



Synthesis, Characterization and Thermal Degradation Study of New Terpolymeric material

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ABSTRACT

This paper deals with the synthesis of new terpolymeric material by using oil bath. The material have been prepared by condensation of monomer i.e. orcinol,guanidine hydrochloride and formaldehyde in acidic medium (2 M HCl) in varying molar ratios. The sample was purified and then characterized by differentspectral methods like ¹H-NMR, IR and UV-visible techniques to elucidate the structure of orcinol-guanidine hydrochloride-formaldehyde(OGF) material. The thermal degradation ability of OGF material was studied using thermogravimetric analysis (TGA) in a static nitrogen atmosphere at a heating rate of 10°C/min. Freeman–Carroll and Sharp–Wentworth methods were used to calculate the thermal activation energy (E_a) and order of reaction (n).

Keywords: Terpolymeric material, orcinol, guanidine hydrochloride , formaldehyde, TGA.

Introduction:

The terpolymeric materials are high molecular weight compounds containing covalent bonds, however they are different from macromolecules. These terpolymers are reported to have better acid resistance, better thermal stability and electrical properties. Recently these materials are of academic interest and also investigated as the materials of electronics and photonics. The thermal degradation study of materials has become a subject of interest and provides information about the nature of species produced at various temperatures due to degradation. Terpolymers having good thermal stability have enhanced the scope for development of some polymeric materials.

Phenolic materials have a large number of practical applications in electronics, insulating materials, protective adhesives, aerospace industries etc. because of their high thermal stability, heat and chemical resistance and electrical insulation properties.

Michael and his coworkers have synthesized, characterized and studied thermal degradation of terpolymer prepared from salicylic acid, guanidine and formaldehyde¹ and 8-hydroxyquinoline-guanidine-formaldehyde.² Thermogravimetric analysis of 8-hydroxyquinoline-melamine-





formaldehyde resin has also been carried out by Gurnule and his coworkers³ and also have been reported the thermal degradation of resin preparing from 4-hydroxyacetophenone, catechol with formaldehyde and calculate the various kinetic parameters.⁴ Rahangdale et al. have been synthesized and studied the thermal degradation and determine their mode of decomposition, activation energy, order of reaction, frequency factor, entropy change, free energy and apparent entropy change.⁵ The preparation and thermal degradation of 2-hydroxy-4-methoxypropiophenone-urea-formaldehyde copolymers have been reported by Patel and his coworkers.⁶ They observed that copolymers prepared using equimolar proportions of reactants are thermally more stable. Terpolymers prepared by condensation of o-cresol and urea with formaldehyde in presence of acid catalyst have also studied for better thermal stability.⁷ Chauhan et al. reported the synthesis of self-crosslinked terpolymer derived from 4-acetylpyridine oxime, formaldehyde and acetophenone and studied the degradation process by using TGA.⁸ Thermogravimetric analysis of copolymer obtained from p-cresol, dithioamide with formaldehyde has also been carried out.⁹ The study of thermal degradation of terpolymer resins has been carried out by many researchers.¹⁰⁻¹² The Freeman – Carroll and Sharp- Wentworth methods have been applied for the calculation of kinetic parameters.¹³⁻¹⁶ Burkanudeen et al. have reported the thermal degradation of anthranilic acid, urea and formaldehyde in DMF as reaction medium.¹⁷ Recently, Dharkar and his coworkers synthesized a terpolymer involving melamine, aniline, and formaldehyde and reported its kinetic parameters on the basis of its thermal degradation.¹⁸

Extensive research work has been carried out on the synthesis, characterization and thermogravimetry of terpolymers by various researchers.¹⁹⁻²⁰

The present work reports on the synthesis and purification of new terpolymeric material derived from orcinol and guanidine hydrochloride with formaldehyde and their characterization by using different spectral and thermal studies.

Experimental:

All the chemicals used as starting materials in the synthesis of the material resin were of AR or chemically pure grade.

