Original Article

http://www.bpasjournals.com/chemistry
DOI: 10.5958/2320-320X.2021.00003.0

Bulletin of Pure and Applied Sciences.
Vol.40 C (Chemistry), No.1
January-June, 2021: P.16-22
Print version ISSN 0970 4620
Online version ISSN 2320 320X

Stress Corrosion Studies of AL 2014 Alloy Using Synthesized Pyrimidin Derivative Inhibitor in Different Concentration of HCl Solution

Abstract

The stress corrosion resistance of AL 2014 in high temperature acidic media using The inhibitors MPPA and AMPO has been evaluated using an autoclave. The liquid melt metallurgy technique using vortex method was used to fabricate AL 2014 alloy. Stress corrosion tests were conducted using weight loss method for different exposure time, normality and temperature of the acidic medium. The corrosion rates of AL 2014 alloy was lower to that of Concentration increases of the inhibitor.

Keywords: Vortex method, Stress corrosion, Autoclave, AL 2014 alloy, Synthesized inhibitor

[1]**Nataraja G***
[2]**Praveen BM**
[3]**Pruthviraj RD**
[4]**Sudhakara A**

Author Affiliations
[1,2]Department of Chemistry, Srinivas University, Mangaluru, Karnataka 575023, India
[3,4]Department of Chemistry, Rajarajeswari College of Engineering, Mysore Road, Bengaluru, Karnataka 560074, India

***Corresponding Author**
Nataraja G,
Department of Chemistry, Srinivas University, Mangaluru, Karnataka 575023, India

E- mail: nataraj.jit@gmail.com

Received on 30.02.2021
Accepted on 23.05.2021

How to cite this article: Nataraja G, Praveen BM, Pruthviraj RD, Sudhakara A. (2021). Stress Corrosion Studies of AL 2014 Alloy Using Synthesized Pyrimidin Derivative Inhibitor in Different Concentration of HCl Solution. *Bulletin of Pure and Applied Sciences-Chemistty,* 40C (1), 16-22.

INTRODUCTION

AL 2014 offer the designer with many added benefits, since they are particularly suitable for application requiring their combined high strength [1], better wear resistance [2], thermal conductivity [3], damping properties [4], and low coefficient of thermal expansion with lower density [5]. These properties of alloy enhance their usage in automotive and tribiological applications. The trend is towards safe usage of MMC parts in the automobile engine, which works particularly at high temperature and pressure environments [6,7]. Particle reinforced alloy has been the most popular over the last two decades. Among them ceramic reinforced AL 2014 are very popular in the recent days. The addition of the ceramic particle not only enhances the mechanical and physical properties, but also it changes the corrosion properties significantly.

Particle reinforced AL find number of applications in several thermal environments especially in the automobile engine parts such as brake drum, brake rotors, cylinders and pistons used at high thermal conditions should have good mechanical properties and resistance chemical attack in air and acidic environment. It is necessary that the detail corrosion behavior of AL composites must be understood thoroughly for high temperature applications. Several authors [8-10] point out that the extent of pitting in AL 2014 increased with increase in volume fraction which may be due to the preferential acidic attack at the matrix –reinforcement interface [11]. The corrosion behavior of is influenced by the nature of matrix alloy, a type of reinforcement and alloying elements [12], in spite of these factors the corrosion behaviour in AL 2014 is a complex nature [13]. The objective of the present investigation is to understand the role reinforcement on the stress corrosion behaviour of AL 2014 at high temperature in varied normalities of Hydrochloric acid solutions. High temperature and pressure in an autoclave is an excellent test for stress corrosion.

EXPERIMENTAL PROCEDURE MATERIAL SELECTION

Here the matrix alloy used as AL 2014 and its composition is given in Table 1.

Table 1: Composition of AL 2014

Elements	**Mg**	**Sn**	**Cr**	**Mn**	**Fe**	**Ni**	**Al**
Percentage (wt%)	0.12	0.34	0.40	0.16	0.74	0.35	Balance

PREPARATION OF AL 2014 ALLOY

The liquid metallurgy route using vortex technique [12] was employed to prepare the alloy A mechanical stirrer was used to create the vortex. This alloy melt was thoroughly stirred and subsequently degassed by passing nitrogen through the melted at a composite rate 2-3 l/min for three to four minutes. Castings were produced in permanent moulds.

