International Journal of Applied Chemistry.
ISSN 0973-1792 Volume 13, Number 3 (2017) pp. 515-523

http://www.ripublication.com

Effect of Nanoclay on Thermal and Flame Retardant Properties of Phosphorylated Epoxy Nanocomposites

Priyanka and J. B. Dahiya*

Department of Chemistry, Guru Jambheshwar University of Science & Technology, Hisar-125001, Haryana, India.

Abstract

In this paper, the effect of nanoclay on thermal degradation and stability behaviour and flammability properties of phosphorylated epoxy nanocomposites is studied. Phosphorylated epoxy nanocomposites were prepared by blending organophosphorus-modified epoxy resin with desired amount of nanoclay (upto 4 wt%) and curing with 4,4'-diaminodiphenyl sulfone (DDS). The thermal properties of samples were analyzed by thermal techniques (TG-DTA). The thermogravimetric analysis showed that the onset temperature of degradation of phosphorylated epoxy is increased by10^{o}C on addition of 4 wt% nanoclay. The flammability behaviour of samples was investigated by UL-94 and Limiting Oxygen Index (LOI) tests. Phosphorylated epoxy nanocomposite (phospho-EP_{1NC}) containing 1 wt% nanoclay showed the best V0 rating in UL-94 vertical burning test.

Keywords: Phosphorylated epoxy, nanoclay, nanocomposites, thermal degradation and stability, flammability

INTRODUCTION

Epoxy resin is used commercially in various industries [1, 2] due to many attractive properties such as excellent adhesion, low shrinkage on cure, electrical properties, chemical and water resistance, easy processing and low cost. But modern market demands also high thermal stability and flame retardancy [3] of epoxy resin for advanced applications in the present scenario. Several approaches such as halogenation and phosphorylation of epoxy resin were attempted to develop the epoxy

with to improve thermal stability and flame retardancy. The halogenated compounds are much less favored owing to emission of toxic gases, while organophosphorus compounds are found to generate very less toxic gases than halogenated compounds and exhibit better flame retardancy [4].

The use of modified nanoclay as reinforcement in polymer composites is increased due to high aspect ratio and low cost of nanoclay. In many research works, organically modified nanoclay has been used to improve mechanical properties of epoxy resins [5]-[7]. Giannelis et. al [8] and Alexander et. al [9] investigated the thermal stability and flammability of epoxy nanocomposites. It was observed that the reinforcement of pure epoxy matrix with nanoclay alone was not sufficiently effective flame retardant. Therefore, it is considered that the use of nanoclay in combination with organophosphorus flame retardant may be more effective for developing the improved flame retardant epoxy system [10]. In view of this, the 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has been chosen as a flame retardant moiety in combination with varying content of nanoclay (up to 4 wt%) for epoxy resin. The effect of nanoclay content on thermal and flammability properties of phosphorylated epoxy (modified with DOPO) was investigated using thermal analysis and flammability test.

EXPERIMENTAL

A. Materials

Diglycidyl ether of bisphenol-A (DGEBA), 4,4$^{'}$-diaminodiphenyl sulfone (DDS), nanoclay namely Nanomer 1.31PS (sodium montmorillonite modified with 15-35 wt% octadecylamine and 0.5-5.0 wt% γ-aminopropyltriethoxysilane with CEC about 145 meq/100gm) were received from Sigma Aldrich, India. The 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was obtained from TCI Chemicals, India, and all the materials were used without any further purification.

B. Preparation of phospho-epoxy samples

The phosphorylated epoxy nanocomposites were prepared by blending mechanically DOPO-modified epoxy with the appropriate amount of nanoclay in a resin kettle and then mixed with DDS as curing agent stoichiometrically. The mixture was transferred to pre-heated mould and cured the material using vaccum oven and hot air oven. The detailed method of preparation has been given elsewhere [11]. The phosphorylated epoxy samples having size $15.5\times11.0\times0.26 cm^3$ were prepared using mould in vacuum oven and hot air oven. The samples were subsequently machined to the required sample size for measuring the flammability properties.

