

Research Article

Effect of UV Exposure on Coir-epoxy Infused Particulate Composite

Savita Dixit and Preeti Verma*

Department of Chemistry, MANIT, Bhopal, India

Abstract

Photo degradation mainly occurs in the lignin which is responsible for the colour changes. The surface becomes richer in cellulose content as the lignin degrades. In contrast to lignin, cellulose is much less prone to UV degradation. The effect of accelerated UV-aging on properties of coir-epoxy infused particulate composites has been studied. Composites are prepared by the hand layup technique at room temperature (25 °C). Composites containing 15% particulates were subjected to accelerated UV-aging in a QUV weatherometer for 24 hrs. The results showed that coir-epoxy infused particulate composites displayed good UV resistance with regard to mechanical properties. The color of the coir-epoxy infused particulate composite changed from dark brown to light brown at the exposed area because of the formation of a thin, strongly degraded surface layer. Differential scanning calorimetry (DSC), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) were also carried out to assess the changes occurring during accelerated weathering. These results show the deterioration of the epoxy matrix leading to crystallization. A decrease in epoxy melting temperature was also noted, due to molecular chain scission and the formation of extraneous groups, such as carbonyls and amine.

Keywords: Photo degradation; Mechanical properties; DSC; XRD; TGA; SEM

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***Correspondence to:** Preeti Verma, Department of Chemistry, MANIT, India

Email: vermapreeti786@gmail.com

1. Introduction

Fiber reinforced polymer composites have been broadly used for applications requiring high rigidity and strength [1-3]. Composites made from natural fibers are low cost, light weight, have enhanced mechanical properties, and are free from health hazards. Despite the attractiveness of natural fiber reinforced polymer matrix composites, they suffer from lower modulus, lower strength, poor moisture, microbial and UV resistance.

Ultraviolet radiation that reaches the Earth's surface comprises about 6% of the total solar radiant flux and has wavelengths between 290 and 400 nm. Since most polymers have bond dissociation energies on the order of the 290 to 400 nm wavelengths in the ultraviolet region, they are greatly affected by exposure to this portion of the solar spectrum. The effect of UV exposure, or photodegradation, is usually confined to the top few microns of the surface. However, in some cases, degradation of the surface of a polymeric component has been shown to affect mechanical properties disproportionately, as flaws that result from surface photodegradation can serve as stress concentrators and initiate fracture at stress levels much lower than those for unexposed specimens.

Durability of natural fiber composites upon exposure to UV-light is of particular concern as UV-light can cause the changes in the surface chemistry of the composites commonly known as photo degradation [4, 5]. The degradation ranges from mere surface discoloration affecting the aesthetic appeal in indoor applications to extensive loss of mechanical

properties [6, 7]. Moreover, the combination of light, moisture, and temperature in outdoor applications can completely destroy the lignocellulosic network, limiting the performance of unprotected wood in outdoor application [8]. The photodegradation of natural fibres like wood is attributed to the degradation of its components namely cellulose, hemicelluloses, and lignin [9].

Lignin and hemicelluloses are more prone to degradation than cellulose by various means [10]. Lignin degrades upon exposure to UV-light and hemicelluloses degrade upon moisture absorption and biological means [11]. Photodegradation in lignin can take place in several ways [12-14]. Figure 1 shows several ways of lignin degradation.

The UV-degradation process is known to be triggered by the formation of free radicals and probably starts with the oxidation of phenolic –hydroxyls [15]. Moreover, singlet oxygen that can be formed by oxygen quenching of photoexcited lignin plays a role in the degradation of lignocellulosic natural fibres like wood [16]. The formed singlet oxygen is a source of peroxides [17], which can initiate the auto-oxidation of carbohydrates and cleavage of lignin [18, 19]. In epoxy resin photo initiation begins with radical induced process (Figure 2).

These radicals may then be oxidised which initiate a chain of photooxidative process. Epoxy resin segment of amine cured epoxy is photoinitiating species. Photo oxidation leads to the formation of carbonyl or amide type moieties as follows (Figure 3). The main objective of this research is to study the effect of UV exposure on mechanical, thermal and microstructural properties of composites.