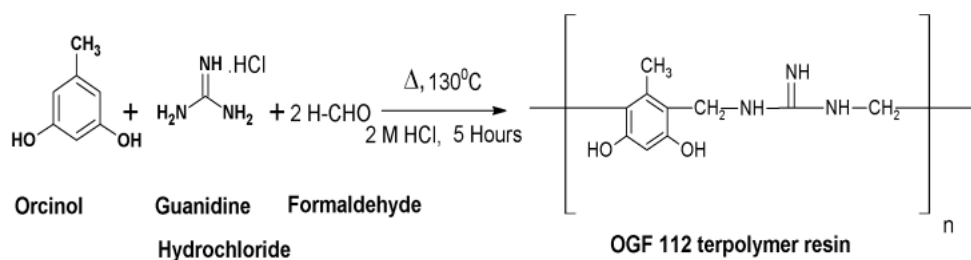
Synthesis of OGF Terpolymeric Material : The terpolymeric material OGF was prepared by condensing orcinol (0.1 mol) and guanidine hydrochloride (0.1 mol) with formaldehyde (0.2 mol) in the presence of acidic medium (2 M HCl) at 130^o C using





conventional oil bath. After 5 hours, the precipitate was obtained. Then this precipitate was filtered and washed with cold water and hot water again and again to remove the soluble impurities. This material resin was also purified by dissolution in 8% NaOH and re-precipitation by drop-wise addition of 1:1 (v/v) of 2 M HCl. The precipitated product was filtered off, washed repeatedly with hot water and dried in a vacuum desiccator over anhydrous calcium chloride.

Similarly, other types of OGF terpolymeric materials have also been synthesized in different molar ratios. i.e. 2:1:3, 3:1:4, 4:1:5.



Reaction scheme: Synthesis of OGF terpolymeric material resin

SPECTRAL ANALYSIS: Electronic absorption spectra of all the OGF materials in dimethyl formamide were recorded on Shimadzu spectrophotometer in the region 190-600 nm and also infrared spectra were recorded on Shimadzu FTIR spectrometer in the region of 4000-400 cm^{-1} at Institute of Pharmaceutical Education and Research, Borgaon (Meghe), Wardha. While $^1\text{H-NMR}$ Spectrum were recorded using Mercury Plus 300 MHz NMR Spectrometer at SAIF, IIT, Bombay. The spectra were recorded in CDCl_3 solvents and TMS was used as reference.

THERMOGRAVIMETRIC ANALYSIS : The modes of thermal degradation of all the OGF materials were analyzed using thermogravimetric analyzer (TA Instruments Model SDT Q600) at a heating rate of $10^\circ\text{C}/\text{min}$ in a static nitrogen atmosphere at SAIF, IIT, Bombay. Based on the results obtained, the degradation pattern, activation energy (E_a) and order of the reaction (n) were calculated by Freeman-Carroll and Sharp-Wentworth methods.^{1-2, 13-16}

Results and Discussion :

The terpolymeric material OGF was orange colour, insoluble in water but partially soluble in N,N-dimethylformamide, dimethylsulfoxide, diethyl ether, ethyl alcohol, acetone, 1,4-dioxane, petroleum ether but completely soluble in NaOH and KOH solutions.

Spectral analysis:

Electronic Absorption Spectra: The electronic spectra of all the ratios of OGF were recorded in spectroscopic grade in absolute ethanol. These gave rise to three



characteristic bands in the region 250-295,315-380 and 418-450nm which is shown in **Figure 1**. These observed positions of bands indicate n-o* transition which may be due to the C-O of the phenolic OH group, the presence of π - π^* transitions in C=N group in conjugation with an aromatic ring while the later may be due to n- π^* transition for the presence of the phenolic hydroxyl group. This observation is in good harmony with the most probable structures of these terpolymeric materials.