C. Techniques used

Thermal analysis (TG/DTA) was performed on the phosphorylated epoxy samples (about 10 mg each) using a thermal analyzer instrument EXSTAR TG/DTA 6300 at a heating rate of 10°C/min from room temperature to 700°C in air at flow rate of 200 ml/min.

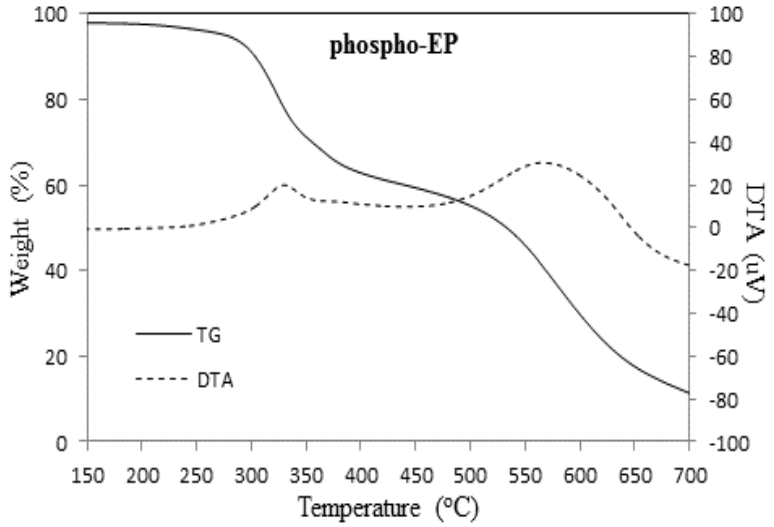
The UL-94 vertical burning test was performed according to the test method ISO 1210 proposed by Underwriter Laboratory Inc. with test specimen bars of size $10.6\times1.3\times0.26cm^3$. Five replicates were carried out for each sample. During vertical burning test, the specimens were subjected to two ignitions. After first ignition of 10 s, time (t_1) for specimen to self-extinguish was noted. Then, immediately, second ignition was performed on same sample for 10 seconds and time (t_2) for specimen to self-extinguish was noted. The surgical cotton below the specimen was observed if there any ignition by flame drippings. If (t_1+ t_2) for each specimen was less than 10 seconds without dripping, 30 seconds without dripping and 30 seconds with dripping, the samples were considered to be V-0, V-1 and V-2 rating material, respectively as per specifications of UL-94 vertical burning test.

Limiting oxygen index (LOI) value was measured using oxygen index apparatus according to the ASTM D2863 specification with specimen size $10.6\times1.0\times0.26cm^3$.

RESULTS AND DISCUSSION

A. Thermal degradation and stability behaviour

TG-DTA thermograms of phosphorylated epoxy and its nanocomposite samples are presented in Figure 1.