SPECIMEN PREPARATION

Three point loaded specimens, typically flat strips of dimension 8mm thickness, 40mm wide and 150mm long was prepared from the composites and the matrix alloy by adopting standard metallographic procedure for the stress corrosion testing. Before subjecting the specimens for the stress corrosion test. It was ground with silicon carbide paper of 1000 grit and then polished in steps of 15 to 3 μm diamond paste to obtain a fine surface finish and degassed in acetone then dried. The samples were weighed up to fourth decimal place using electronic balance.

Autoclaves are often used for high temperature and pressure applications. The Teflon coatings protect the autoclaves from severe aggressive environments. shows a bracket used to load corrosion specimen to be placed in autoclave. The specimen was supported at both ends and bending stress was applied using a screw equipped with a ball to bear against specimen at a point midway between the end supports. For calibration a prototype specimen of same dimensions was used and stressed to the same level. In a three point loaded specimen the maximum stress that occurs at the mid-length of the specimen, decreases linearly to zero at the ends. The specimens were subjected to one third of matrix alloy's ultimate tensile strength. For each test two litres of different normalities of HCl solution, prepared was used. After loading the specimen in to the holder and placing the same in autoclave. Then the required normality acid solution of 2 litres was added as corrodant. Then autoclave was closed and heated to test temperature with increase in inside pressure. Different composites with varying percentages of reinforcement were subjected to test with different temperature, different normality and corroded for various duration of 10, 20, 30, 40, 50 and 60 minutes respectively. After the corrosion test, the specimen was immersed in Clark's solution for 10 minutes and gently cleaned with a soft brush to remove adhered scales. Then after drying, the specimens were accurately weighed again. Weight loss was calculated and converted to corrosion rate expressed in mils penetration per year (mpy) [14].

SYNTHESIS OF CORROSION INHIBITORS

The inhibitors MPPA and AMPO were synthesized by the method re- ported in literature. Chalcone was synthesized by stirring a mixture of benzaldehyde (0.1mol), 4-methoxyacetophenone (0.1 mol) and small amount of sodium hydroxide in ethanol (50 mL). A mixture of the chalcone (0.05 mol), malononitrile (0.05 mol) and ammonium acetate (0.4 mol) in ethanol (80 mL) was refluxed on a water bath for 14–16 h to synthesize 2-amino-3-cyano-6-methoxypyridine. The compounds MPPA and AMPO were obtained by refluxing a mixture of 2-amino-3-cyano-6-methoxypyridine (0.04 mol) with formamide (0.04 mol) and urea (0.04 mol) respectively, on an oil bath. The synthetic route of inhibitors (MPPA and AMPO) is shown in Scheme 1 and the structure of inhibitors is shown in Fig The purity of the inhibitors was checked by thin layer chromatography (TLC). The IR and ^{1}H NMR spectra of inhibitors MPPA and AMPO are given in supplementary materials as Figs. S1 and S2, respectively. The melting point, yield, IR, ^{1}H NMR and ^{13}C data of the synthesized compounds are given below:

