02

DSC Graph:-03



Melting point and solubility of Cd(^{i}OBut)$_2$.Mo$_n$O$_x$(^{i}OBut)$_4$-Glyptal polymer

Table 3 Temperature Rangeand Solubility

Cd-Mo (0.025) +glycerol +phthalic anhydride	Temperature Rangeand Solubility's				
Solvent ⇩	45^{0}C	60^{0}C	80^{0}C	100^{0}C	110^{0}C
H_2O	X	X	X	X	X
CC_{l4}	X	X	X	X	X
ButiOH	X	X	X	X	X
Benzene	X	X	X	X	X
Toluene	X	X	X	X	X
1,4Dioxane	X	X	X	partially	YES

Results and Discussions

SEM, TGA and DSC Analysis of $Cd(^{i}OBut)_2.Mo_nO_x(^{i}OBut)_4$-Glyptal polymer

The miscibility between the organic polymeri.e.$Cd(^{i}OBut)_2.Mo_nO_x(^{i}OBut)_4$-Glyptal polymer phase and the nanocomposites phase was investigated by SEM and TGA. TheSEM images of the polymer hybrids are in Fig. 05 and 06, showthe phase separation at a magnification of about 3000X to 6000X. The white particles, whose size could be estimated tobe around 0.2544nm, indicate a nanocomposites phase(7,8). On the other hand, inthe case of the transparent hybrid polymers, the results suggest a homogeneous dispersion between the organicpolymer and the nanocomposites phase about 200 ◦C. The small apparent mass change at the end of the experiment is an corresponding to the furnaceswitching off. The thermal behavior of all the compositionswas investigated by sequentially firing both powder and fragmentsamples at temperatures between 500–800◦C for 20◦C/min anddetermining the crystalline products formed at each temperatureby XRD.

In TGA analysis graph 02, the weight of the sample is continuously recorded as a function of temperature. The hybrid organic polymer has change in weight of sample due to dehydration and decomposition as a function of temperature. In 250◦C first decrease 13.02% and 0.3918 mg of sample and maximum weight decreases of shown at between 250◦C to 418◦C i.e. 86.69% and 2.609 mg. it's results shows that the maximum stability in course of reaction time as a reagents. In DSC analysisGraph:-03, the heat absorbed or emitted by a system is observed by measuring temperature flow rate. In these, adiabatic calorimetric measurement for specific heat and enthalpy transition of polymeric composites (9-12). Heat energy 64.70 J/g absorption max. 318◦C, the degraded & heat evolved enthalpy transition temperature is 340.29 to 359.98◦C.

$Cd(^{i}OBut)_2.Mo_nO_x(^{i}OBut)_4$-Glyptal polymer almost insoluble in all organic solvent i.e. n-Hexane, Benzene, Toluene and water etc. but partially soluble in dioxane at temperature range 100-110^{o}C. The very small amounts of metal nanoparticles when added to the metal glyptal polymer has been shown the partially conductivity. We have determined the melting point by open capillary method. It is stable at very high temperature and the range are between 165-187^{o}C.

Conclusion

The XRD, SEM, TGA and DSC analysis ensures the insertion of metal nanoparticles in glyptal polymer. We have successfully synthesized **$Cd(^{i}OBut)_2.Mo_nO_x(^{i}OBut)_4$-Glyptal polymer**in a versatile and bio safe approach, at room temperature.A single source catalyst,simple economic and environmentally safe which will make it suitable for various applications in organometallic reagent. Dispersion of nanoparticles between organic polymers improves the thermal stability, organometallic properties and surface phenomenon. XRD analysis have confirmed that synthesized particle are multiphase anataseCd($^{i}OBut)_2.Mo_nO_x(^{i}OBut)_4$-Glyptal polymer and their average nano size isapproximately 0.2544 nm to 0.8492 nm. We expect that this synthesis technique would be extended to prepare many other important metal oxide nano structures.

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