Synthesis, Characterization and Thermal Properties of Photoresponsive Epoxy Resin Containing Benzylidene Units in the Main Chain

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ABSTRACT

A photoresponsive epoxy resin containing benzylidene units in the main chain has been prepared from bis (4-hydroxybenzylidene) cyclohexanone and epichlorohydrin using solution polycondensation method. The resulting compound possessed both the oxirane ring and benzylidene units. Thus, it has been highlighted in practical applications. The chemical structure of epoxy resin was characterized by Fourier transform infrared (FT-IR) and (1H, 13C) nuclear magnetic resonance (NMR) spectroscopies. The photolysis via [2π + 2π] cycloaddition reaction of the epoxy resin in the chloroform solution was studied by the UV-irradiation (350 nm). The thermal properties results show that the resulting epoxy resin is stable until 350 °C and its glass transition temperature is about 140 °C, which they were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively, to demonstrate its potential in the industrial coatings.

Introduction

Epoxy resins are among the most multipurpose materials due to their beneficial properties such as good thermal stability, chemical resistance, strong adhesion and higher electrical properties. These properties provide various applications for epoxy resins including high performance composites, adhesives, coatings, flooring, electrical-electronic laminates and low-viscosity (Ferdosian, 2015; Longhi, Zini, Kunst, & Zattera, 2017; Maiorana et al., 2016). Photoresponsive polymers are defined as the polymers that have been photosensitive groups, which are undergo to crosslinking, chain scission, or other chemical reaction under the light irradiation, leading to the change in various physical properties such as solubility, adhesive strength, softening point, or changing from liquid to solid and vice versa (Xiong, del Campo, & Cui, 2019). Photoresponsive polymers are also widely used as a polymeric photoresist in the field of microelectronics. Currently, they are of broad interest because they possess a combination of a good thermal stability, photosensitivity, and dielectric constant. However, the Photoresponsive polymers could be undergo either photo polymerization or photo cross linking upon UV irradiation. Among these photochemical reactions, the photo polymerization under UV light has been highlighted in practical applications. Due to the rapid cationic polymerization rate and good physical properties of the final products, some of the epoxy compounds have found a considerable use in many applications including photolithography, coating resins, and adhesives (Balaji, Grande, & Nanjundan, 2003; Hwang, Lee, & Jung, 2000; Kim, Ban, Kaihua, & Choi, 2003; Rehab & Salahuddin, 1999; Subramanian, Krishnasamy, Nanjundan, & Reddy, 2000). The UV radiation curing process has become a powerful tool to increase the crosslinking mechanism in the photoresist and to selectively modify the physicochemical characteristics of the irradiated areas. The polymers that containing the cinnamic ester and bis benzylidene groups have been used in the studying of photo transformation phenomenon that occur under UV irradiation. The photosensitivity of these materials is mainly attributed to the π electron density of the photoactive chromophore. Many properties such as, high photosensitivity, film forming ability, good solubility before irradiation changed to resistance toward solvents, plasmas, and etching agents after UV exposure and thermal stability are very important for a photopolymer to be used as a photoresist (Balaji, Grande, & Nanjundan, 2004; Reiser, 1989). Evaluation of Epoxy nanocomposites to improve resistance to degradation was reported by (Awad, Fellows, & Mahini, 2019), the epoxy nanocomposite containing 0.5% MWCNT had improved thermal stability and resistance to degradation compared to the bare epoxy resin. A novel and facile strategy was suggested by (Yao et al., 2015), to make a thermosetting epoxy resin/thermoplastic system with both shape memory and self-healing properties. A new class of a thermotropic main chain liquid crystalline polyesters containing bisbenzylidene and pyridine units were synthesized by a solution polycondensation in a previous work (Deepa, Balamurugan, & Kannan, 2010), showing resistant to a high temperature and good thermal stability. Also, a photosensitive epoxy resin containing a bis (4-hydroxy -3-methoxy benzylidene) acetone was synthesized by (Balakrishnan & Murugavel, 2009), exhibiting a highly soluble in the polar solvents and good thermal stability. In this study,

a new photoresponsive epoxy resin containing bis benzylidene units in the main chain was synthesized for the microelectronics and coatings applications and its chemical structure was characterized. The thermal properties of the resulting epoxy resin were investigated by TGA and DSC analyses.

EXPERMENT

2.1. Materials

2,6 bis (4- hydroxybenzylidene)cyclohexanone (BHBCH) was prepared and characterized in our previous article (Mohamed, Kuo, Mahdy, Ghayd, & Aly, 2020). Ethanol absolute, sodium hydroxide, epichlirohydrin and chloroform were purchased from Sigma-aldrich.