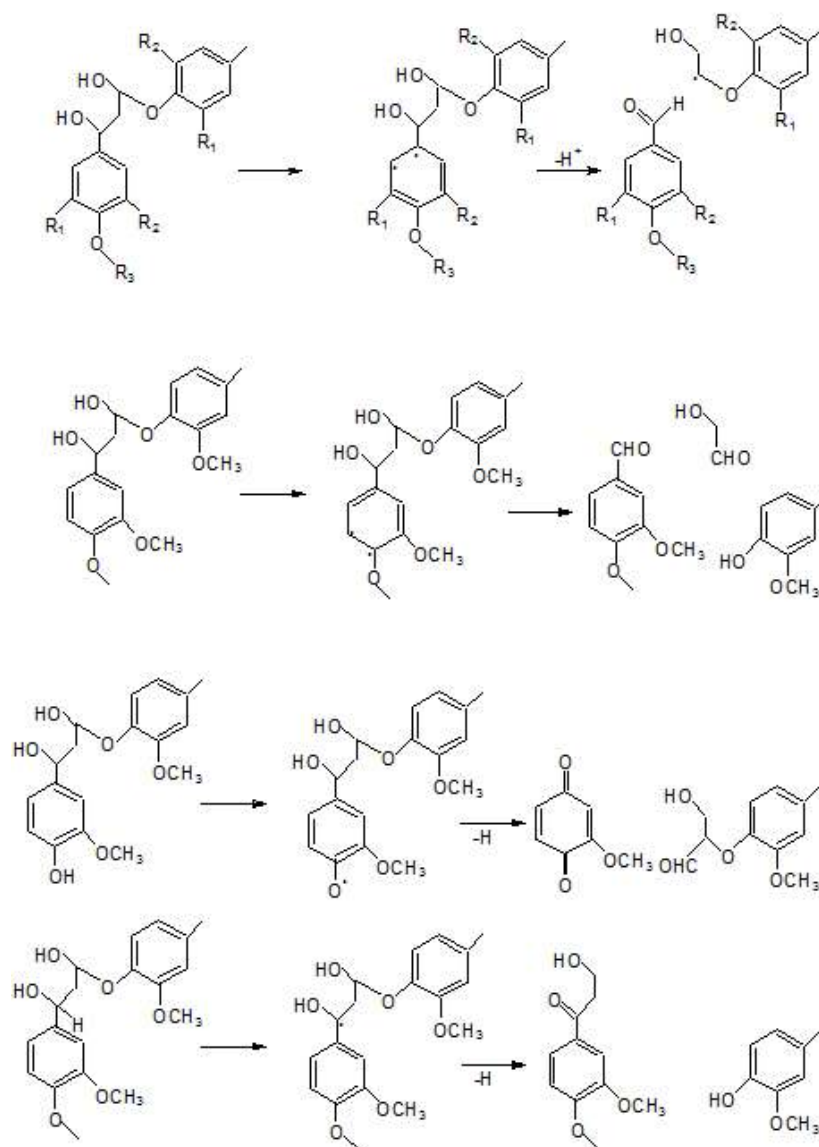


Figure 1 represents different ways of lignin degradation

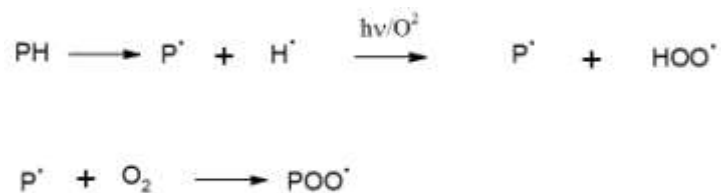


Figure 2 represents photoinitiation process of epoxy

P= Polymer

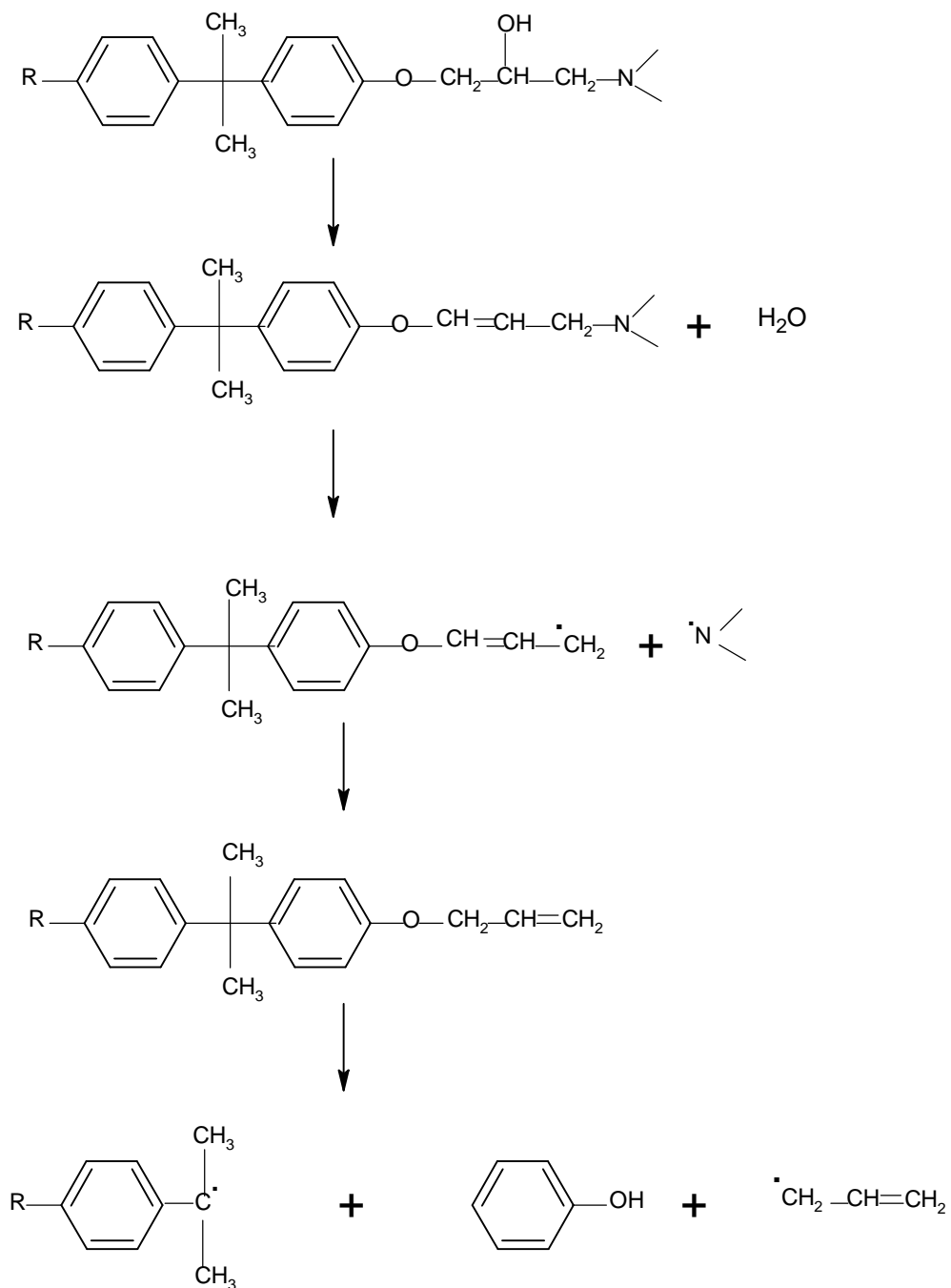


Figure 3 represents photodegradation of epoxy

2. Materials and Methods

2.1 Composite Fabrication

Coir used in this study was collected from local religious places of Bhopal, India. The matrix material was epoxy resin with polyamine (hardener) was used to improve interfacial adhesion between fiber and particulate. Cow dung was used as particulate material (25 BSS) in coir-epoxy composite. Coir fibers were cleaned manually and washed with tap water. Fibers were dried in an air oven at 60°C for 24 hrs. in order to remove moisture. Coir fibers were ground into 25 BSS using mixer grinder. Coir epoxy infused particulate samples were prepared by mixing constituents (coir 15%, cow dung 15% and epoxy 70%). After mixing, the mixture of constituents was transferred into iron molds and then pressed using a hydraulic press. Composite samples were prepared by using compression molding technique.

2.2 UV Exposure

For UV Exposure composite sheets were cut into dumbbell shaped and rectangular (according to ASTM D 638 and ASTM D 790) specimen. Samples were exposed to ultraviolet light in a QUV spray with solar eye irradiance control weatherometer to simulate outdoor exposure. Test conditions were continuous uv exposure for 24 hours, then dried and weighed on completion of the test.

