



Thermal Stability Analysis of PbO/ISO-UP Resin Composites

Harish Venkatreddy*, Ashok Godekere Visweswaraiiah[†],
Shivaprasad Nambihalli Gopalakrishna[‡] and Niranjana Prabhu
Thippeswamy[♦]

Abstract

Composites of Isophthalate based unsaturated polyester (ISO-UP) resin with various concentrations of lead monoxide (PbO) filler were fabricated and investigated for degradation kinetics & thermal stability of the composites. The thermogravimetric data have been treated with Freeman-Carroll & Horowitz-Metzger methods and results were discussed. The filler concentration effect on thermal stability & degradation kinetics of composites were also discussed. Neat sample was observed to exhibit one stage degradation while the filled composites undergo degradation at two stages. Further, with the increased filler content in the composite the initial degradation temperature values (IDT) as were found to decrease from 337°C for neat polymer to 304°C for 50% filled composite whereas presence of filler slows down the degradation process. Among the two classical degradation kinetic theories used, Freeman-Carroll method yields almost close activation energies from 18.295KJ/mol to 20.029KJ/mol while Horowitz-Metzger method yields activation

* Department of Physics, Government First Grade College, Shikaripura - 577427, India. Email: harishvenkatreddy@gmail.com

† Department of Physics, Government College (Autonomous), Mandya - 571401, India. Email: ashok.godekere@gmail.com

‡ Department of Physics, Government First Grade College, Chamarajanagara - 571313, India. Email: ngsprasad1981@gmail.com (*Corresponding Author*)

♦ Department of Chemistry, MS Ramaiah University of Applied Sciences, Bangalore - 560054, India, Email: niranjan1975@gmail.com

energies from 17.919KJ/mol to 13.198KJ/mol. Both methods indicate that thermally stability of composites increase at lower filler loading but tend to decrease at higher filler loading.

Keywords: Thermogravimetry, Degradation kinetics, Polymer composites, Unsaturated polyester.

Introduction

Materials such as high-density concrete, metals or metal alloys or lead bricks are often used as general radiation shielding materials for radiation shielding purpose [1, 2]. Many of these materials cannot be used under all conditions due to their bulk nature and lack of service flexibility [1]. As a solution, high density polymer composites of different polymer-filler combinations have been recommended as flexible radiation shields [3]. Many such shields are used in radiotherapy, x-ray radiography, personnel and equipment near nuclear reactors, space applications, etc. Polymer materials have advantages in cost, flexibility, molding, and volume reduction after use, etc. but inferior as radiation shields compared to metals [4]. Several investigators have fabricated and investigated variety of polymer composites filled with various metal or metal oxides for radiation shielding applications. Few to mention are, Landler *et al.*, have fabricated composites of Polyethylene and lead compounds [5]. MacLeod *et al.*, have prepared highly filled thermoplastic compositions of PbO (81 % by weight) in an ethylene/vinyl acetate copolymer, without plasticizer for attenuation of electromagnetic radiations [6]. Rizwan Hussain *et al.*, have studied the shielding properties of polyethylene glycol-lead oxide composites [7]. Abdul Aziz *et al.*, fabricated Styrene-Butadiene rubber/Lead oxide composites as gamma radiation shields and also studied their thermal and mechanical properties [8, 9]. Pavlenko *et al.*, investigated the radiation-protective characteristics of a thermoplastic polystyrene composite material filled with a high-dispersion modified lead oxide [10]. H Chai *et al.*, have prepared and characterized novel, flexible, x-ray shielding materials containing tungsten and bismuth(III) oxides [11]. O Evcin *et al.*, have investigated the production of barite and boroncarbide doped radiation shielding polymer composite panels [12]. Bagheri *et al.*, have thermal resistance, tensile properties, and

gamma radiation shielding performance of unsaturated polyester/nanoclay/ PbO composites [13]. Demir *et al.*, studied gamma ray and neutron shielding characteristics of polypropylene fiber-reinforced heavyweight concrete exposed to high temperatures [14]. Akman *et al.*, presented gamma attenuation characteristics of CdTe-doped polyester composites [15]. Mona M. Gouda *et al.*, have fabricated nano tin oxide/dimethyl polysiloxane reinforced composite as a flexible radiation protecting material [16]. Literature review reveals that in many such investigations to evaluate polymer composites, radiation shielding characteristics was considered as only main parameter and no other characteristics of polymer composites such as their stability to thermal, chemical, electrical, radiation, corrosive environments in addition to mechanical flexibility were given importance. Polymer composite shields during their service life, are inevitably exposed to different degrading environments. Hence these characteristics also play important role to evaluate and label a material as flexible and excellent radiation shield. Particularly high temperature environments, may setup degradation reactions in the polymer composites and affect the performance of these radiation shields. Hence, in this direction, authors propose to fabricate new polymer composite combination using lead monoxide (PbO) as recommended filler [17,18] with density (9.82g/cc) and a stable unsaturated polyester containing stable benzene rings and isophthalate groups recommended as radiation resistant and chemically resistant polymer [19]. These polymer composites fabricated and investigated for radiation shielding, thermo-mechanical stability, chemical stability and thermal stability. The details of thermal stability and kinetic parameters of thermal degradation evaluated using thermogravimetric analysis method [20] have been presented in this paper.

Materials and Methods

Polymer composites of commercial grade ISO-UP resin and PbO powder with different compositions (0, 5, 10, 20, 30, 40 & 50% by weight of filler) were casted into 3 mm thick sheet form using open mould method [21] and labeled as S1 to S7 respectively. Beyond 50% of filler addition, uniform distribution of filler is quite difficult in open mould casting method due to increased agglomeration and also settling of

filler. These composites characteristics for radiation shielding [21, 22], thermomechanical stability [23] and chemical stability [25] have been investigated and reported elsewhere. The details of FTIR, SEM and powder XRD thermal stability and kinetic parameters of thermal degradation evaluated using thermogravimetric analysis method in addition to FTIR, SEM and powder XRD investigations have been presented in this paper.