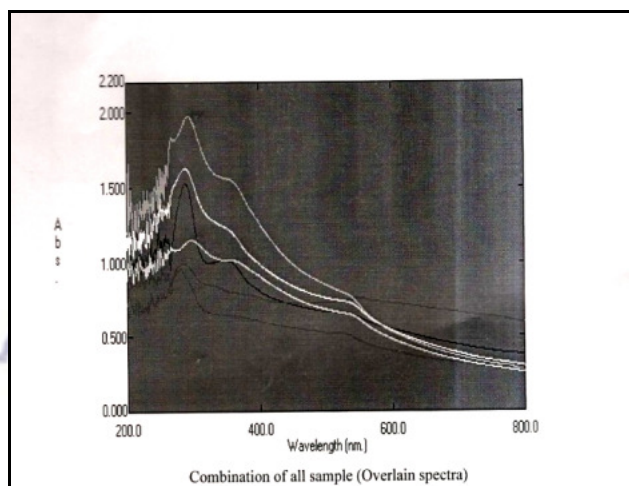


Figure 1 - Electronic Absorption Spectra of OGF (combine)

FTIR spectra: The IR spectrum provides useful information about the linkages and the functional group present in the terpolymeric material. The Infra-Red spectra of all the OGF materials are presented in **Figure 2** and IR spectral data are tabulated in **Table No.1**.

The assignment of vibrational frequencies is mainly based on the data available in the literature.

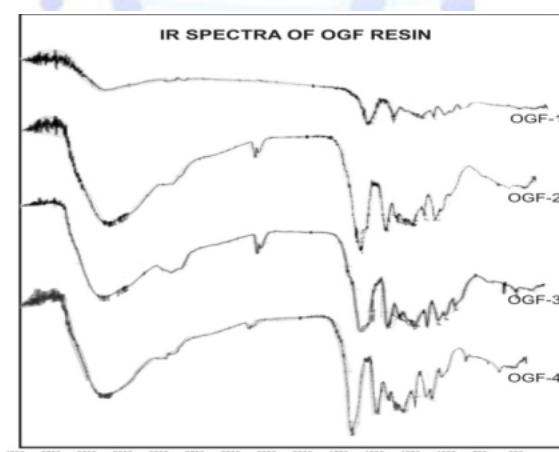


Figure 2 - FTIR Spectra of OGF(Combine)

Table 1- FTIR spectral data of OGF

Assignment	Observed band Frequency (cm ⁻¹)	Expected band Frequency (cm ⁻¹)	References
Phenolic -OH stretch	3450-3500	3750-200	[1,2]
-N-H stretch (imide)	3200	3500-800	[1,2]
-N-H bend(imide)	680	800-600	[1,2]
Aromatic ring vibration	1440	1600-450	[1,2]
Methylic bridge (-CH ₂) modes Rock	741	800-710	[1,2]
Methylic bridge (-CH ₂) modes Bend	1420	1460	[1,2]
Methylic bridge (-CH ₂) modes Wagging	1320	1300-200	[1,2]
C=N (imines)	1616	1690-630	[1,2]
-substituted benzene ring	690	710-690	[1,2]

¹H-NMR spectra: All the OGF materials shows same type of proton NMR spectra and represented in **Figure 3**. The NMR spectra of OGF terpolymeric material show a signal appearing at δ 7.38 ppm may be aromatic proton. The broad signal appearing in the region δ 6.2-6.4 ppm may be due to phenolic proton (intermolecular hydrogen bonding). The signal appearing in the region δ 6.5-8 ppm may be due to C=N. The signal appearing in the region δ 2.3-3.2 may be due to Ar-CH₂-N moiety. The signal appearing in the region δ 3.5-8 ppm due to -NH- bridging. The sharp signal appearing at δ 1.2 ppm may be due to methyl group of orcinol moiety of resin. [1,2]

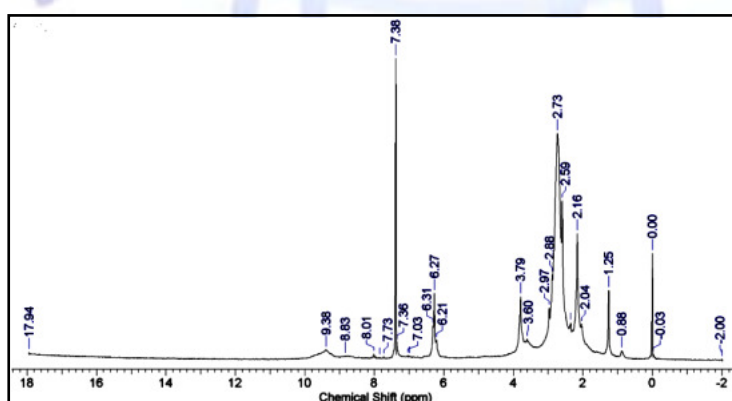


Figure 3 -¹H-NMR spectra of OGF

Thermogravimetric analysis: The thermogravimetric analysis is an effective and useful technique to measure the thermal stability of the materials. The thermal analysis of all the OGF materials have been carried out and the thermograms &



kinetic plots are given in Figure 4–15 and the data of parameters are given in Table No.2.

