



A selective reaction of polyhydroxy fullerene with cycloaliphatic epoxy resin in designing ether connected epoxy star utilizing fullerene as a molecular core

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Abstract

A novel ether connected epoxy star like polymer was synthesized by selective reaction of water soluble polyhydroxy fullerene (fullerenol) with a commercial grade cycloaliphatic epoxy resin (CY-230, Ciba Geigy) in heterogeneous medium at ambient alkaline condition using tetrabutylammonium hydroxide as phase transfer catalyst. The reaction went well in such conditions and the hydroxy groups of fullerenol underwent selective nucleophilic addition reaction with polar carbonyl groups of the epoxy resin with the formation of a hemiketal. The progress of the reaction was monitored by FTIR analysis of the product formed. The disappearance of characteristic FTIR bands of fullerenol (at 1593.2, 1381.2, and 1068 cm^{-1}) and the typical carbonyl peak (at 1725 cm^{-1}) of parent epoxy resin and also changes of broad hydroxy peak (at 3431 cm^{-1}) of fullerenol into a sharp peak (at 3396.6 cm^{-1} , indicating reduced hydrophilicity) in the reaction product clearly demonstrated the chemical attachment of the epoxy units to the fullerene core. Multiple epoxy units (about 8–10) were attached to fullerene core. Non-reactivity of fullerenol towards DGEBA epoxy resin (LY 556 Ciba Geigy) in similar conditions further supports our result. The thermal properties of the product were influenced by the presence of fullerenol and exhibits higher thermal stability compared to parent epoxy. A probable reaction mechanism for the reaction has also been discussed.

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1. Introduction

Molecular architecture leading to the formation of highly branched polymers having hyperbranched, dendritic, and star-like structures are becoming fascinating field of recent research. The interest lies with their ability to form monofunctional and monodisperse materials of known high molecular mass (within molecular dimension range) having globular three-dimensional structure, which may lead to greater encapsulation. Fullerene, an electron-deficient polyolefin, exhibits a variety of outstanding electronic, conducting, and magnetic properties and can be a potential candidate as a molecular core in designing such type of molecular architect. A significant advantage in functionalization of fullerene and its derivatives by polymeric materials via chemical reactions will be to

provide an encapsulation of fullerene clusters having conducting properties by a polymeric insulating layer. The incorporation of fullerene may also considerably modify the physical and chemical properties of the parent polymers. These novel materials may find outstanding applications in sophisticated electronic devices and various other fields. Moreover, the incorporation of reactive fullerene functionality would provide sites for further functionalization, including functionalization by methods that would fail for original polymers. In spite of their potential future applications, only few star like polymers containing fullerene has been reported so far. A novel star-like $\text{C}_{60}(\text{CH}_3)_x(\text{PAN})_y$ copolymer was synthesized by the reaction of living *n*-butyl-terminated polyacrylonitrile (PAN) with C_{60} in a heterogeneous medium followed by end-capping with methyl iodide [1]. Similar star-like $\text{C}_{60}(\text{PMS})_{1-3}(\text{CH}_3)_{1-3}$ copolymers have also been reported [2]. Reaction of living anionic polystyrene (PS) with C_{60} gives novel star-like $\text{C}_{60}(\text{PS})_x$ polymers [3,4]. Star-like

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$C_{60}(PS)_x$ polymeric materials via free-radical polymerization have also been reported [5–8]. Further, it has been demonstrated that combination of polyol function and the ball shape C_{60} cage in fulleranol (a polyhydroxy fullerene) enrich their utilization as a spherical molecular core in the design of dendritic, star shape polymers. Chiang et al. [9] have synthesized urethane-connected polyether star-like polymer as a soluble material containing six chemically bonded polymer arms per C_{60} (polydispersity index of 1.45) utilizing fulleranol as a molecular core. They have also reported the remarkable advantages of incorporation of polyhydroxylated fullerene in the poly(urethane-ether) network giving high performance elastomers with greatly enhanced tensile strength, elongation, and thermo-mechanical stability in comparison with their linear analogs or conventional polyurethane elastomers cross-linked by trihydroxylated reagents [10]. Recently, the same group has synthesized conducting star polymers using polyfunctionalized C_{60} -core and oligoaniline arms with upto 16 aniline units per arm [11–13]. The synthesis involves nucleophilic substitution of nitro groups in monodisperse nitrofullerenes by hexadecaniline in the presence of triethylamine at 50 °C for 6 h. This type of poly(oligoanilinated) C_{60} star-burst macromolecules were found promising in improving physical and mechanical properties of the materials without greatly compromising their inherent conductivity and thermal stabilities. In these series of utilizing functionalized fullerene as core moiety for the synthesis of star-like polymers, we here report the synthesis of novel ether connected star like polymer by selective reaction of fulleranol with cycloaliphatic epoxy resin (CY-230) in heterogeneous medium at ambient alkaline condition. It is noteworthy to mention here that this is the first time we are reporting a fullerene core epoxy star-like polymer where the parent epoxy resin contains two active functional moieties, i.e. carbonyl and epoxy in the molecule. The beauty of the present work was the judicious selection of reagents and reaction conditions and the significance of the work was the simplicity of process adopted and the high selectivity of the chemical reaction. It has been observed that the hydroxy groups of fulleranol selectively underwent nucleophilic addition reaction with the carbonyl groups of the epoxy resin only. The progress of the reaction and chemical attachment of the polymeric arms has been monitored by FTIR analysis of the reaction product. Substantial weight gain and thermal behaviour of the product clearly demonstrate the formation of star-like product.