2.2. Synthesis of epoxy resin

The epoxy resin was synthesized using the following procedure: in the three necked round bottom flask 0.00546 mol, 1.7 g of BHBCH in a 30 ml isopropanol was dissolved and then 0.5 mol, 25 ml, of epichlirohydrin was added. After that 10 wt %, 0.01 mol of sodium hydroxide was added dropwise into the reaction mixture with stirring at 80 °C for 8h. The resulting product was kept at room temperature for 12h and the solvent was removed by a rotary evaporator then the excess of epichlorohydrin was separated by a vacuum distillation. The final product was washed by water and ethanol, a yellowish solid product was obtained. (Yield: 82.4 %). IR (KBr, cm-1): 1659 (C=O Stretch), 1599 (C=C stretch), 1508 (C-C stretch of aromatic ring), 1257 cm-1 (Ar-O-C asymmetric stretch), 1028 cm-1(C-O-C stretch), 915 cm-1(C-O vibration of epoxy ring). UV-vis λmax (chloroform) = 365 nm (-C=C-).

Characterizations

The solubility of the epoxy resin was tested in several of organic solvents. The chemical structure of epoxy resin was identified by Fourier transform infrared (FTIR) spectroscopy on a potassium bromide pellets from 400 to 4000 cm^{-1} on a Shimadzu 2110 PC(Assiut University, Egypt). Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) was performed using DTG-60H at heating rate of a 10 °C/min in a nitrogen atmosphere (Assiut University, Egypt). DSC scan was obtained using a DSC Q20 V24.11 Build 124 calorimeter in a nitrogen atmosphere at a heating rate of a 10 °C/min (Assiut University, Egypt). The photoresponsive of the synthesized epoxy resin was studied by UV spectrophotometr, in the solution method. The epoxy resin was dissolved in chloroform (0.0002M) and was irradiated by Herolab uv-6 S/L LW 365nm at a distance of 10 cm from the sample at various intervals of time followed by UV absorption measure on spectrophotometry, respectively. This procedure was repeated until the reduction in absorption was completed.

Results and discussion

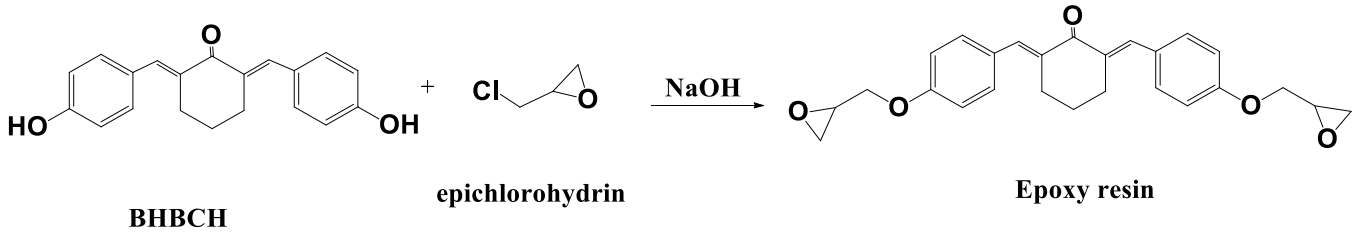
The epoxy resin containing benzylidene moiety was synthesized by a solution polycondensation reaction of BHBCH with epichlorohydrin using NaOH as catalyst (scheme 1). The solubility of the prepared epoxy resin in various organic solvents was tested in a test tube. It was found that the resulting epoxy resin was highly soluble in the polar solvents such as, THF, DMF and methanol at room temperature and was insoluble in nonpolar solvents. The FT-IR analysis of the synthesized epoxy resin is shown in Figure 1. In this spectrum, it was observed that the band at 1660 cm-1 is attributed to the C=O stretching

and the band at 1598 cm-1 is attributed for to C=C olefinic stretching. The symmetric stretching vibration of C—O (epoxy ring) is observed at 914 cm-1. The broad band at 3420 cm-1 is attributed for the vibrations of the hydroxyl group and a strong band at 2923 cm^{-1} is due to the C—H stretching vibrations.^{1}H-NMR spectrum of the resulting epoxy resin is shown in **Figure 2(a)**.