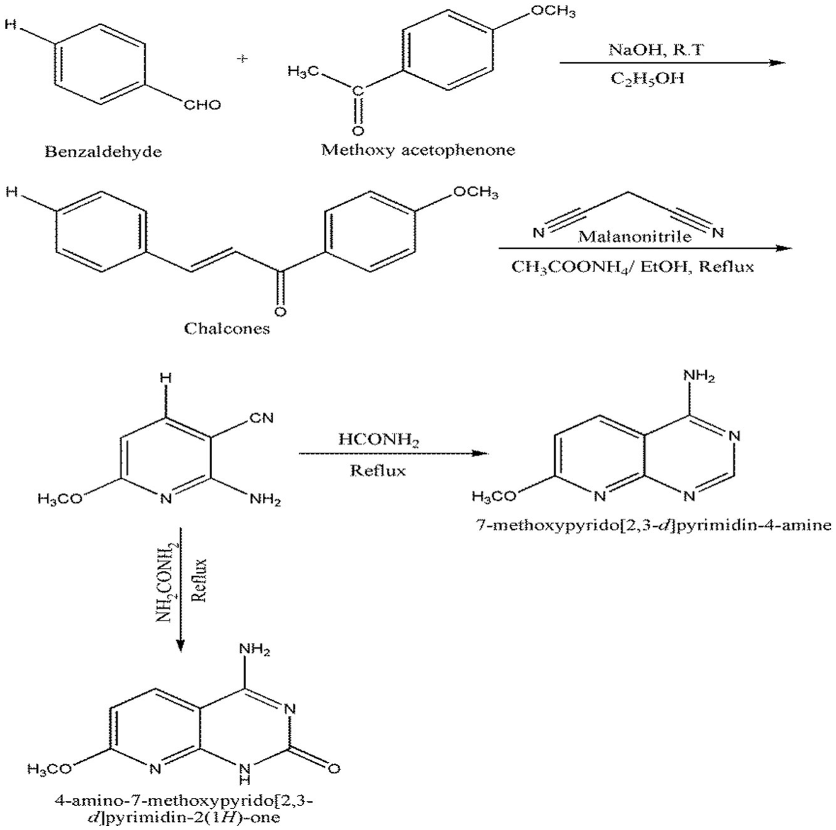

Figure 1: Synthetic route of inhibitors 7-methoxypyrido [2,3-d] pyrimidin-4-amine (MPPA) and 4-amino-7-methoxypyrido[2, 3-d] pyrimidin-2(1H)-one (AMPO).

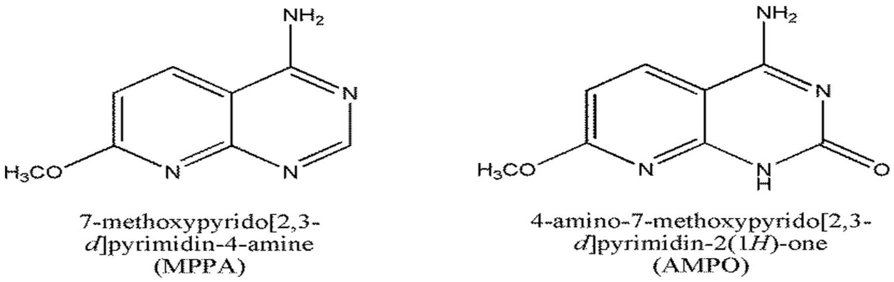

Figure 2: Structure of inhibitors 7-methoxypyrido [2, 3-d] pyrimidin-4-amine (MPPA) and 4-amino-7-methoxypyrido [2,3-d] pyrimidin-2(1H)-one (AMPO).

CORROSION TEST

Corrosion rate decreases with increase in the concentration of inhibitor with respect to matrix alloy [15]. Figure 4 shows stress corrosion rate vs. exposure time of AL 2014 with and without inhibitor at 100°C in Different Concentration HCl. The corrosion rates of both matrix alloy and AL 2014 with and without inhibitor increase with increase in exposure time. The plot of stress corrosion rate vs. different concentrations of HCl at exposure temperature of 100°C and exposure time of 30 minutes. The stress corrosion rates of specimens increase with the concentration of HCl. the stress corrosion rates of matrix alloy and composites in Different Concentration HCl at different temperatures. All figures clearly show the decrease in corrosion rate monotonically with increase concentration of inhibitor content. In other words greater the concentration of inhibitor greater will be the corrosion resistance.

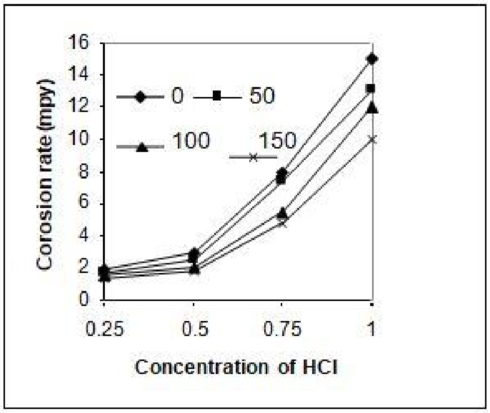

Figure 3: Corrosion rate v/s Concentration of HCl at 100°C

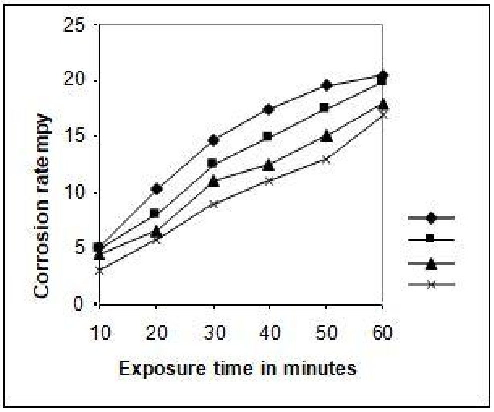

Figure 4: Corrosion rate v/s exposure time at 100°C in Different Concentration HCl