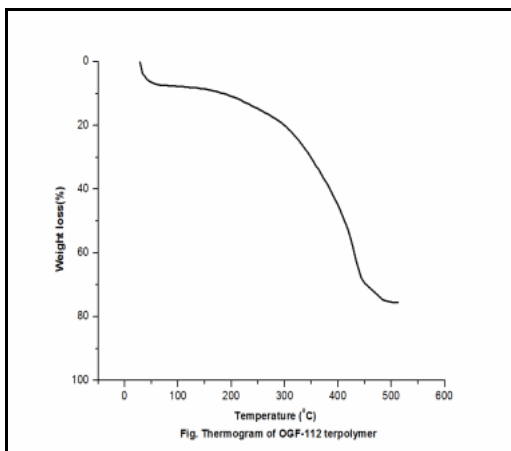


Figure 4 - Thermogram of OGF-112

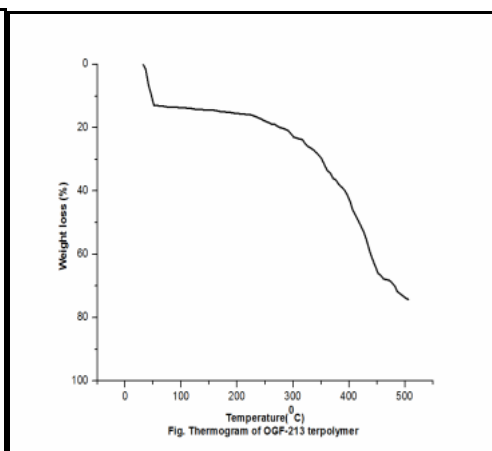


Figure 5 - Thermogram of OGF-213

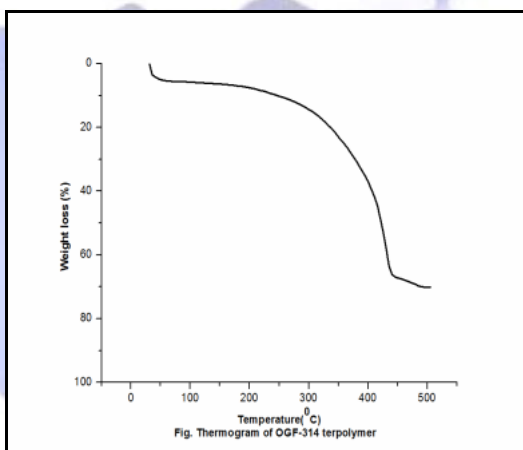


Figure 6 - Thermogram of OGF-314

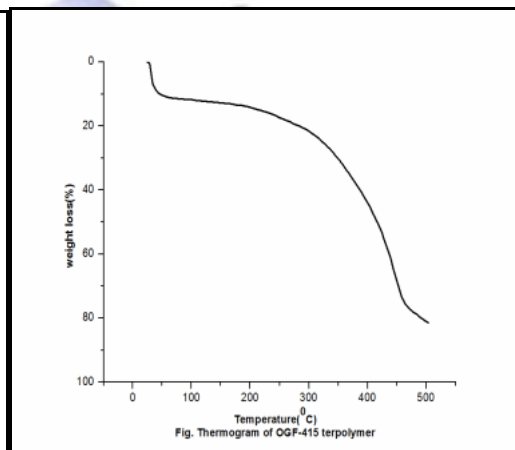


Figure 7 - Thermogram of OGF-415

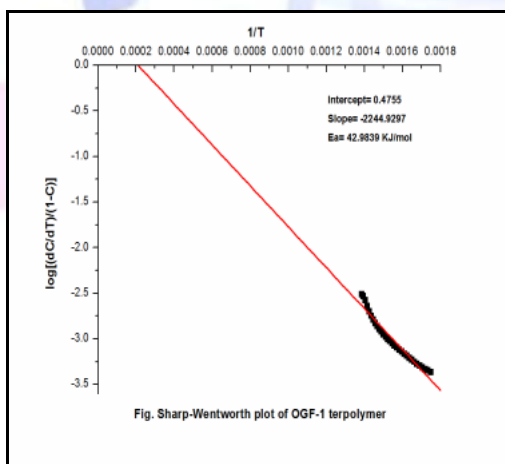