Table 1. FT-IR, ^{1}H-NMR and ^{13}C-NMR results of the resulting epoxy resin

Analysis methods	Results
FT-IR(ν, cm^{-1})	C=O(1660),C=C(1598), C-O epoxy ring(914), -OH(3420), C-H(2923)
^{1}H-NMR(δ, ppm)	C-H oxiran ring(3.26), CH_2 oxirane ring(2.6), CH_2-O moiety(3.90-4.20), olefinic protons(7.35-7.37), aromatic ring(6.86-7.67)
^{13}C-NMR(δ, ppm)	C-H oxiran ring(44.6), CH_2 oxirane ring(50.01), CH_2-O(66.8-70.33), CH_2 cyclohexanone (23.01-28.48), phenyl group(114.61-158), C=O(190.4)

Scheme 1. Synthesis of epoxy resin



BHBCH **epichlorohydrin** **Epoxy resin**

Scheme 2. Photochemical reactions of Bis (benzylidene) cyclohexanone based epoxy resin.

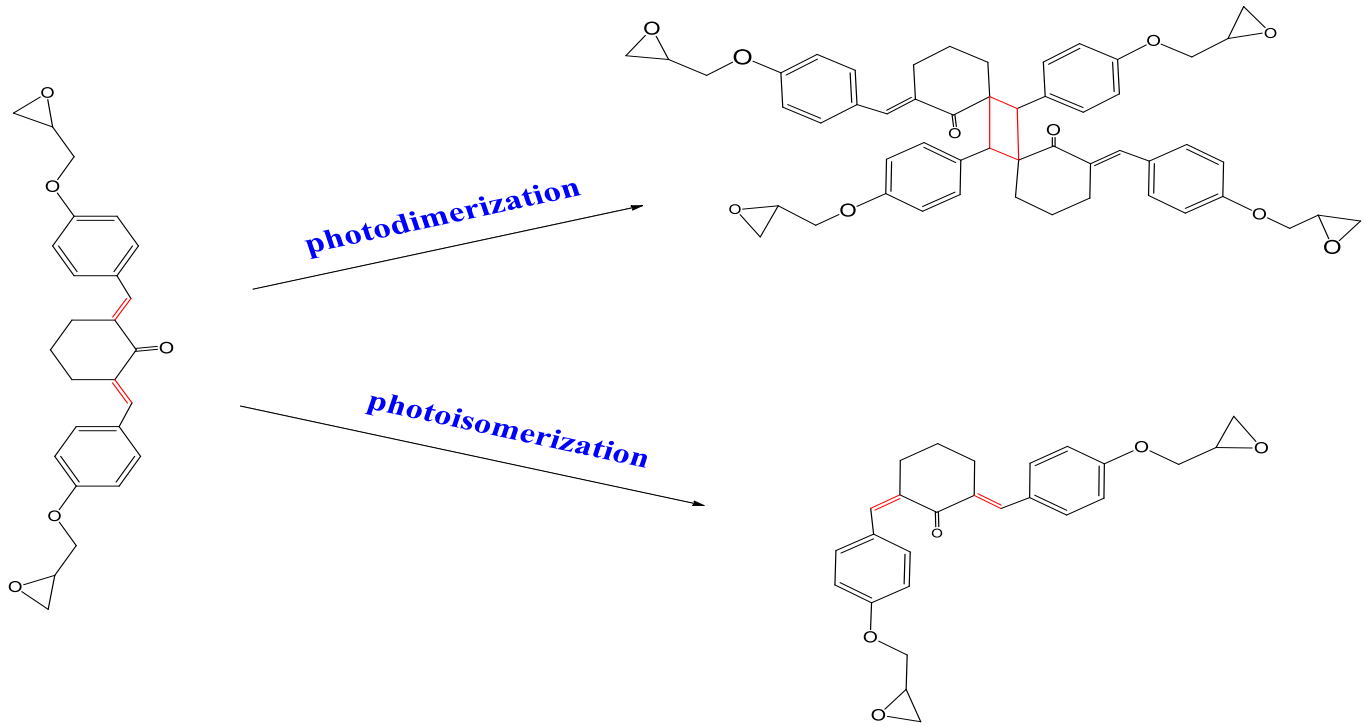
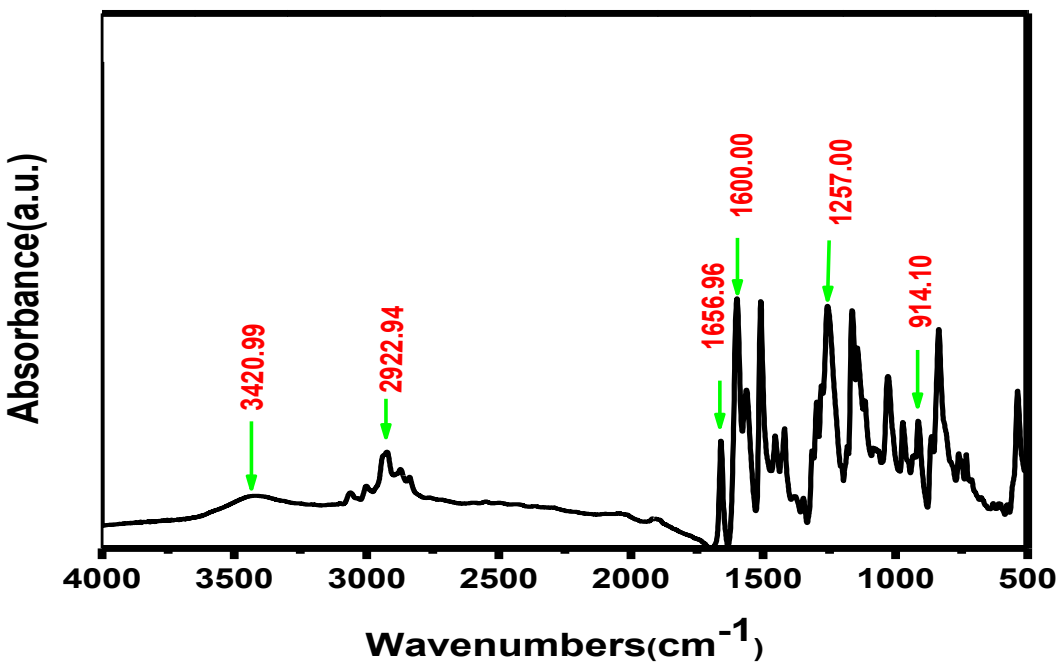