The composite samples were investigated for polymer-filler interaction using Spectrum RX-FTIR Spectrometer, PerkinElmer, USA. Gold plated fractured surfaces of neat polymer and filled composites were observed under Scanning electron microscope (S-4700 Cold FE-SEM, Hitachi High Technologies America, Inc., Annexure-V) to examine the nature of polymer-filler binding, the filler particle size and dispersion in the composite. Powder X-ray diffraction measurements were done on pristine polymer and filled composites to investigate the physical structure of the composite samples for 2θ ranging from 10° to 60° using Cu-K α line of MiniFlex-II, Rigaku Benchtop X-ray diffractometer. The composite samples of about 3 to 6 mg weight were characterized for thermal degradation using Thermo-gravimetric Analyzer (TGA), TA Instruments, USA. The samples were heated in air atmosphere at a heating rate of $10^\circ\text{C}/\text{minute}$ from 26°C (room temperature) to 800°C . TGA data were analyzed for degradation onset temperature or initial degradation temperature (IDT), temperature at maximum degradation rate, degradation rate maximum and residual weight.

Thermogravimetry has been accepted as reliable, exact and fast method for studying kinetics of thermal decomposition. In order to evaluate degradation kinetic parameters such as activation energy, reaction order and pre-exponential factor from weight loss data, classical laws of kinetics have been used²⁰.

Using the general formulation, the chemical reaction rate ($d\alpha/dt$) in terms of the degree of conversion (α), can be shown as

$$\frac{d\alpha}{dt} = k_n(1-\alpha)^n \quad (1)$$

where k_n is the specific rate with kinetic reaction of order n and α is the normalized weight loss.

Differential technique was used to find the reaction rates ($d\alpha/dt$) by incorporating heating rate into the temperature and weight-fraction data. Applying Arrhenius kinetics to degradation process, the rate constant, the absolute temperature, T and the activation energy E_a were related as.

$$k_n = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

Where A be the pre-exponential factor and R be the gas constant.

For thermal decomposition, the overall rate equation of conversion α in Arrhenius form was expressed by combining the above two equations as,

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) (1-\alpha)^n \quad (3)$$

Considering a constant heating rate: $\frac{dT}{dt} = \beta$, above equation can be transformed as,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) (1-\alpha)^n \quad (4)$$

Using equations similar to those above and applying appropriate approximations several thermal degradation kinetic theories have been discussed. Among them, following Freeman-Carroll [25] and Horowitz-Metzger [26] are quite popular methods for the discussion of thermal degradation kinetics using single heating rate.

Freeman-Carroll method

Freeman and Carroll derived a straight-line equation for thermal degradation as,

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = n - \frac{E_a}{2.303R} \frac{\Delta(1/T)}{\Delta \log W_r} \quad (5)$$

Where dw/dt = rate of decrease/change of weight,

W_r = final weight loss - total weight loss up to time t

E_a = activation energy, T = Temperature, n = reaction order

A straight-line plot between $\frac{\log(dw/dt)}{\log W_r}$ vs $\frac{1/T}{\log W_r}$ yields activation energy (E_a) as the slope with reaction order (n) as Y-axis intercept.

Horowitz-Metzger method

Horowitz-Metzger has given a straight-line equation for thermal degradation through single-reaction pyrolysis process which leads only to gaseous products as follows,

$$\ln \left\{ \ln \frac{W_0}{W} \right\} = \frac{E_a \theta}{RT_e^2} \quad (6)$$

Where W = Weight of sample at time t , W_0 = Initial sample weight, $\theta = T - T_e$, T_e = temperature at $W/W_0 = 1/e$ and T = temperature at time t and, E_a = activation energy.

A straight-line plot of $\ln\{\ln W_0/W\}$ vs. θ gives E_a from slope.

Results and Discussion

FT-IR transmittance spectra of the composite samples have been shown in figure 1 and observed band data are shown in table 1. The broad peak observed in the range of 3504 to 3547 cm^{-1} shows the hydroxyl group present in ISO-UP resin. The 3028 cm^{-1} peak indicates the aliphatic C-H stretching in styrene. It shows the possible presence of unreacted styrene monomer in the polymer. The range of 2,927 – 2934 cm^{-1} peaks show the occurrence of methylene group asymmetric stretching. The -CO group present in the polymer shows absorption in the range from 1,724 to 1,727 cm^{-1} . The peaks in the range 1602 to 1606 cm^{-1} and 1017 to 1018 cm^{-1} are due to the polystyrene. The 1494 and 731 cm^{-1} peaks indicate the mono substituted benzene rings and the peak at 701 cm^{-1} shows the presence of iso or meta substituted benzene rings. The peaks at 1270 and 1244 cm^{-1} indicate the aromatic ketone groups in the polymer network. The peaks at 3061, 1645 and 1156 to 1075 cm^{-1} are due to the presence of unsaturated carbon bonds [27, 28, 29].