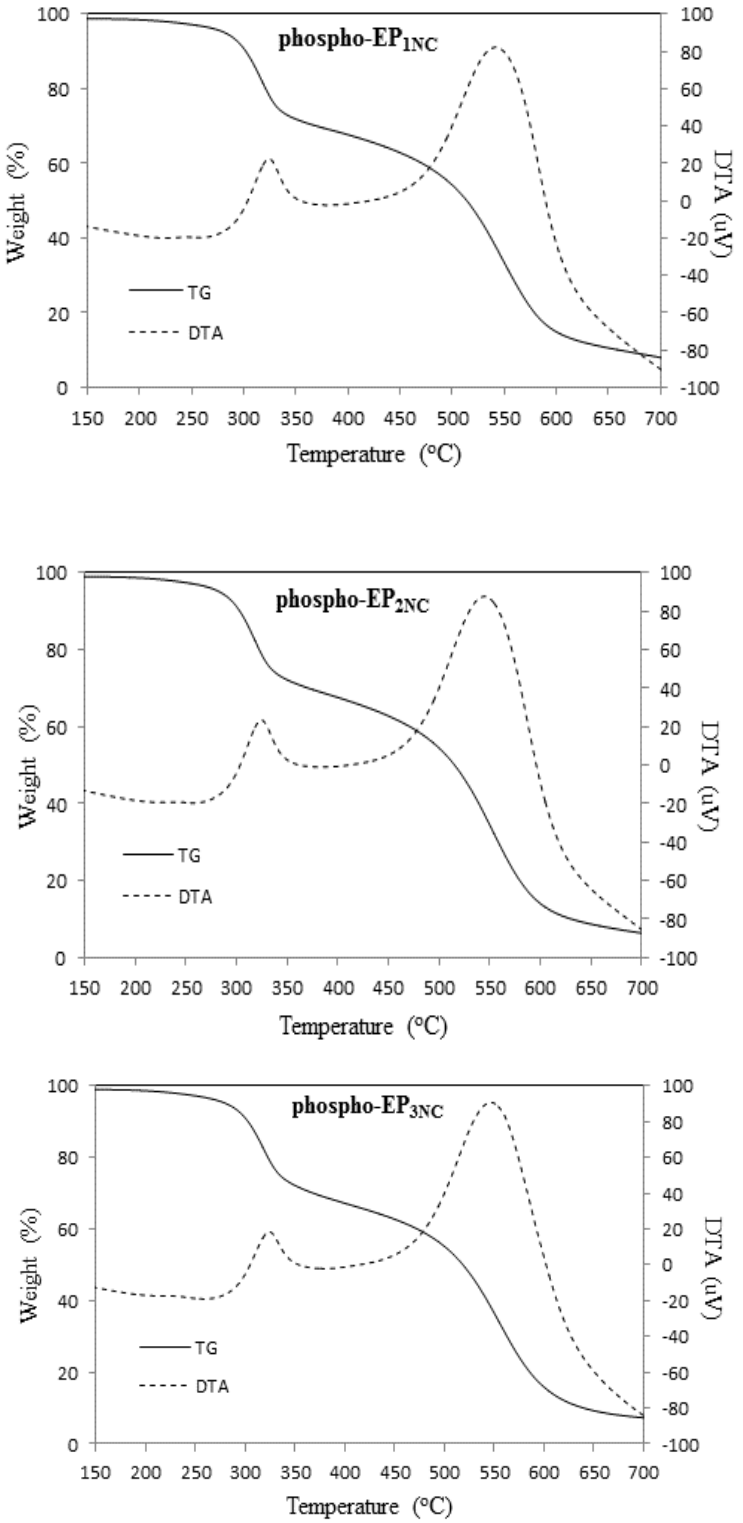


Figure 1: TG-DTA thermograms of phosphorylated epoxy samples

The various parameters such as T_{onset} (temperature at 5% weight loss), T_{mid} (temperature at 50% weight loss) and the char yield at 650°C are observed for comparing thermal stability. TG-DTA data are given in Table 1.

Table 1: TG-DTA data of phosphorylated epoxy samples in air atmosphere

Sample	TG data							DTA data		
	Stage	Temp. range (°C)	Wt. loss (%)	DTG (°C)	T_{onset} (°C)	T_{mid} (°C)	Char yield (%)	DTA peaks (°C)		Nature of peak
								Initiation	Maximum	
phospho-EP	1st 2nd 3rd	100-353 353-430 430-700	29.4 9.9 49.2	323 368 580	276	533	17.5	232 440	330 565	Exo Exo
phospho-EP_{1NC}	1st 2nd	100-400 400-700	32.3 59.7	316 545	282	514	10.6	256 430	316 528	Exo Exo
phospho-EP_{2NC}	1st 2nd	100-401 401-700	32.6 61.0	317 548	283	515	8.7	255 431	317 531	Exo Exo
phospho-EP_{3NC}	1st 2nd	100-419 419-700	34.4 58.3	319 553	281	518	9.2	260 430	314 556	Exo Exo
phospho-EP_{4NC}	1st 2nd	100-427 427-700	35.9 56.8	318 553	286	521	9.1	285 429	315 557	Exo Exo

From TG thermogram of phospho-EP sample indicates the thermal degradation in three stages. The onset degradation temperature of phospho-EP is found to be 276°C. The weight loss during first stage of phospho-EP sample up to 353°C is attributed to dehydration, breakage of some ether linkages and P−O−C bonds of epoxy network [12]. The weight loss of about 10% in second stage of degradation in the temperature range of 353 - 430 °C is due to further breakage of ether linkages, carbonyl group and start of oxidation process. In the third stage of thermal degradation, the major weight loss of phospho-EP takes place in the temperature range 430-700°C in air atmosphere, and this weight loss is due oxidative decomposition and volatilization of polyaromatic products. The oxidative decomposition of sample is supported by exothermic maximum at 565°C in DTA thermogram (Table 1). After thermal degradation of phospho-EP sample the significant amount of residue of 17.5 wt% at 650°C is observed at the cost of volatile and flammable products.