Figure 8- Sharp-Wentworth plot of OGF-112

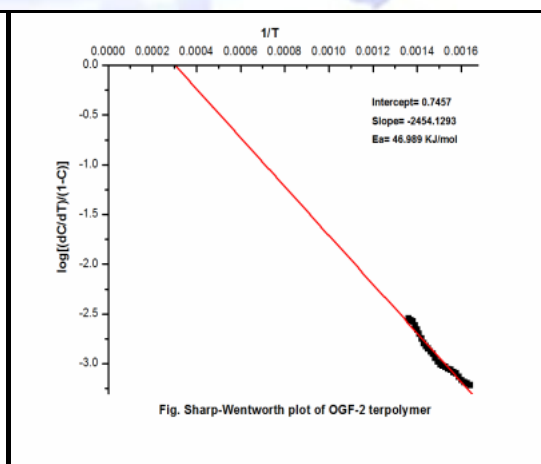


Figure 9- Sharp-Wentworth plot of OGF-213



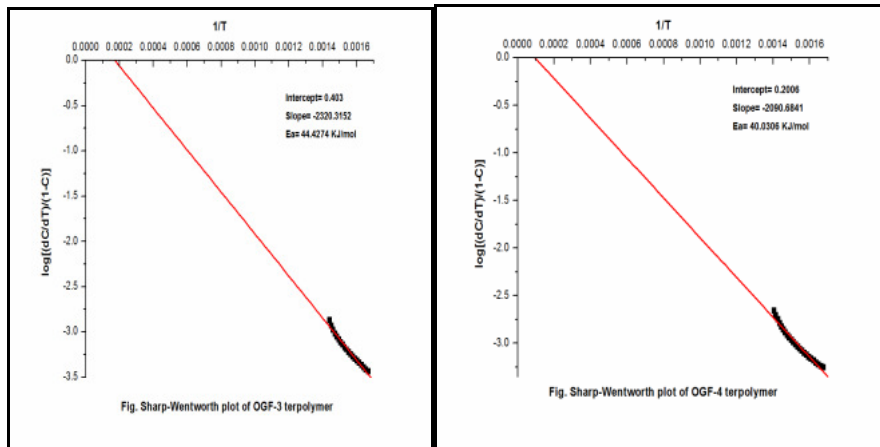


Figure 10- Sharp-Wentworth plot of OGF-314 Figure 11- Sharp-Wentworth plot of OGF-415

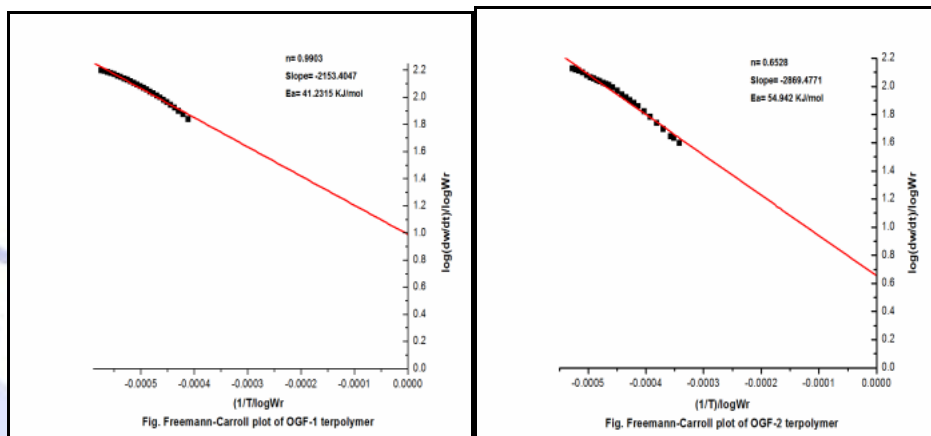


Figure 12 –Freeman-Carroll plot of OGF-112 Figure 13 –Freeman-Carroll plot of OGF-213