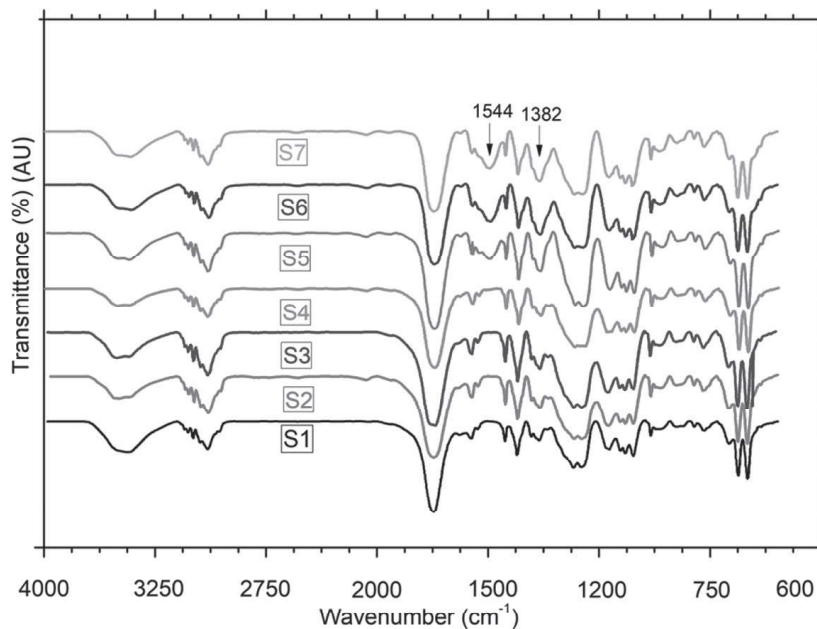


Figure 1. FT-IR spectra of the composites.

IR Band (cm ⁻¹)	Group
3504 to 3547	-OH
3028	C-H stretching in Styrene showing presence of unreacted Styrene
2927 to 2934	-CH ₃ Asymmetric stretching
1724 to 1727	-C=O
1602 to 1606 and 1017 to 1018	Polystyrene
1494 and 731	Mono substituted Benzene ring
701	iso or meta substituted Benzene ring
1270 and 1244	Aromatic ketone groups
3061, 1645 and 1156 to 1075	-C=C-, unsaturated carbon double bonds

Table 1. FT-IR peak data of the composites.

From the plots it is evident that none of the absorption peaks of the pristine polymer undergo modification either as peak shift or disappearance of characteristic peaks indicating that the filler at all its concentrations in the composite has a little or no effect on chemical structure of the polymer matrix. However, at higher concentrations (above 30% wt. fraction) a new peak was observed at wave number

1544 cm^{-1} and also a peak at 1382 cm^{-1} shows modification in peak intensity. These observations may be attributed to the nature of the polymer and filler interactions which may not be the type of chemical interactions but merely a physical or a mechanical locking of the filler in the matrix of polymer chains.

Scanning electron microscope pictures recorded on fractured surfaces of neat polymer and filled polymer (S5, 30% weight PbO filled composite) are shown in figures 2, 3 and 4. Figure 2 shows the brittle surface fracture of neat polymer with regularly graded ridges having average width as 10 microns. In addition, there are wider and lighter streaks departing from the ridges which represent the fraying or detachment of ribbon-like strands from the ridges during fracture. It is a common fracture mode in neat thermosets [21].

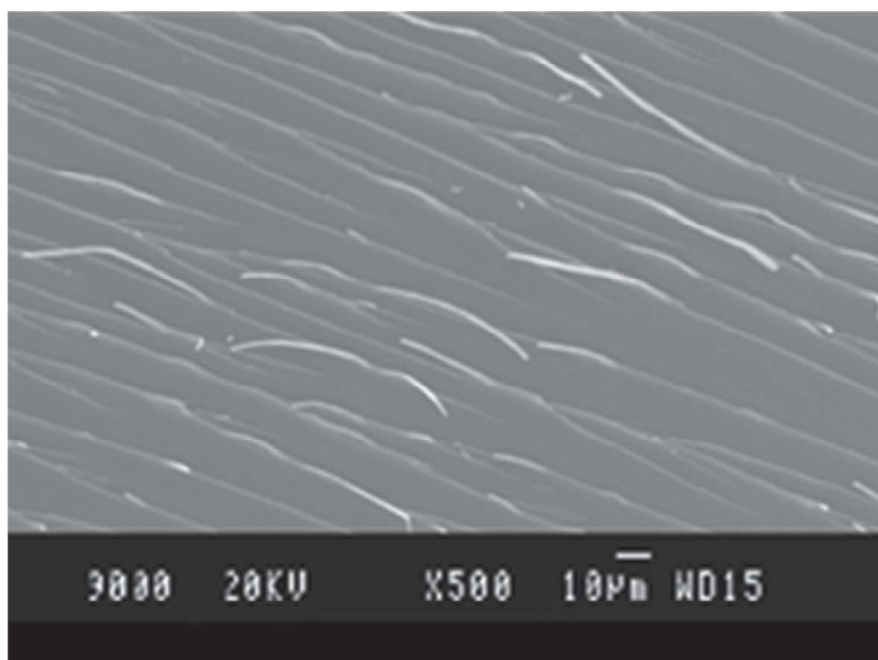


Figure 2. SEM image of neat polymer.

Figure 3 and 4 show the dispersed morphology of the filler in fractured surface at low and high magnification of 30% filled content respectively. With an average inter particle distance of about 10 μm , the filler particles have a good dispersability with an average size of about 5.36 μm [21]. From figure 3, one can see filler particles having radial fronts at one end link with at least one or more particles along the ridge path. The presence of filler particles in the matrix creates

such a radial path (crack propagation) quite different than observed for the neat resin. The crack propagation in neat polymer is almost straight due to the absence of filler. Presence of filler particle along ridges and creation of radial fronts influence the progression of the crack in filled composites. With more filler loading, the ridges become less pronounced due to decreased tension in the matrix resulting in a smoother surface during fracture.