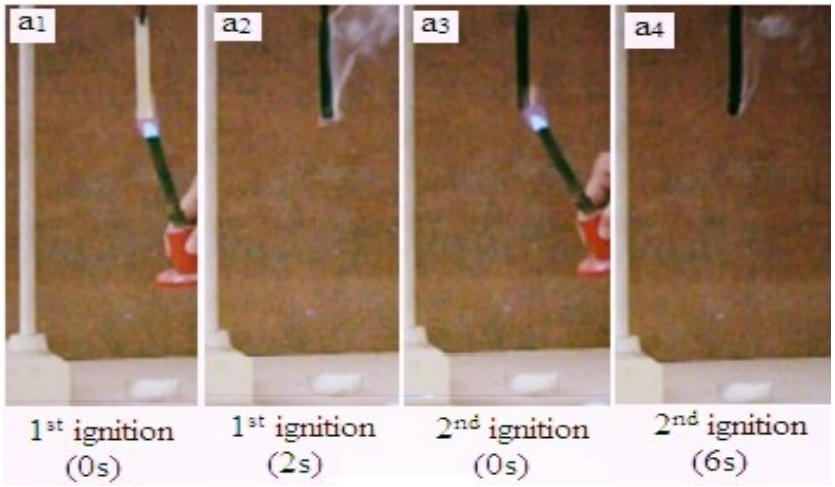
Phosphorylated epoxy nanocomposite samples (phospho-EP_{1NC}, phospho-EP_{2NC}, and phospho-EP_{3NC}) show two stages of thermal degradation instead of three stages of base phospho-EP sample. The phospho-EP_{1NC} shows two stages of degradation in the temperature ranges 100-400°C and 400 to 700°C with corresponding weight losses of 32.3 and 59.7%, respectively. On inclusion of 1 wt% nanoclay to phosphorylated epoxy for phospho-EP_{1NC} sample, the T_{onset} is found increased by 6°C due to formation of nanocomposites. But the T_{mid} is decreased by 19°C. The maximum of

endothermic peak (528ºC) in DTA curve is also decreased by 37ºC. Generally, nanoclay affects the thermal stability of the nanocomposites by two ways, one is due to surface protection to oxygen thereby increasing the stability, and the other is due to the catalysis effect toward the polymer degradation. In phosho-EP_{1NC} sample containing 2.5 wt% phosphorus and 1% nanclay, the surface protection effect is dominant in beginning of the degradation but later during second stage of degradation the catalyzing effect becomes dominant. Hence, the thermal stability and char yield of nanocomposite is decreased at higher temperature.

Further addition of nanoclay to phosphorylated epoxy upto 4 wt%, the onset temperature of degradation increased by 10ºC in comparison to phosphorylated epoxy sample (phospho-EP). The decomposition temperature at which 50 % weight loss, (T_{mid}) is slightly increased on further increase in addition of nanoclay upto 4 wt% by 7ºC in comparison to phospho-EP_{1NC}. The exothermic DTA peak in curve is also observed at higher temperature by 29ºC for phospho-EP_{4NC} sample containing 4 wt% nanoclay in comparison to phospho-EP_{1NC}. Thermogravimetric results of samples reveal that there is medium effect of nanoclay addition on the thermal degradation and stability behaviour of phosphorylated epoxy resin.

B. Flammability properties

The flame retardant properties of epoxy samples can be studied by Underwriter Laboratory (UL-94) vertical burning test and limiting oxygen index (LOI), which is a measure of flammability of materials. UL-94 VB test determines the upward burning characteristics of a polymeric material. LOI is defined as the minimum fraction of O_2 in O_2-N_2 mixture that is just sufficient to sustain combustion of the specimen after ignition. The images of UL-94 VB test for phosphorylated epoxy samples (phospho-EP_{1NC}, phospho-$EP_{2NC}$and phospho-EP_{3NC}) are shown in Figure 2, and the results of UL-94 and LOI tests of samples are listed in Table 2.