Figure 1. IR spectrum of epoxy resin



In this spectrum, the characteristic proton resonances of the oxirane ring appeared as a singlet signal at 3.26 ppm which is assigned to CH (methine), and the signal at 2.67 ppm is assigned to CH_2 (methylene). The signals at 3.90 - 4.20 ppm are assigned to ─CH_2─O─ moiety. The signal at 7.35-7.37 ppm is assigned to the olefinic protons. The signals at 2.82-2.84 ppm are assigned to CH_2 methylene (cyclohexanone). The multiple signals at 6.86-7.67 ppm are assigned to protons of the aromatic ring. ^{13}C - NMR spectrum of the resulting epoxy resin in $CDCL_3$ is shown in **Figure 2(b).** In this spectrum, the characteristic carbon resonances of the carbon oxirane ring (methylene, methine) appear at 44.6 and 50.01 ppm. The signals at 68.8-70.33 ppm are assigned to ─CH_2─O─ moiety. The signals at 23.01-28.48 ppm are attributed to the CH_2 (cyclohexanone). The multiple signals between 114.61 -158.79 ppm are attributed to the aromatic carbons of the phenyl group and the one at 190.4 ppm is due to the carbon of carbonyl group. All the FT-IR, ^{1}H-NMR and ^{13}C-NMR results are summarized in **Table 1.**

The thermal properties of the resulting epoxy resin were studied by thermogravimetric analysis and differential scanning calorimeter. The TGA thermogram of the synthesized epoxy resin (**Figure 3**) show three stages of thermal degradation of epoxy resin, and the maximum weight loss of 90% occurred in the temperature from 350 to 650 °C. Furthermore, its start thermal degradation temperature was at about 350 °C. (Tuohedi & Wang, 2021). It was found that the LCS-epoxy resin had the start degradation temperature of 200 °C, which is much less than that reported in this study. The Td5, Td10 and char yield at 600 °C of the resulting epoxy resin are 314, 345 °C and 28%, respectively. These results are higher than those reported for epoxy resin (DGEBAGY260) and