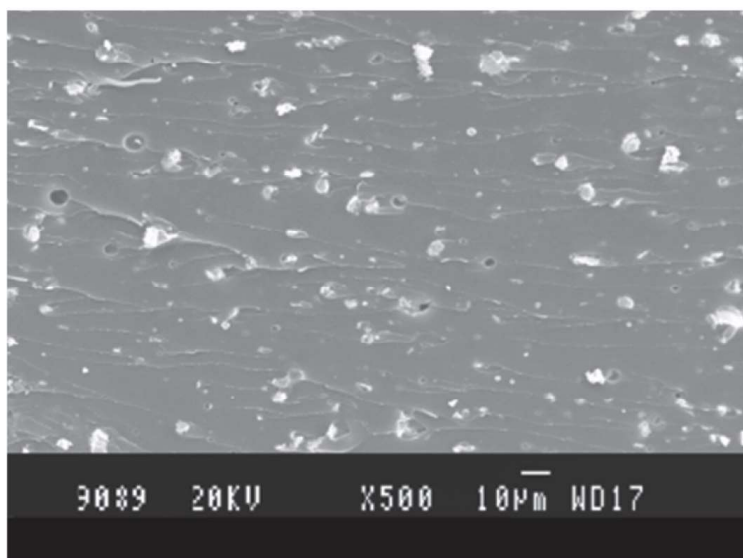


Figure 3. SEM image of 30% weight PbO filled (S5) composite.

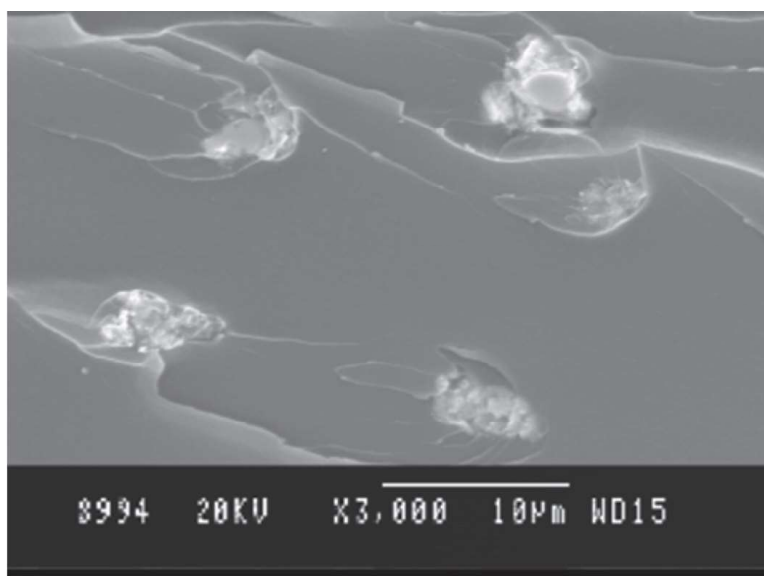


Figure 4. SEM image of 30% weight PbO filled (S5) composite (high resolution).

Powder x-ray diffractograms of neat polymer and filled composites are shown in figure 5. A broad peak centered around 19.20 degree and diffused scattering from 30 to 60 degrees with some minor peaks observed for neat polymer, show mainly the amorphous nature of the neat sample S1.

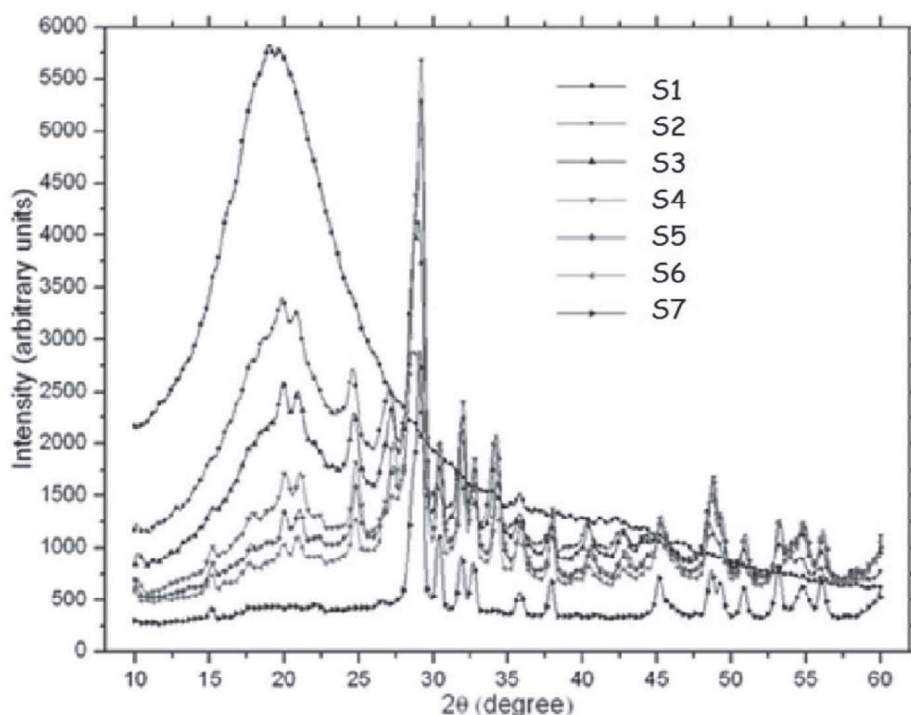


Figure 5. Powder x-ray diffractograms of neat polymer and filled composites (S1 to S7 downwards in order)

The observed broad peak and diffused scattering pattern is mainly due to their long chain structure with a relatively large number of defects. Further, the presence of polymer crystallites if any are relatively very small with a large surface to volume ratio enhance the contribution of interfacial disorganization on the diffraction pattern [30, 31, 32]. In figure 5, the patterns observed for filled composites are the result of overlapping of peaks due to both polymer and the filler. Prominent & relatively sharp peaks observed at 2θ values equal to 29.12, 30.35, 32.62, 37.80, 45.21, 49.33, 50.76, 53.14 & 56.10 degrees refer to the scattering from the filler particles. In all the samples these peaks were found to be unique and remain in the same positions. The peaks observed are found to be in good agreement with ICDD-JCPDS database [33]. Further, the additional minor peaks observed

at 2θ values equal to 24.66, 27.14, 34.22, 40.43, 42.74, etc degrees in the samples S2 to S7 are attributed to scattering from polymer layers formed around filler particles. These observations also do not provide any information on possible chemical interaction between polymer and filler in the composite.