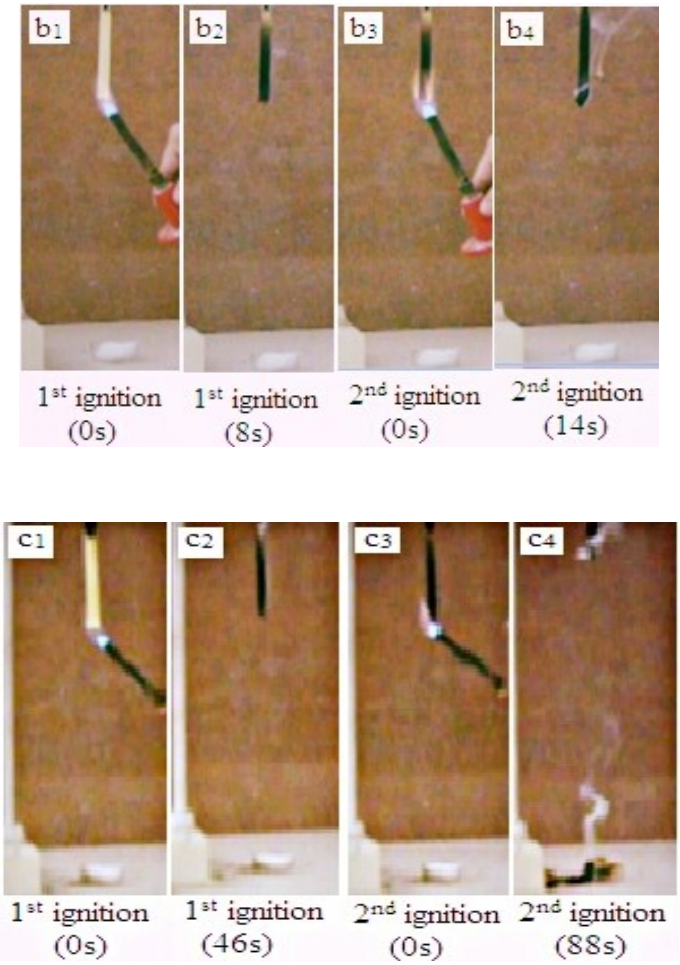


Figure 2: UL-94 VB test images of (a) phospho-EP_{1NC}, (b) phospho-EP_{2NC}, and (c) phospho-EP_{3NC} samples

Table 2: Flammability data of phosphorylated epoxy samples

Sample	UL-94 VB test						LOI (%)
	t_1 (s)	t_2 (s)	d_1	d_2	Smoke release	Rating	
phospho-EP	2	4	-	-	negligible	V0	27.3
phospho-EP_{1NC}	2	6	-	-	small	V0	25.0
phospho-EP_{2NC}	8	14	-	-	small	V1	26.0
phospho-EP_{3NC}	46	88	8	9	significant	BC,NR	27.0
phospho-EP_{4NC}	55	32	13	2	significant	BC,NR	27.6

t_1 and t_2 - average burning time in seconds after the first and second applications of flame;
d_1 and d_2 - average number of drips after the first and second applications of flame;
NR - no rating; BC - burn up to clamp.

Phosphorylated epoxy sample (phospho-EP) extinguishes itself within 2 seconds after 1st flame application and 4 seconds after 2nd application of flame, respectively without any dripping. It is classified as UL-94 V0 rating. On addition of 1 wt% nanoclay to phosphorylated epoxy, the rating remains same (V0) but rating reduces to V1 rating on 2 wt% nanoclay addition for phospho-EP_{2NC}. Phosphorylated epoxy nanocomposites (phospho-EP_{3NC} and phospho-EP_{4NC}) burn up to clamp with significant smoke on 2nd application of flame with dripping and therefore, give no rating. LOI value of phosphorylated epoxy sample (phospho-EP) is 27.3, which decreased to 25.0 on addition of 1 wt% nanoclay. On further addition of nanoclay up to 4 wt%, LOI value increased to 27.6. In the present study, the significant correlation between the results of UL-94 VB and LOI tests is not seen.