2.3 Mechanical Properties

2.3.1 Tensile Strength

Dumbbell shaped samples of biodegraded composites with dimension 150 x 10 x 3.5 mm were tested according to ASTM standard D638. Samples were tested to failure under tension at a

crosshead speed of 1.5 mm using an Instron1 tensile tester. An extensometer was attached to the gauge section of the sample for strain measurement. Five samples were tested for different time period of the composite. Tensile strength, failure strain, and tensile modulus were recorded.

2.3.2 Flexural Strength

Flexural test of biodegraded composite was conducted on the Instron Machine Model 5567 according to ASTM D790. The samples, with dimensions 80 × 10 × 3 were tested at a cross-head speed of 3 mm/min at room temperature. The support span for the flexural test was 51 mm. All the reported values for the tests were the average of seven specimens.

2.4 Microstructural study

Scanning electron microscopy (SEM) images of the surface of the biodegraded composite were taken to study the morphology of the surface degradation of composite. Electron micrographs were obtained by using JEOL JSM 6390A before and after biodegradability test at an accelerating voltage of 10 KV in low vacuum. The specimens were coated with 99.99% pure gold to prevent electrical discharge.

2.5 FTIR

FTIR was done for functional group identification in composites. FT-IR spectra of composite sheets before and after degradation were recorded by means of Shimadzu Fourier transform infrared spectrophotometer in the 4,000-400 cm⁻¹ frequency range and averaged over 64 scans. A few milligrams of composite samples ground in a mortar. Ground composite was mixed with KBr and pressed into pellets for FTIR analysis. FT-IR

analysis provides information about the chemical structure of the material. Several indicator bands in the spectra that refer to functional groups represent the components, the presence or absence of which indicate the degradation or stabilization process.

2.6 XRD

The structure of the particulate in the polymer matrix was evaluated with XRD measurements. A Rigaku 200B X-ray diffractometer (45 kV, 100 mA) equipped with Cu KR radiation with a wavelength 0.1546 nm and a curved graphite crystal monochromator at a scanning rate of 0.5 %/min was used for this purpose.

2.7 Thermogravimetric Analysis

Thermo gravimetric analysis (TGA), Differential thermo gravimetric analysis (DTA) and Differential scanning calorimetry (DSC) analysis were performed with TGA Q500 (Perkin Elmer instrument). Samples were scanned from room temperature to 700°C at the heating rate of 10°C/

min. Melting point and enthalpy of composites were calculated by the instrument.

3. Results and Discussion

3.1 UV Exposure

Weight and colour loss in composite sample were observed after UV exposure. The color of the coir-epoxy infused particulate composite changed from dark brown to light brown at the exposed area because of the formation of a thin, strongly degraded surface layer. 6-7% weight loss was observed due to UV exposure.

3.2 Mechanical Testing

Tensile and flexural strength of composites decreases after UV exposure. Tensile and flexural strength were found to decrease from 31.5 to 17.2 MPa and 115 to 72 MPa respectively. The change in mechanical properties after UV exposure are clearly shown in the Figure 4 (a & b).

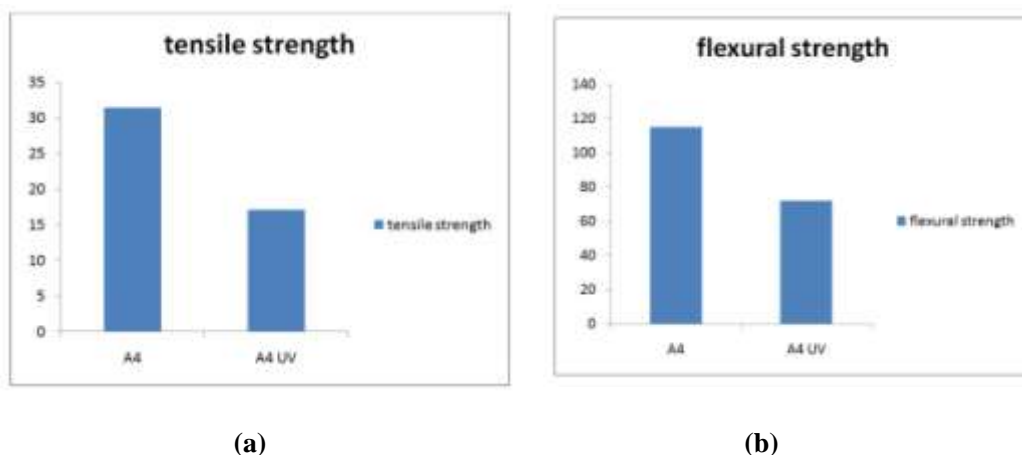


Figure 4 represents change in mechanical properties of composite due to UV exposure (a) Tensile Strength (b) Flexural strength

3.3 SEM

Figure 5 illustrates the scanning electron micrograph (SEM) results for coir epoxy infused cow dung composite before and after UV exposure.