Thermograms and derivative thermograms of the composite samples are shown in figures 6 and 7 respectively. Pristine polymer S1 was observed to undergo one-stage degradation process in a temperature region from 300°C to 400°C whereas the filled composite samples undergo two-stage degradation with a temperature range extending from 300°C to about 750°C. The weight loss which occurs before IDT may be attributed to the removal of volatile content present in the polymer such as water and un-reacted styrene [34, 35]. The residual weight % left after 750°C indicates the amount of lead monoxide filled in the composite sample which is quite stable at these temperatures.

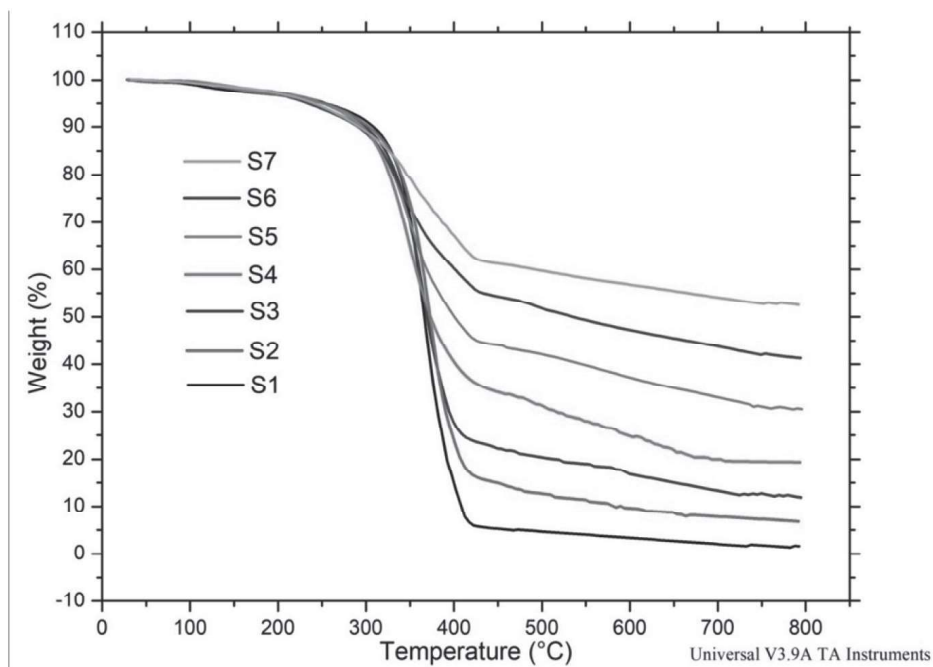


Figure 6. TGA Thermograms of the composites.

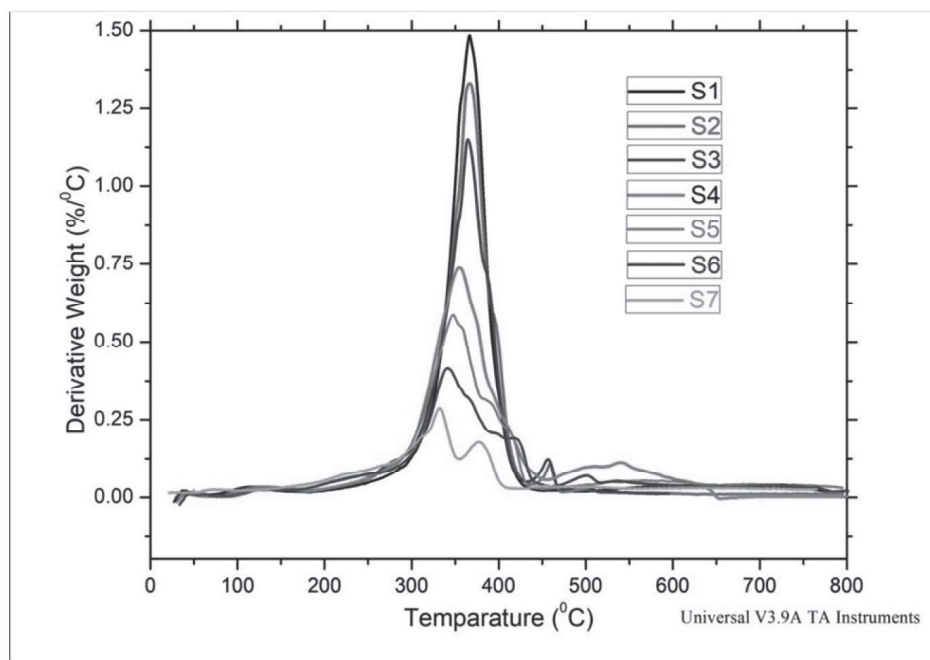


Figure 7. Derivative thermograms of the composites.

It is evident from the results of analysis of the TGA data shown in table 2 and associated figures 6 and 7 that IDT values decrease from 337°C to 304°C with increasing filler content in the composites. T_{max} , the temperature at which maximum degradation rate occurs was also observed to decrease from 367°C (for S1) to 343°C (for S7). However, the degradation rate and also the maximum degradation rate R_{max} values decrease with increased filler concentration in the composite. The decrement in IDT values might be possible due to the the bigger filler particles (average particle size 5.36 μ m) present in between the polymer molecules which generally reduces the crosslink density of the polymer and thereby affect the thermal properties. [21] Hence the presence of the filler in the composite retards the degradation rate but favours the onset of degradation process. Also, the decrease in maximum degradation rate may be attributed to the reason that the particulate filler present in the composites influence the degradation process of polymer molecules which are in contact with them. These polymer molecules show more stability to external temperature effect and hence do not degrade easily. Further from figures 6 & 7, it was observed that the first stage of degradation of both the pristine and filled composites was observed below 400°C and can be attributed to degradation process of the polymer component of the composite

which is not in contact with the filler. The above reason can be verified by determining the temperature $T_{1/2}$ at which 50% of the polymer content present in the composite undergoes degradation. The $T_{1/2}$ values determined were observed to spread over a narrow range of temperatures from 360°C to 365°C which directly indicates that no role played by the filler in degradation of the polymer molecules which are not in contact with the filler and values of $T_{1/2}$ are shown in table 2. The second stage of degradation was observed only in filled composites from about 400°C and ends up at around 750°C. This can be attributed to degradation of the polymer molecules which are in contact with the filler and the rate of degradation is slower than that of the first stage. This fact may be due to the presence of strong adhesion interaction between the polymer and filler.