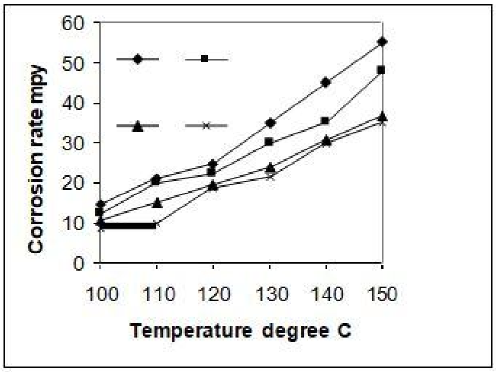

Figure 5: Corrosion rate vs. exposure temperature for 30 minutes exposure in Different Concentration HCl

CORROSION MORPHOLOGY

Visual examinations of the specimens after the stress corrosion experiments has shown few deep pits, flakes and cracks formed on the unreinforced matrix alloy and the cracks was perpendicular to the axis of the specimen. Whereas more wide spread superficial pitting was observed and few or no cracks were seen on the surface.

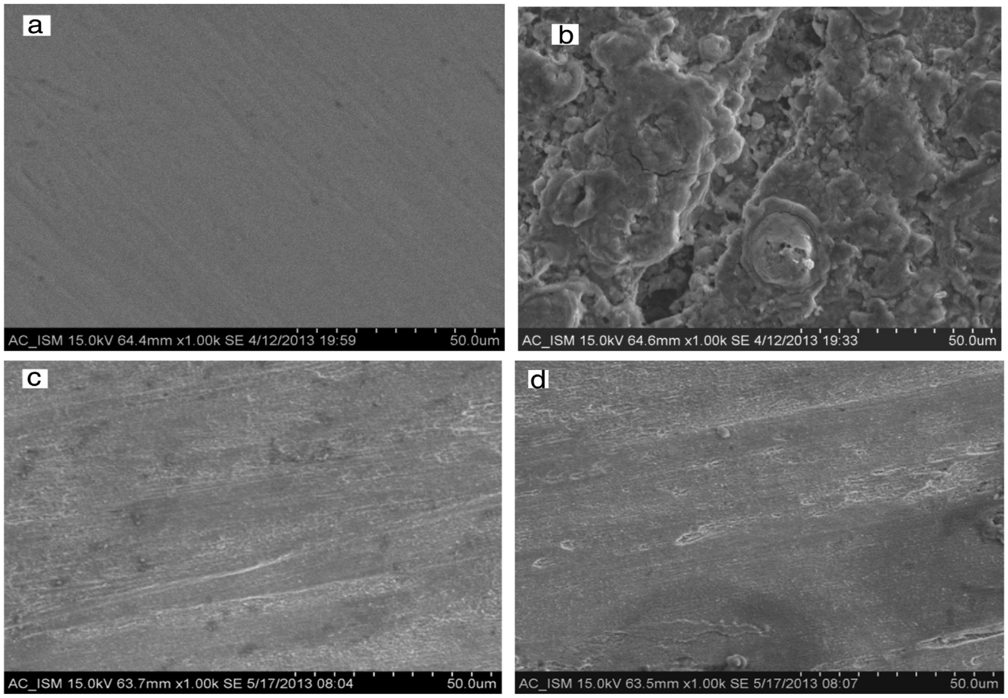

Figure 6: SEM image of AL 2014 in 1M HCl solution (a) before immersion (polished), (b) after immersion without inhibitor, (c) with inhibitor MPPA, (d) with inhibitor AMPO.