epoxy resin (diglycidyl adipate) in previous works (Longhi et al., 2017; Maiorana et al., 2016). DSC analysis of the synthesized epoxy resin is shown in Figure 4. In this figure, the melting point, glass transition temperature and curing exothermic peak of the synthesized epoxy resin are 136, 140, and 337°C, respectively. This Tg value (140 °C) of epoxy resin is higher than that of the blend containing 70 vol % epoxy resin and 30 vol % PDCPD in a previous work (Rohde, Le, Krishnamoorti, & Robertson, 2016). All the thermal results were summarized in Table 2. The photo reactivity property of a new epoxy resin was studied in a chloroform solution after it was irradiated under UV light and the structural changes were monitored by UV spectrophotometer. The representative spectral changes in photolysis of epoxy resin in a solution state at various intervals of time is shown in **Figure 5.** The absorption maximum at around 360 nm corresponds to π→π* transition of the olefinic double bond present in the main chain. The decreasing in the intensity after irradiation may be ascribed to the gradually disappeared of the double bond of bis (benzylidene) cycloalkanone chromophores and the formation of cyclobutane ring at 280 nm, due to the 2π + 2π cycloaddition reaction (Balamurugan & Kannan, 2008; Lin, Chien, Chen, & Juang, 2017). An isobestic point was observed at around 312 nm which may be due to the cis-trans isomerization of olefinic double bond present in the main chain (Scheme 2). The absorption at 360 nm has completely disappeared after 60 min of the irradiation process. The rate of conversion of >C=C< to —c—c— was calculated using the expression, [(A0 − At)/ (A0 – A)] × 100, where A0 , At and A are the absorption intensities of >C=C< at irradiation times, 0, t and A time after which there is no more important change in the absorption (Balakrishnan & Murugavel, 2009). The conversion percentage is plotted against the time of irradiation as shown in Figure 6. The a change in color from a pale yellow to a clear red during the successive irradiation of bis benzylidene based epoxy resin was observed in the solution as shown in Figure 7. This may be ascribed to the formation of cis conformation which is further confirmed by the appearance of a new absorption peak around 500 nm.

Table 2. Thermal results obtained from TGA and DSC analyses

Samples	[a] T_{d5} (°C)	[b] T_{d10} (°C)	[c] Char yield (%) at 600°C	Tg °C (by DSC)	References
Epoxy resin	314	345	28.6	140	This work
Epoxy resin ($DGEBA_{GY260}$)	240	300	12	-	[2]
Epoxy resin (diglycidyl adipate)	297	311	-	77	[3]

[a] T_{d5} is the temperature when the weight loss of polymer reaches its 5%.
[b] T_{d10} is the temperature when the weight loss of polymer reaches its 10%.
[c] Char yield (%) at 600°C is the remaining mass after completely degrading the polymer.