Among the two kinetic theories applied, Freeman-Carroll plots shown in figure 8 and Horowitz-Metzger plots shown in figure 9 yield straight line plots and quite acceptable in different stages of degradation process. The kinetic parameters determined from these theories are shown in table 2.

Table 2. Results of thermo-gravimetric analysis of the composites.

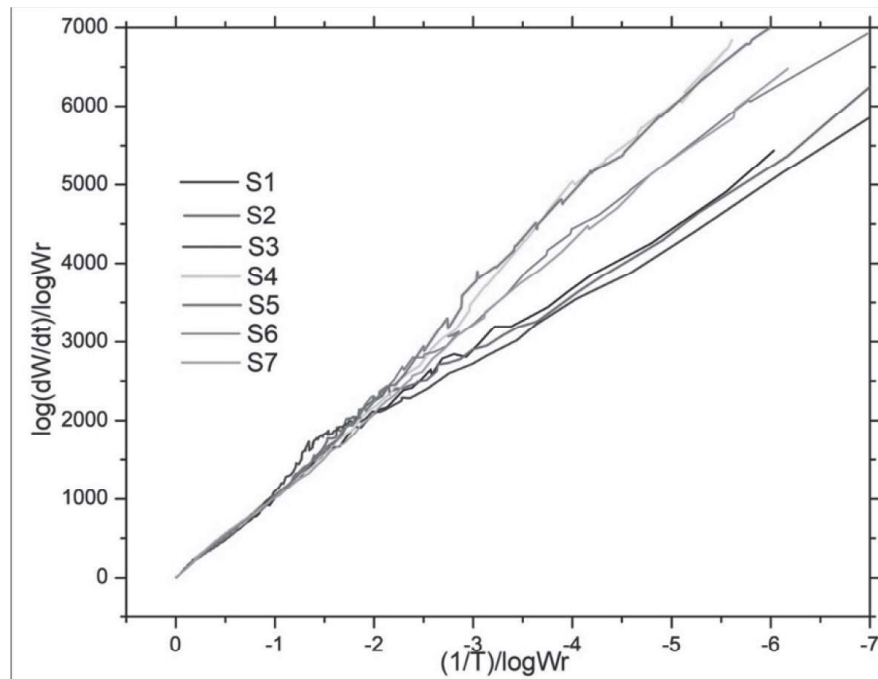


Figure 8: Freeman-Carroll plots of the degradation kinetic analysis.

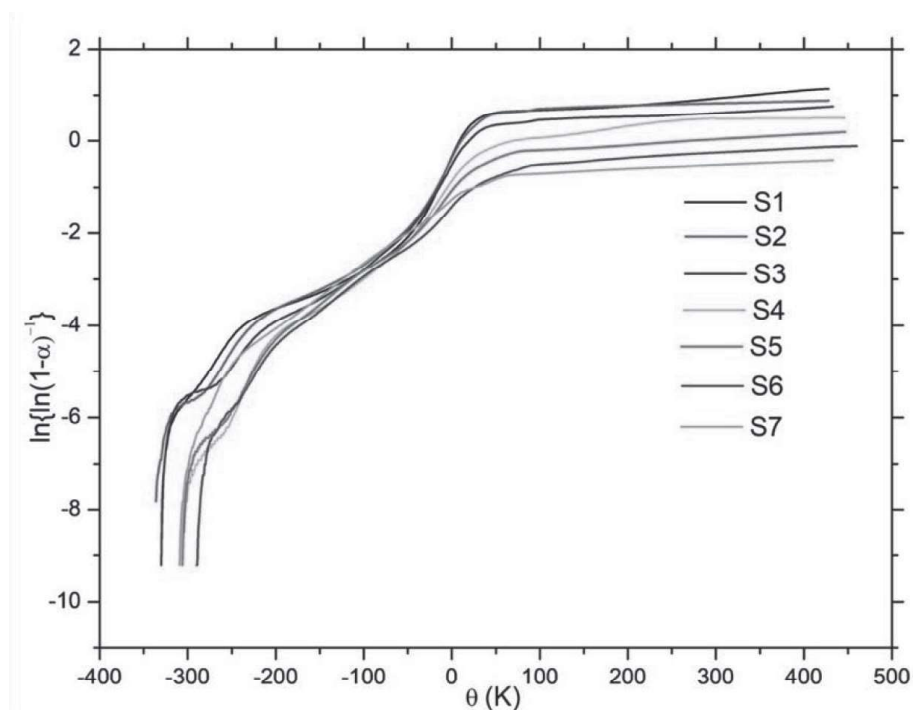


Figure 9: Horowitz-Metzger plots of the degradation kinetic analysis.