From figures degradation after UV exposure can be clearly observed.

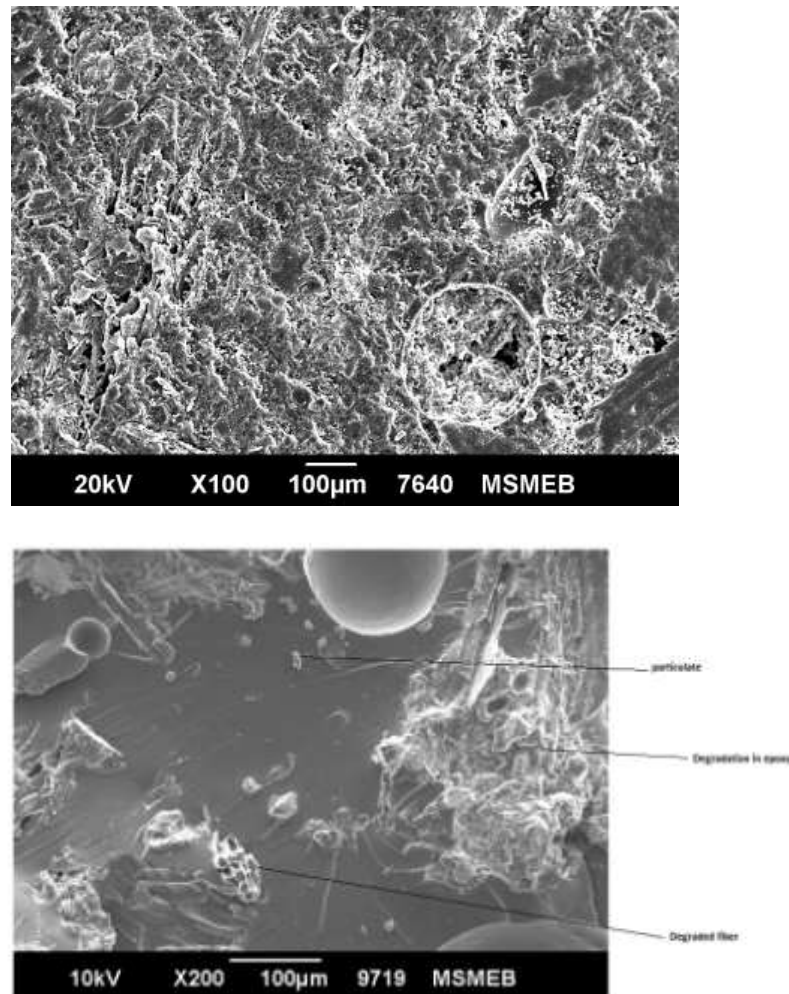


Figure 5 represents the microstructures of composite before and after UV exposure

3.4 FTIR

As can be seen in Figure 6, the intensity of the peak around 3400 cm^{-1} , which is evidence of OH band, is decreased after UV exposure of composites. The intensity of the band around 1730 cm^{-1} increased due to formation of ester band. The

intensity peak for aromatic ring at 1508.2 cm^{-1} is increased after UV exposure. A strong peak at 1730 cm^{-1} in the FTIR spectrum indicates the presence of acetyl group in the composite. Peak at 2820 cm^{-1} reveals the presence of a carbonyl group.