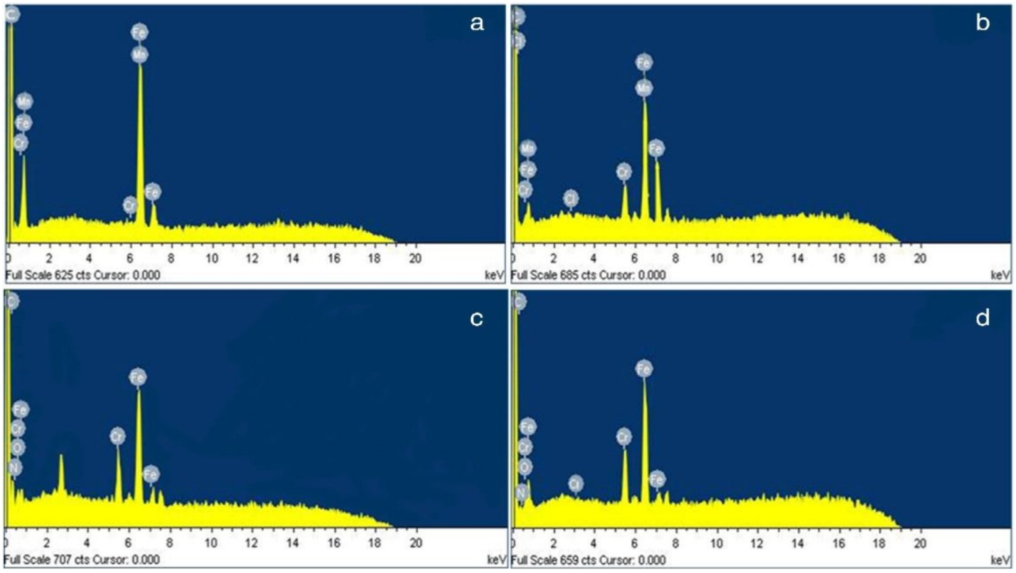

Figure 7: EDX spectra of AL 2014 specimens (a) polished, (b) after immersion without inhibitor, (c) With 100 ppm AMPO, (d) with 150 ppm MPPA.

RESULT & DISCUSSION

Hydrogen has been found to evolve when aluminium, was exposed to boiling water [16]. If the alloy alike AL 2014 was taken in acid solution like HCl then there will be liberation of hydrogen due to the slow dissolution of alloy. It may be due to the chemical reactions shown below.

$Al + 2HCl \longrightarrow AlCl_2 + H_2\uparrow$ ……………….. (1)
$Al + 2H_2O \longrightarrow Al(OH)_2 + H_2\uparrow$ …………….. (2)
$2Al + 6H_2O \longrightarrow 2Al(OH)_3 + H_2\uparrow$ ………..(3)

The reaction rates for the above reactions are directly influenced by external variables such as exposure temperature of acidic solutions, exposure area of the specimen, concentration of hydrogen in solution, specimen exposure time and area of specimen exposed. Various researchers [17,18] has reported in their papers on static corrosion that the corrosion rate of the matrix alloy and the reinforced composites decrease with increase in exposure time. There may be possibility of conversion of hydroxide of aluminium into non-porous oxide layer, which prevents further corrosion. However the percentage of aluminium was only between 26-28% but in the case of Zinc formation of oxide layer was ruled out. Hence the corrosion takes place and increases with the increase in temperature, normality of HCl and exposure time. Corrosion rates for matrix alloy and reinforced composites increased with increase in the normality of corrodant like HCl. The corrosion rates in different concentration HCl was more when compared to the corrosion rates in 0.25N, 0.5N and 0.75N HCl solutions. This is due to the increase in concentration of hydrogen in corrodant. Temperature also plays an important role in the corrosion properties. Two factors with respect to temperature, which influences on corrosion factor. These energy of activation of hydrogen ions and the temperature variation of hydrogen gradient.

Cocentration of inhibitor are inert and not expected to affect the corrosion mechanism of alloy The corrosion results indicate the improvement of corrosion resistance as the cocen of inhibitor increased in the alloy. This shows the direct or indirect influence of inhibitor on the corrosion properties of the alloy. Several authors [19,20,21] point out that the extent of pitting in AL 2014 alloy increased with increase in concentration fraction which may be due to the preferential acidic attack at the matrix –reinforcement interface [22]. The corrosion behavior of is influenced by the nature of matrix alloy, type of reinforcement and alloying elements [23], in spite of these factors the corrosion behavior in AL2014 was a complex nature[24]. But nature of bond between reinforcement and matrix plays an important role in the corrosion property.

CONCLUSION

Corrosion rate increases with solution temperature. Concentration of inhibitor hence it is not involved in galvanic corrosion with alloy. Normality of HCl plays significant role in the corrosion of AL 2014. The increase in hydrogen evolution results in higher corrosion rate. Corrosion rate increases with increase in time of exposure and temperature. The extent of corrosion damage is reduced with increasing inhibitor cocen. Which may be due to increase in tensile strength and bonding strength of the alloy Material loss from corrosion is significantly higher in the case of AL 2014.

REFERENCES

1. Karaaslan A, Kaya I, Atapek H. (2017). Effect of aging temperature and of retrogression treatment time on the microstructure and mechanical properties of alloy AA 7075. *Metal Sci Heat Treat,* 49, 9-10.