Sample	wt% of PbO filler in composite	IDT (°C)	$T_{1/2}$ (°C)	1 st Stage Degradation		2 nd Stage Degradation		Activation Energy (E_a) KJ/mol	
				T_{max} (°C)	R_{max} (wt%/°C)	T_{max} (°C)	R_{max} (wt%/°C)	Freeman Carroll	Horowitz Metzger
S1	0	337	365	367	1.4851	---	---	18.295	17.919
S2	5	336	364	367	1.3323	459	0.1074	18.386	18.367
S3	10	330	362	364	1.1496	457	0.1226	19.180	18.332
S4	20	310	360	349	0.7379	535	0.1123	20.886	17.834
S5	30	308	363	347	0.5854	566	0.05313	20.261	16.920
S6	40	305	360	336	0.4152	418	0.1790	19.443	15.348
S7	50	304	363	343	0.2867	391	0.1721	20.035	13.198

Table 2. Results of thermo-gravimetric analysis of the composites.

Activation energy values evaluated by both methods are comparable. Activation energy values which range from 18 to 20 KJ/mol evaluated from Freeman-Carroll method do not provide much information on filler concentration effect on thermal stability of the composites. However, those evaluated from Horowitz-Metzger method show a decrement from 18 to 13 KJ/mol with the increased filler concentration in composites. Slight thermal stability decrement of the composites with increased filler concentration and these results

verify the cause for the decrease in IDT values discussed above. Both methods indicate that thermally stability of composites increase at lower filler loading but tend to decrease at higher filler loading. The reaction order determined from Freeman-Caroll was found to be between 1 and 2, and the degradation reactions may be concluded as not of first order [25].

These composites were fabricated with a primary intention of application in gamma radiation shielding. In terms of radiation shielding efficiency, S7 appears to be the best composite because radiation attenuation coefficients depend linearly on density of the sample [21, 22]. However, in terms of thermal stability as a primary parameter, S5 with 30% by weight filler loading may be concluded as best sample. IDT values and other parameters evaluated from first stage of degradation won't contribute for this conclusion but from the parameters of second stage of degradation, S5 shows higher T_{\max} (566°C) and lowest rate of degradation R_{\max} (0.05313 wt%/°C). Hence S5 may be concluded as best sample from the point of thermal stability.

Conclusions

The PbO filled ISO-UP resin composites were investigated for the degradation kinetics & thermal stability of the composites. The effect of filler concentration on degradation kinetics & thermal stability of the composites was also discussed. Neat polymer was supposed to be brittle which undergoes brittle fracture with regularly graded ridges while the presence of filler influences radial propagation of cracks during fracture in filled composites. Brittleness may be affected due to presence of filler. X-ray diffraction studies reveal no changes in characteristic patterns of the filler and too little influence of filler on structure of polymer matrix. Neat sample was observed to exhibit one-stage degradation whereas filled composites exhibit two-stage degradation. Further, with the increased filler ratio in the composite the IDT values as well as degradation rate were observed to decrease in first stage of degradation. Presence of filler slows down the rate of degradation process. From the second stage of degradation, S3 appears to be thermally stable compared to other compositions. Thermal degradation kinetics were observed to follow Freeman-Caroll

and Horowitz-Metzger methods. The activation energies obtained from both of these methods were comparable and the degradation process was found not to be of first order. Better understanding of the structure as well as polymer-filler interactions may help to draw conclusions on the thermal degradation of these composites. It may also help to improve these composites on their performance as excellent radiation shields. Present study provides scope for adoption of more advanced particle dispersion to dimensions at nano scale and composite fabrication methods in fabrication of more efficient radiation shielding materials.

Author Contribution Statement: **Harish Venkatreddy:** Investigation, Data curation, Writing- Original draft preparation, Reviewing and Editing. **Ashok Godekere Visweswaraiiah:** Investigation, Supervision, Data curation, **Shivaprasad Nambihalli Gopalakrishna:** Conceptualization and Methodology, **Niranjana Prabhu Thippeswamy:** Data curation and Validation.

Declaration of competing interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Declaration on funding/financial support: The authors declare that no financial aid/funding was received from any agency for study presented in this paper.

Acknowledgements: None

References

- [1] Andrew Holmes-Siedle and Len Adams, "Hand Book of Radiation Effects", 2nd Ed, Oxford Univ. Press, 2002.
- [2] A.B Chilton, J. K Shultis, R. E Faw, "Principles of Radiation Shielding", Prentice Hall Inc., New Jersey, 1984.
- [3] J. W. T. Spinks and R. J. Wood, "An Introduction to Radiation Chemistry"; Wiley-Interscience: New York, 1964.
- [4] F. A. Bovey, "The Effect of Ionizing Radiation on Natural and Synthetic High Polymers", Wiley-Interscience, New York, 1958.
- [5] Landler, Yvan Lebel, Pierre, "Mixing of Polyethylene and lead compounds", Pneumatiques, Patent No: FR 1384603, GB 1034533, 1965.

- [6] MacLeod, John Murdo Servant, Raymond Hector, "Highly filled thermoplastic compositions for attenuation of electromagnetic radiations", Du Pont Canada Inc., Patent No: EP 372758, CA 2003879, JP 02223899, US 5278219, 1990.
- [7] Rizwan Hussain, Zia Ul Haq, Din Mohammad, "A study of the shielding properties of polyethylene glycol-lead oxide composite", *J. Isla. Aca. Sci.*, 10, 1997.
- [8] M.M Abdul Aziz, A. S Badran, A.A.Abdel-Hakem, F.M.Healy, A.B. Moustafa, "Styrene-Butadiene rubber/Lead oxide composites as gamma radiation shields", *J. App. Poly. Sci.*, 42, 1073. 1991
- [9] M.M.Abdul Aziz and S.E. Gawaily, "Thermal and mechanical properties of styrene-butadiene rubber/lead oxide composites as gamma radiation shields", *Polymer degradation and stability*, 55, 269, 1997.
- [10] V. I. Pavlenko, V. M. Lipkanskii and R. N Yastrebinskii, "Calculations of the Passage of Gamma-Quanta through a Polymer Radiation-Protective Composite", *J. Eng. Phys. Thermophys* 2004, 77, 11.
- [11] H Chai, X Tang, M Ni, F Chen, Y Zhang, D Chen, Y Qiu , "Preparation and properties of novel, flexible, lead-free X-ray shielding materials containing tungsten and bismuth(III) oxide", *J Appl Polym Sci.* 2016, <https://doi.org/10.1002/app.43012>
- [12] O Evcin, A Evcin, N Bezir, K Günoğlu, B Ersoy, "Production of barite and boroncarbide doped radiation shielding polymer composite panels", *Acta Phys Pol* 132:1145–1148. 2017, <https://doi.org/10.12693/APhysPolA.132.1145>
- [13] K Bagheri, SM Razavi, SJ Ahmadi, M Kosari, H Abolghasemi, "Thermal resistance, tensile properties, and gamma radiation shielding performance of unsaturated polyester/nanoclay/PbO composites", *Radiat Phys Chem.*, 146, 5–10, 2018.<https://doi.org/10.1016/j.radphyschem.2017.12.024>
- [14] İ Demir, M Gümüş, HS Gökçe, "Gamma ray and neutron shielding characteristics of polypropylene fiber-reinforced heavyweight concrete exposed to high temperatures", *Constr Build Mater* 257:119596. 2020, <https://doi.org/10.1016/j.conbuildmat.2020.119596>