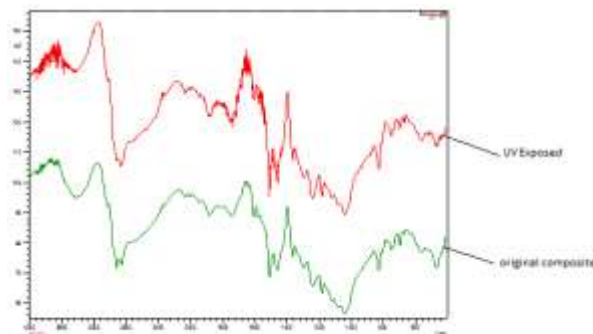


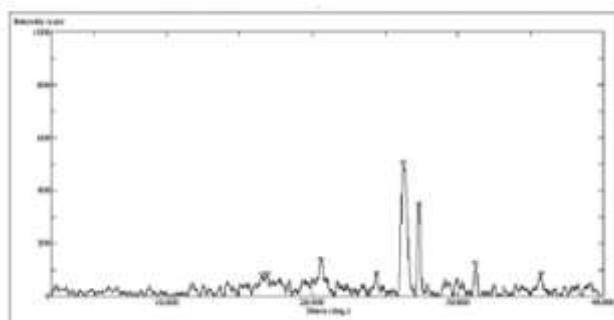
Figure 6 represents FTIR spectra of composite

3.5 XRD

XRD pattern of before and after UV exposure is shown in Figure 7. From XRD study it is observed that crystalline of composite reduces after UV

exposure from 41.83% to 29.38%. The diffractograms of A4 display a well-defined main peak around $2\theta = 22.5^\circ$, which is the characteristic of cellulose. This peak disappeared after UV exposure due to degradation of cellulose.

(a)



(b)

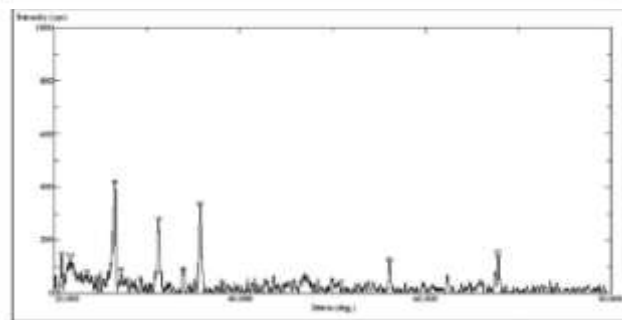


Figure 7 represents XRD pattern of composite (a) before exposure (b) after UV exposure

3.6 Thermogravimetric analysis

Samples were scanned between room temperature to 700oC to determine thermal degradation of coir-epoxy infused cowdung composite. TGA analysis were performed before and after UV exposure of samples. Table 1 represents % weight loss of normal and UV

exposed composite samples at different temperatures. Table 2 represents melting point and enthalpy of fusion of normal and UV exposed composite samples. Result shows subsequent effect of UV exposure on thermal properties of composite.

Table 1

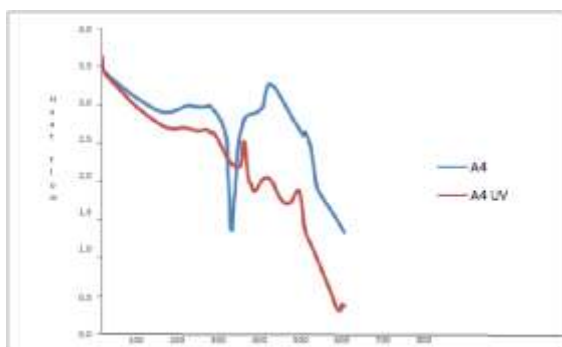
Temperature	A4	A4 UV
100-150	.03	0.59
150-200	.40	1.99
200-250	.60	2.60
250-300	.9	3.89
300-350	3.8	22.97
350-400	1.86	35.09
400-450	1.84	26.48
450-500	0.9	21.32
500-550	1.45	4.6
550-600	1.25	5.88
600-650	0.4	6.66

Table 2

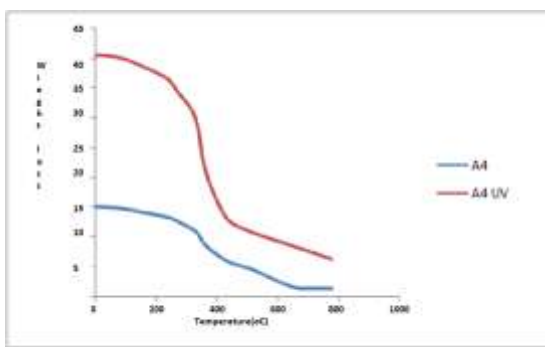
	A4	A4 UV
Melting point(°C)	346.48	273.59
Enthalpy of fusion	650.29	64.59

Figure 8 represents TGA and DSC graphs of composite before and after UV exposure. From the graphs declination of melting point of composite is observed.