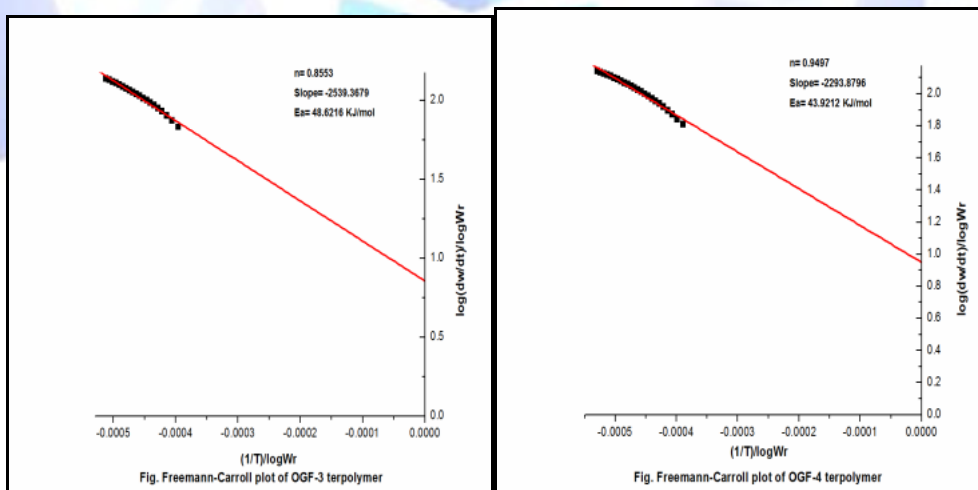


Figure 14 –Freeman-Carroll plot of OGF-314 Figure 15 –Freeman-Carroll plot of OGF-415

From the thermograms, it is seen that by raising the temperature from 28^o-513^oC, the material lost their weight continuously. All the OGF materials show only one stage of decomposition from 40^o-495^oC. The results are suggestive for significant difference in the energy of activation of different OGF materials. These aromatic materials have found to exhibit a good magnitude of the thermal





activation energy of decomposition process. The order of reaction at the stage of decomposition was calculated to be nearly unity.

The kinetic parameters resulted into conclusion that all these terpolymeric materials show approximately same trend of degradation mechanism.

Table 2 - Kinetic and thermodynamic Parameters of OGF materials

Terpolymeric materials	Half decomposition Temperature (K)	Activation Energy(E_a) (KJ/mol)		Order of reaction(n)
		FC	SW	
OGF-112	684.06	41.2315	42.9839	0.9903
OGF-213	691.71	54.942	46.989	0.6528
OGF-314	695.9	48.6216	44.4274	0.8553
OGF-415	690.7	43.9212	40.0306	0.9497

Conclusion:

The terpolymeric materials OGF were synthesized by condensation of orcinol and guanidine hydrochloride with formaldehyde in the presence of acid catalyst using conventional method in different molar ratios. The material OGF is orange colour, insoluble in water but partially soluble in ethanol, diethyl ether, N,N-dimethyl formamide, dimethyl sulphoxide, acetone, 1,4-dioxane, petroleum ether. From IR, UV-Visible and $^1\text{H-NMR}$ spectral studies the proposed structure of the OGF material was confirmed. From TGA, it is seen that the energy of activation evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be nearly equal indicating the common reaction mode of decomposition while degradation pattern follows nearly the first order kinetics.

Acknowledgements:

The authors wish to express their sincere thanks to the Principal, J.B.College of Science, Wardha(India) for providing the necessary facilities and rendering their valuable guidance. The authors also like to thank SAIF, Punjab University, Chandigarh, SAIF, IIT, Bombay and Principal, Institute of Pharmaceutical Education And Research, Borgaon(Meghe), Wardha for their services for spectral and thermal analysis.

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