- [15] F Akman, H Ogul, MR Kaçal, H Polat, K Dilsiz, O Agar, "Gamma attenuation characteristics of CdTe-doped polyester composites", *Prog Nucl Energy*, 131, 103608, 2021. <https://doi.org/10.1016/j.pnucene.2020.103608>
- [16] Mona M. Gouda, Mahmoud I. Abbas, Sabbah I. Hammoury, Kareman Zard & Ahmed M. El-Khatib, "Nano tin oxide/dimethyl polysiloxane reinforced composite as a flexible radiation protecting material", *Scientific reports*, 2023, <https://doi.org/10.1038/s41598-023-27464-z>
- [17] S Harry, John V Katz and Milewski. "Handbook of Fillers for Plastics", Springer, 1987.
- [18] George Wypych, "Handbook of Fillers", William Andrew Inc., 1999.
- [19] H Hansmann, "Compendium-Composites; ASM hand book on Polyester resins", ASM International, Ohio, USA, 2003.
- [20] L. H Zhang, H Gong and J. P Wang, "Thermal decomposition kinetics of amorphous carbon nitride and carbon films", *J. Phys. Condens. Matter*, 14, 1697, 2002.
- [21] V Harish, N Nagaiah, T Niranjana Prabhu, K. T Varughese, "Preparation and Characterization of Lead Monoxide Filled Unsaturated Polyester Based Polymer Composites for Gamma Radiation Shielding Applications", *J. App. Poly. Sci.*, 122, 1503, 2009.
- [22] V Harish, N Nagaiah, H G Harish Kumar, "Lead oxides filled isophthalic resin polymer composites for gamma radiation shielding applications", *Indian J Pure & Appl Phys*, 50, 847-850, 2012.
- [23] V Harish, N Nagaiah, T Niranjana Prabhu and K. T Varughese, "Thermo-Mechanical Analysis of Lead Monoxide Filled Unsaturated Polyester Based Polymer Composite Radiation Shields", *J. App. Poly. Sci.*, 117, 3623-3629, 2010.
- [24] V Harish, T Niranjana Prabhu and N Nagaiah, "Effect of Lead Monoxide as a Filler on Chemical Stability of Unsaturated Polyester Radiation Shields", *Chemical Science Transactions*, 4(1), 2015, DOI:10.7598/cst2015.968
- [25] E. S Freeman and B Caroll, "The Application of Thermoanalytical Techniques to Reaction Kinetics: The Thermogravimetric

- Evaluation of the Kinetics of the Decomposition of Calcium Oxalate Monohydrate”, *J Phys Chem*, 62, 394, 1958. <http://dx.doi.org/10.1021/j150562a003>
- [26] H. H Horowitz and G. A Metzger, “New Analysis of Thermogravimetric Traces”, *Anal. Chem.*, 35, 1464, 1963. <https://doi.org/10.1021/ac60203a013>
- [27] John Scheirs, Timothy E. Long, *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, Wiley Series In Polymer Science, 2003, ISBN 0-471-49856-4
- [28] M. Paauw and A. Pizzi, A FT-IR Analysis Method for Simple Unsaturated Polyesters, *J. Appl. Polym. Sci*, Vol 42(5), 1377-1384, 1991. <https://doi.org/10.1002/app.1991.070420521>
- [29] M. Paauw and A. Pizzi, Completion of Unsaturated Polyesters Analysis by FTIR spectra, *J. Appl. Polym. Sci*, Vol 48, 931-934, 1993. DOI:10.1002/APP.1993.070480517
- [30] L E Alexander, “X-Ray Diffraction Methods in Polymer Science, Wiley-Interscience New York. 1979.
- [31] B.D. Cullity, “Elements of X-Ray Diffraction”, Addison-Wesley, Quarry Bay, Hong Kong. 1978.
- [32] V. K. Pecharsky and P. Y. Zavalij, “Fundamentals of Powder Diffraction and Structural Characterization of Materials”, 2nd Edn, Springer Science+Business Media, NY-USA. 2008
- [33] ICDD-JCPDS, PCPDFWIN v1.3, 38-1477, Newtown Square, Pennsylvania, USA. 1997
- [34] J. F McCabe and R. W Wassell, “Thermal expansion of composites”, *J. Mat. Sci. Mat. In Med.*, 6, 624, 1995. DOI:10.1007/BF00123441
- [35] S. H Kandil, A. A Kamar, S. A Shaban, N Taymour and S. E Morsi, “Dimensional change in dental polymeric composite materials”, *Eu. Poly. J*, 24, 1181, 1998. [https://doi.org/10.1016/0014-3057\(88\)90108-5](https://doi.org/10.1016/0014-3057(88)90108-5)