2. Experimental

2.1. Materials

[60] Fullerene (C_{60}) was obtained from MER Co. (purity >99.5%). The sample purity was checked by UV/Vis

absorption, ^{13}C NMR, and was used without further purification. Commercial grade cycloaliphatic epoxy resin (CY-230, Ciba Geigy Product, epoxy equivalent 4.1–4.5 eq/kg) as pale yellow viscous liquid and DGEBA epoxy (LY-556, Ciba Geigy Product, epoxy equivalent 5.2–5.4 eq/kg) as white viscous liquid were used. Methanol and tetrahydrofuran (THF) (all HPLC grade, E Merck) were used as received. Sodium hydroxide and tetrabutyl ammonium hydroxide (TBAH) (all analytical grade, E Merck) were used as received.

2.2. Methods

2.2.1. Synthesis of polyhydroxy fullerene (fullerenol)

Several methods have been reported for the synthesis of fulleranol [14–19]. The fulleranol used in these reactions were prepared by the reaction of fullerene in toluene and aqueous sodium hydroxide at ambient temperature using TBAH as phase transfer catalyst [19]. The structure of the resulting fulleranol was characterized by elemental analysis and various spectroscopic methods (IR and ^{13}C NMR) to consist of an average of 15–18 hydroxy groups per fullerene and also compared with the reported values. The fulleranol was first air-dried and then under reduced pressure before subjecting to further chemical reaction.

2.2.2. Synthesis of fullerene-cored epoxy star polymer

The condensation reaction between cycloaliphatic epoxy resin and fulleranol was performed in a two-phase system at room temperature (25 °C) in alkaline condition in presence of air. A 150 ml THF solution of cycloaliphatic epoxy (5.5 g) was vigorously stirred with 350 ml aqueous solution of fulleranol (100 mg) containing sodium hydroxide (3 g) and few drops of TBAH at room temperature. To completely eliminate the possibility of cross-linking reaction, an excess of epoxy resin (approximately 10 equivalent of epoxy group to each OH group of fulleranol) was used. After 48 h, a brown sludge precipitated out at the bottom. After removal of THF by decantation and evaporation under reduced pressure, the aqueous sludge was further stirred for 30 h after adding 2 g more sodium hydroxide. After the reaction was over, the red-brown product was allowed to precipitate overnight by adding large excess of methanol into the reaction mixture. The product was collected by centrifugation from the aqueous methanolic solution. The thick red-brown mass was washed several times with water, followed by methanol to remove sodium hydroxide, TBAH, and unreacted resin (if any) completely. The product was then first air-dried and finally under reduced pressure to remove traces of water to obtain a red-brown solid powder mass (450 mg).

In a similar manner a slight excess of one equivalent of epoxy per each OH group of fulleranol was reacted under similar condition. In this case also 100 mg of fulleranol produced 450 mg of red-brown product.

2.2.3. Reaction of fulleranol with DGEBA epoxy resin

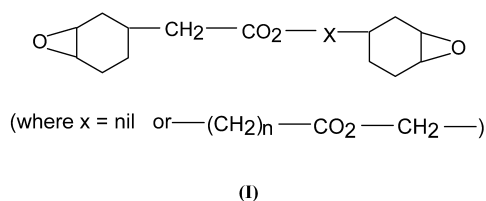
The reaction of fulleranol with DGEBA epoxy resin (LY-556) (in a ratio of 10 equivalent of epoxy for each OH group of fulleranol) was carried out under similar alkaline condition at ambient temperature. No reaction occurred in this case.

2.3. Characterization

FT-IR spectra were recorded on a Nicolet Magna IR 750 Spectrometer, using KBr pellets. Thermal properties were measured using a Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments) attached to a Thermal Analyst 2100 (Du Pont Instruments) thermal analyzer, at a heating rate of 10 °C/min under N₂ atmosphere.

3. Results and discussion

The cycloaliphatic epoxy resins are a class of compound formed by the Tischenko condensation of tetrahydrobenzaldehyde followed by the epoxidization of the dienes by peracids. The commercial grade cycloaliphatic epoxy resin (CY-230) employed in the present reaction was a pale yellow viscous liquid containing both epoxy and carbonyl functional groups in its structure (I). This resin could be converted into the corresponding C₆₀ core ether connected epoxy star-like polymer as insoluble, red-brown solid powder in high yield (more than four and half times the mass of starting fulleranol were obtained) by reaction with fulleranol in heterogeneous medium at ambient alkaline condition using TBAH as phase transfer catalyst.