2. Venugopal T, Srinivasa Rao K, Prasad Rao K. (2016). Studies on friction stir welded AA7075 aluminum alloy. *Trans Indian Inst Metals,* 57(6), 659-63.

3. Rao K Srinivasa, Rao K Prasad. (2015). Pitting corrosion of heat-treatable aluminium alloys and welds: a review. *Trans Indian Inst Met*, 57(6), 593-610.

4. Ranganatha R. (2017). Multi-stage heat treatment of aluminum alloy AA7049.Trans *Nonferrous Met Soc China*, 1570-5.

5. Su JQ. (2018). Microstructural investigation of friction stir welded 7050-T651aluminium. *Acta Mater,* 51, 713-29.

6. Hassan KhAA, Norma AF, Price DA, Prangnell PB. (2015). Stability of nuggetzone grain structures in high strength Al- alloy friction stir welds during solution treatment. *Acta Mater,* 51(7), 1923e36.

7. Sullivan A, Robson JD. (2018). Microstructural properties of friction stir welded and post weld heated 7449 aluminum alloy thick plate. *Mater Sci Eng,* 478, 351e60.
8. Feng JC, Chen YC, Liu HJ. (2016). Effect of post weld heat treatment on microstructure and mechanical properties of friction stir welded joints of 2219-O aluminum alloy. *Mater Sci Technol,* 22(1), 86-90.
9. Cina B and Gan R. (2015). Reducing the susceptibility of alloys, particularly aluminum alloys, to stress corrosion cracking. United States Patent 3856584; 24.
10. Cina B, Zeidess F. (2016). Advances in the heat treatment of 7000 type aluminum alloys by retrogression and re-aging. *Mater Sci Forum,* 102-104.
11. Oliveira Jr AF, de Barros MC, Cardoso KR, Travessa DN. (2016). The effect of RRA on the strength and SCC resistance on AA7050 and AA7150aluminum alloys. *Mater Sci Eng*, 379A. 321-6.
12. Autar K. Kaw, (1997). Mechanics of Composite Materials, Vol. 1, CRC Press LLC, Florida, USA.
13. Ayman, M. Atta, Manar, E., Abdel-Raouf, Shimaa, M., Elsaeed, Abdel-Azim, A., Abdel-Azim, (2006). Compressive Properties and Curing Behaviour of Unsaturated Polyester Resins in the Presence of Vinyl Ester Resins Derived from Recycled Poly(ethylene terephthalate), Journal of Polymer Research, 12(5), 373-383.
14. Basara C, Yilmazer U, Bayram G., (2005).Mechanism of reinforcement in a nanoclay/polymer composite. *Journal of Applied Polymer Science*, 98, 1081- 1086.
15. Ben R Bogner, (2005). Composites for Chemical Resistance and Infrastructure Applications, Elsevier, pp30-35.
16. Beyer G, (2001). Nanocomposites - A new concept for flame retardant polymers, *Polymer News*, 26 (11), 370-378.
17. Beyer G, (2001).Nanocomposites II: A new flame protection system for polymers. *International Polymer Science and Technology,* 28 (10), 1-5.
18. Beyer G, (2004). Nanotechnology application for polymers - improved flame retardancy for polymers and cables by nano composites, *Gummi Fasern Kunststoffe,* 57 (5), 309-314.
19. Beyer G, (2005). Nanocomposites as a new concept for flame retardancy of polymers, IRC 2005: Proceedings of the North European International Rubber conference, Maastricht, The Netherlands, London, IOM Communications, pp 327-337.
20. Bhuvaneswary M.G. and Eby Thomas Thachil, (2008). Blends of natural rubber with unsaturated polyester resin, *International Journal of Polymeric Materials*, 57, 1-12.
21. Blumstein A, (1965). Polymerization of adsorbed monolayers–II, Thermal degradation of the inserted polymer. *Journal of Polymer Science A*, 3, pp 2665 – 2673.
22. Blumstein A., S. Vilasagar, S. Ponrathnam, S. B. Clough, R. B. Blumstein, G. Maret, (1982). nematic and cholesteric thermotropic polyesters with azoxybenzenemesogenic units and flexible spacers in the main chain, journal of polymer science: polymer physics edition, 20(5), 877–892.
23. Bourbigot, S., Devaux, E., Flambard, X., (2002). Flammability of polyamide- 6/clay hybrid nanocomposite textiles. *Polymer Degradation and Stability,* 75(2), pp 397-402.
24. Bryan Harris, (1999). Engineering Composite Materials, The Institute of Materials, London.