Figure 2. (a) 1H and (b) 13C –NMR of epoxy resin

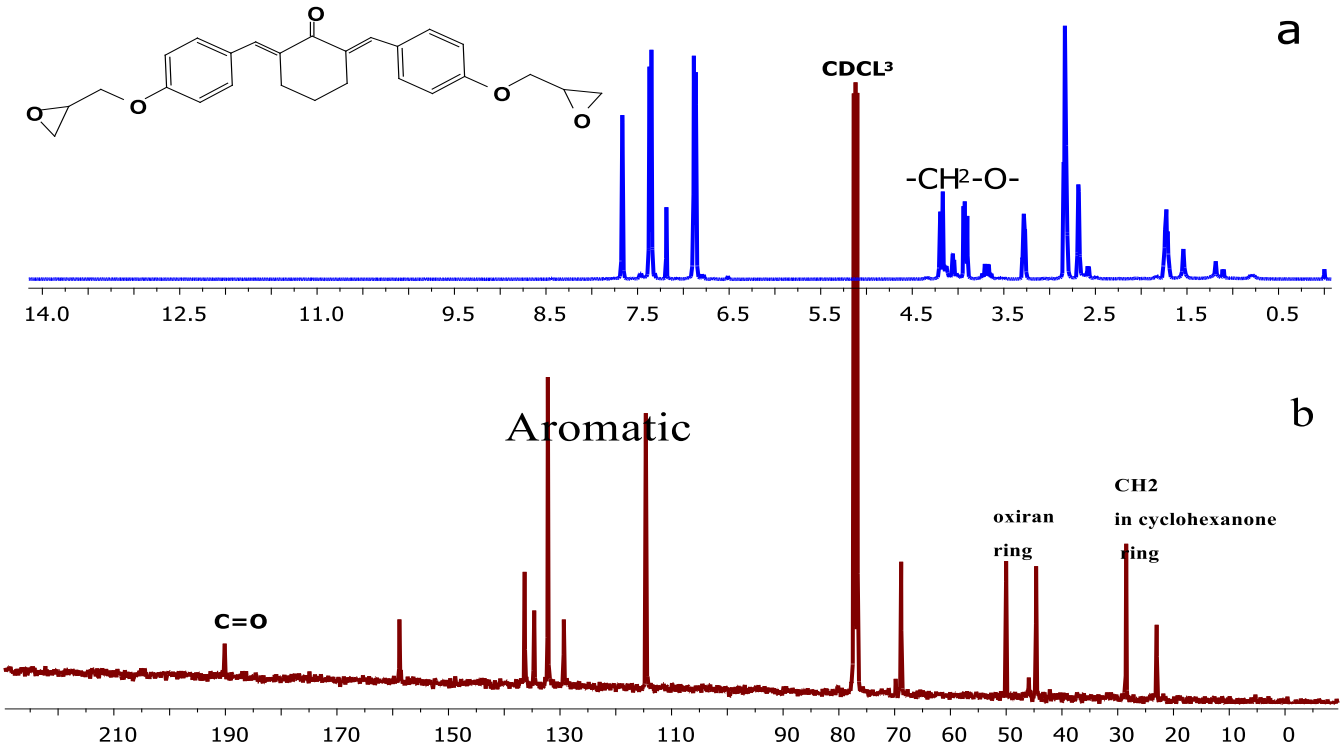


Figure 3. TGA thermogram of epoxy resin

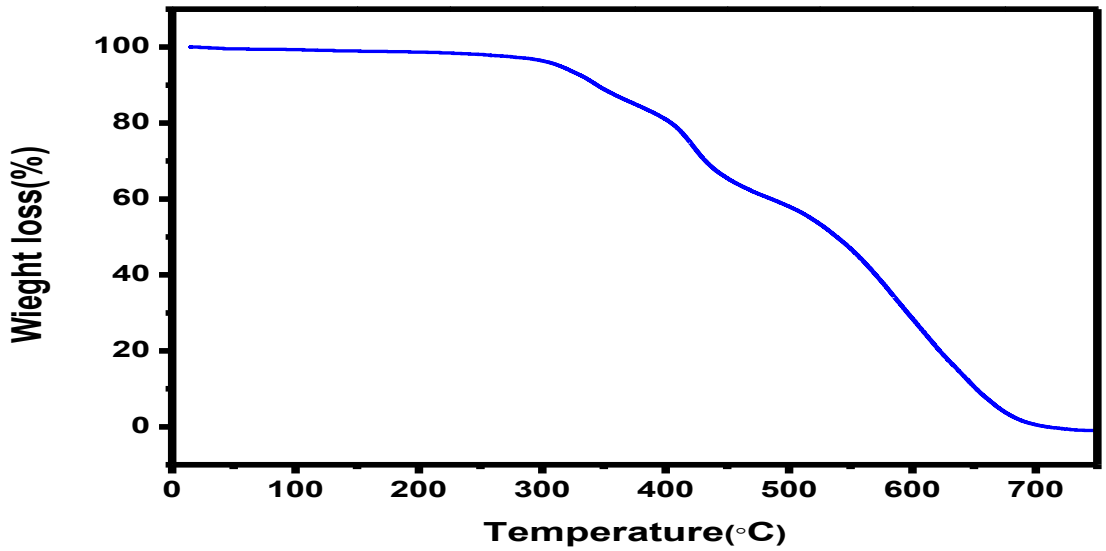


Figure 4. DSC thermogram of epoxy resin

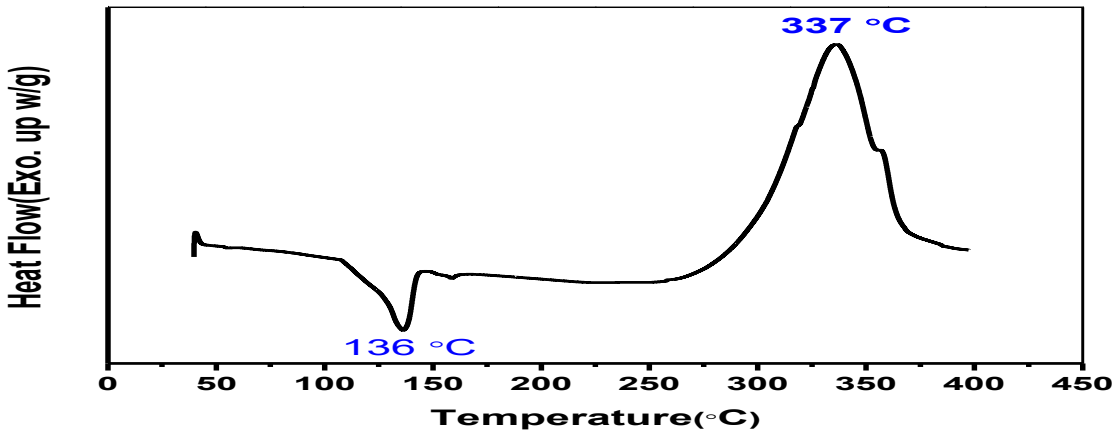


Figure 5. Changes in UV spectral characteristics during photolysis of epoxy resin in chloroform solution at various time intervals.