Decrease of 20% and 90% in melting point and fusion enthalpy of composite was observed after UV exposure respectively.



(a)



(b)

Figure 8 represents thermograms of composite before and after UV exposure (a) DSC (b) TGA

4. Conclusion

The following conclusions can be drawn from above experiment:

1. Weight and colour loss were observed after UV exposure.
2. Mechanical properties of composite are also decreasing.
3. Degradation of epoxy matrix had occurred leading to crystallization and surface cracking.
4. Epoxy melting point decreases due to molecular chain scission and the formation of the carbonyl group.

5. Acknowledgement

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6. References

1. Agarwal BD and Broutman LJ. Analysis and performance of fiber composites, New York: Wiley and Sons (SPE Monograph); pp 355 1980
2. Chu PF. Glass fiber- reinforced polypropylene. In Karian HG, editor. Handbook of propylene and polypropylene composites. New York: Marcel Dekker, pp 263-334 1999
3. Turkovich VR and Erwin L. Fibre Fracture in Reinforced Thermoplastic Processing. *Polymer Engineering Science*. 1983, 23 743-749
4. Stark NM and Matuana LM. Ultraviolet weathering of photostabilized HDPE/wood flour composites. *Journal of Applied Polymer Science*. 2003, 90: 2609-2617
5. Matuana LM, Kamdem DP and Zhang J. Photoageing and Stabilization of Rigid PVC/Wood-Fiber Composites. *Journal of Applied Polymer Science*. 2001, 80:1943-1950
6. Kiguchi M and Evans PD. Photostabilization of wood surfaces using a grafted bezophenon UV absorber. *Polymer Degradation and Stability*. 1998, 61: 33-45
7. Matuana LM and Kamdem DP. Accelerated Ultraviolet Weathering of PVC/Wood-Flour Composites. *Polymer Engineering and Science*. 2002, 42:1657-1666
8. Muller U, Ratzsch M, Schwanninger M, Steiner M and Zobl H. Yellowing and IR-changes of spruce wood as result of UV-irradiation. *Journal of Photochemistry and Photobiology B*. 2003, 69: 97-105
9. Dence CW. The determination of lignin. Springer-Verlag, pp 33-61 1992.
10. Harper S. Developing Asbestos Free Calcium Silicate Building Boards. *Composites*. 1982, 13:123-138
11. Anglesa MN, Ferrandob F, Farriola X and Salvadoa J. Suitability of steam exploded residual softwood for the production of binderless panel. Effect of the pretreatment severity and lignin addition. *Biomass and Bioenergy*. 2001, 21:211-224
12. Tour U, Warishi H, Schoemaker HE and Gold MH. Oxidation of phenolic arylglycerol .beta.-aryl ether lignin model compounds by manganese peroxidase from Phanerochaete chrysosporium: oxidative cleavage of an .alpha.-carbonyl model compound. *Biochemistry Journa*. 1992, 31:4986-4995

13. Bao W, Fukushima Y, Jensen KA, Moen MA and Hammel HE. Oxidative degradation of non-phenolic lignin during lipid peroxidation by fungal manganese peroxidase. *FEBS Letters*. 1994. 354: 297-300
14. Kirk TK, Tein M, Kersten PJ, Mozuch MD and Kalyanaraman B. Ligninase of Phanerochaete chrysosporium. Mechanism of its degradation of the non-phenolic arylglycerol beta-aryl ether substructure of lignin. *Biochemical Journal*. 1986, 236:279-287
15. D.N.S.Hon. Weathering and photochemistry of wood. wood and cellulosic chemistry. Chapter 11, New York: Marcel Dekker, pp. 513-546, 2001
16. Beckert W and Lauke B. Critical discussion of the single-fibre pull-out test: does it measure adhesion? *Compos. Sci. Technol*. 1997, 57:1689-1706
17. Schmidt J, Kimura F and Gray DG. IR and UV Spectroscopic Study of Borohydride Reduced Mechanical Pulp During Monochromatic and Wide Band Irradiation. *Research on Chemical Intermediates*. 1995, 21:287-301
18. Argyropoulos DS, Heitner C and Schmidt JA. Observation of quinonoid groups during the light-induced yellowing of softwood mechanical pulp. *Research on Chemical Intermediates*. 1995, 21:263-274
19. Wypych G. Data on specific polymer, chapter 14, pp.275-410