CONCLUSION

The effect of nanoclay on thermal degradation and stability, and flammability behaviour of phosphorylated epoxy is studied in this paper. The major weight loss of phospho-EP takes place in the last stage of degradation in the temperature range 430-700ºC in air atmosphere due oxidative decomposition of epoxy and volatilization of polyaromatic products giving rise to 17.5% char yield at 650ºC, which is supported by DTA exothermic peak at 565ºC. On inclusion of 1 wt% nanoclay to phosphorylated epoxy for phospho-EP_{1NC} sample, the T_{onset} is found increased by 6ºC due to formation of nanocomposites. Phosphorylated epoxy sample (phospho-EP) is classified with highest V0 rating in UL-94 flammability test. On addition of 1 wt% nanoclay to phosphorylated epoxy, the rating remains the same (V0 rating) but it reduces to lower rating on increasing the addition of nanoclay.

ACKNOWLEDGEMENTS

The research fellowship (JRF) of Council of Scientific and Industrial Research (CSIR), New Delhi, India, to Mrs. Priyanka is gratefully acknowledged.

REFERENCES

[1] Ahmadi, S.J., Huang, Y.D. and Li, W., 2004, "Synthetic routes, properties and future applications of polymer-layered silicate nanocomposites," J. Mater. Sci., 39(6), pp. 1919-1925.

[2] Iijima, T., Tomoi, M., Suzuki, A., and Kakiuchi, H., 1999, "Toughening of epoxy resins by modification with reactive elastomers composed of butyl acrylate and glycidyl (meth) acrylate," Eur. Polym. J., 27(9), pp. 851-858.

[3] Azeez, A.A., Rhee K.Y., Park S.J. and Hui D., 2013, "Epoxy clay

nanocomposites-processing, properties and applications: A review," Comp. Part B: Eng., 45(1), pp. 308-320.

[4] Wang, P. and Cai, Z., 2017, "Highly efficient flame-retardant epoxy resin with a novel DOPO-based triazole compound: Thermal stability, flame retardancy and mechanism, "Polym. Degrad. Stab., 137, pp. 138-150.

[5] Bhattacharya, M., and Bhowmick, A.K., 2010, "Synergy in carbon-filled natural rubber nanocomposites. Part I: Mechanical, dynamic mechanical properties, and morphology," J. Mater. Sci.,45(22), pp. 6126-6138.

[6] Zhao, Z., Gou, J., Bietto, S., Ibeh, C., and Hui, D., 2009, "Fire retardancy of clay/ carbon nanofiber hybrid sheet in fiber reinforced polymer composites," Comp. Sci. Tech., 69(13), pp. 2081-2087.

[7] Wang, K., Chen, L., Wu, J., Toh, M.L., He, C. and Yee, A.F., 2005,"Epoxy nanocomposites with highly exfoliated clay: mechanical properties and fracture mechanisms," 38(3), pp. 788-800.

[8] Giannelis, E.P., Krishnamoorti, R.K.,and Manias, E., 1999, "Polymer silicate nanocomposites: Model systems for confined polymers and polymer brushes," Adv. Polym. Sci.,138, pp. 107-147.

[9] Alexander, M., and Dubois, P., 2000, "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials," Mater. Sci. Eng. Rep., 28(1-2), pp. 1-63.

[10] Jangra, P. and Dahiya J.B., 2017, Effects of nanoclay and flame retardant additives on glass transition temperature, thermal stability and flammability of epoxy composites, "Mater. Res. Innov., DOI: 10.1080/14328917.2017.1325059.

[11] Priyanka, and Dahiya, J.B., 2017 "Phosphorylated epoxy nanocomposites: Study of structure and mechanical properties," Asian J. Res. Chem. (Communicated).

[12] Zhu, S., and Shi, W., 2003, "Thermal degradation of a new flame retardant phosphate methacrylate polymer, "Polym. Degrad. Stab., 80(2), pp. 217-222.