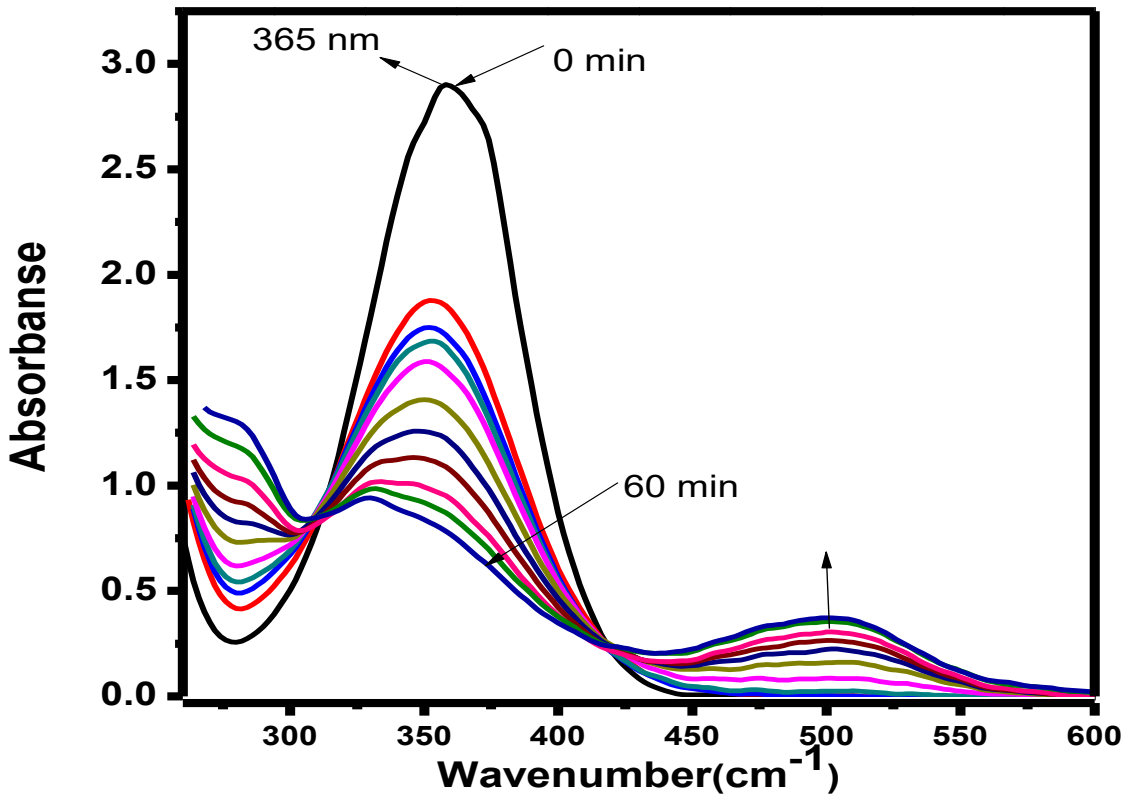


Figure 6. Rate of disappearance of >C=C< epoxy resin

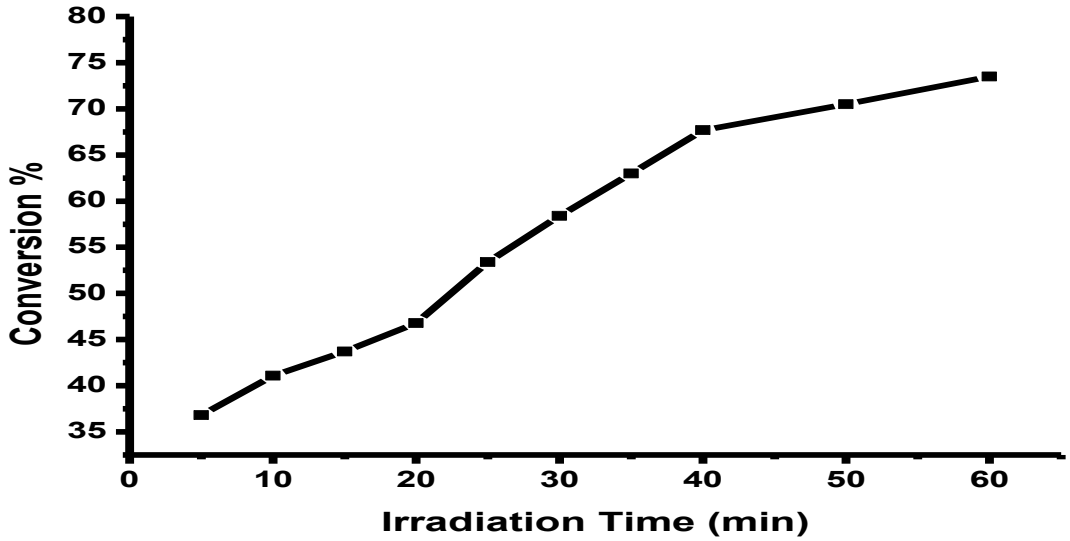
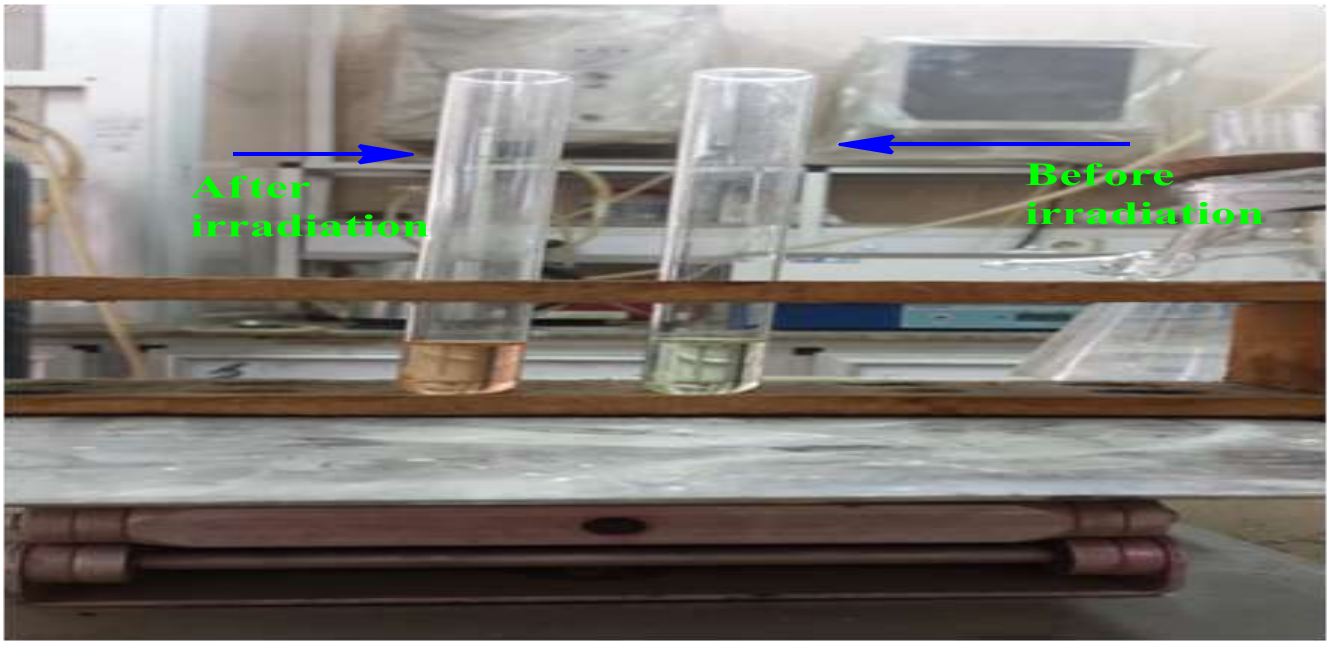


Figure 7. The change in color from a pale yellow to a clear red during the UV irradiation (350 nm) of the Bis benzylidene based epoxy resin.



Conclusions

We have successfully prepared the photoresponsive and thermoset epoxy resin from BHBCH and epichlorohydrin for the microelectronics and coatings applications. The chemical structure of the resulting epoxy resin was characterized by FTIR, (1H, 13C) NMR and UV analyses. The thermal properties show that the resulting epoxy resin was stable up to 350 °C and its Tg was a high value (140 °C), which is an important result to the choice of adhesives/sealants for raised temperature applications. The UV absorption results show that the bis benzylidene cyclohexanone moiety can undergo a photo isomerization, photo dimerization reactions under the influence of a UV irradiation. The observed solubility, thermal stability, and photo reactivity for the resulting epoxy resin suggest that this epoxy resin may be used as a negative photoresist.

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