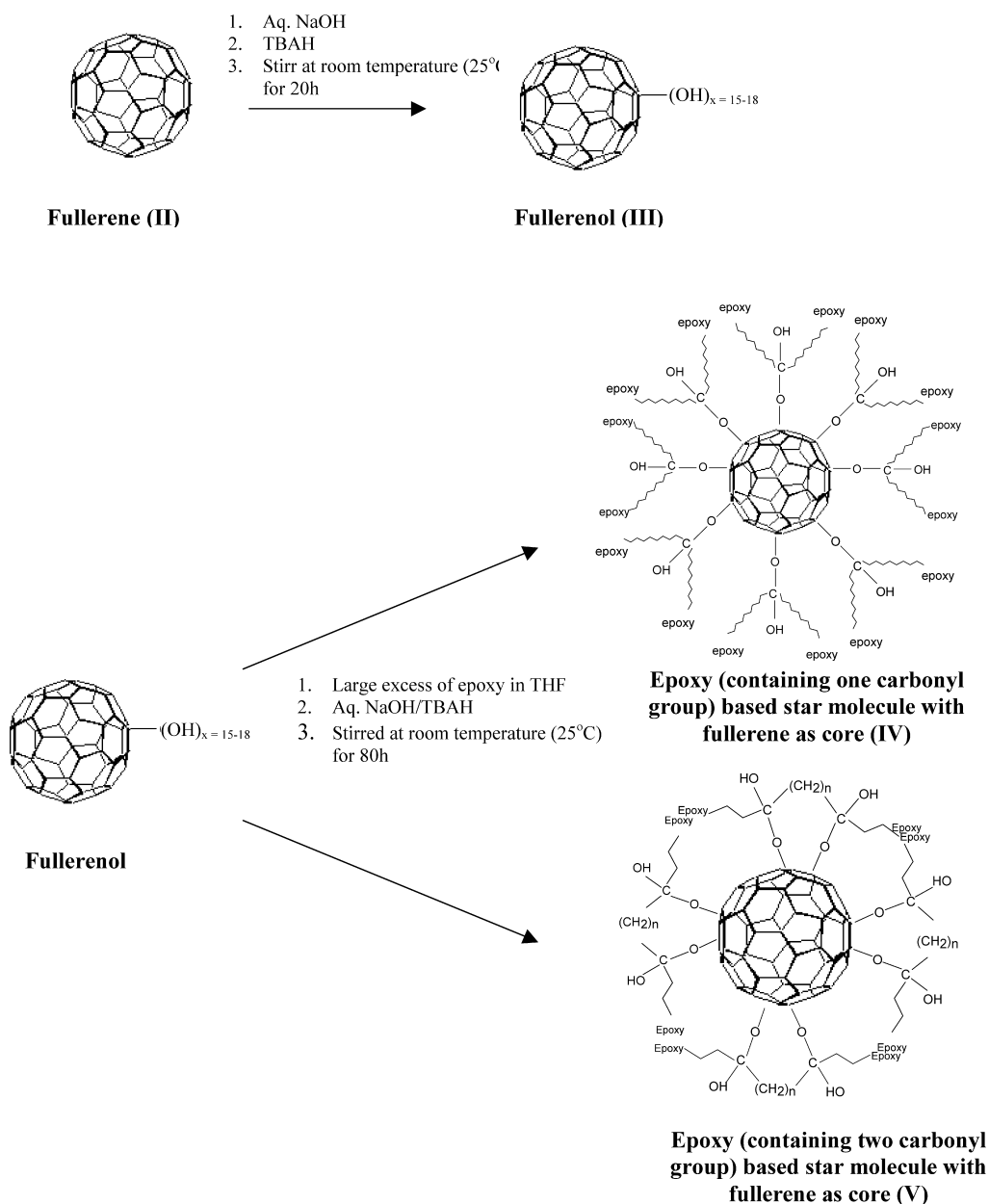


3.1. Selectivity of reaction

It has been observed that in alkaline condition the hydroxy groups of fulleranol selectively and exclusively react with the carbonyl groups of resin only. No reaction with epoxide groups was observed under such conditions. Progress of the reaction was easily monitored by the decrease in intensity of the typical carbonyl IR peak at 1725 cm⁻¹ of the resin, until it disappeared completely. Disappearance of carbonyl peak and the appearance of sharp hydroxy peak at 3396.6 cm⁻¹ in the product also suggested that the reaction of alcohol groups with carbonyl groups proceed only via hemiketal formation and not via transesterification reaction (Scheme 1). It must be men-

tioned that in the reaction Scheme 1, for easy depiction of the reaction sequence, only one hydroxy group have been shown to be bonded to fullerene, though in actual molecule number of hydroxy groups may be between 15 and 18. Also, shown in the scheme the reaction of one hydroxy group of fullerene with one carbonyl group of epoxy (IV), though in actual case it might be that two hydroxy groups of same fullerene core are reacting with two carbonyl groups of epoxy resin with the formation of a stable star like cyclic ring structure (V).

The FT-IR spectra of fulleranol [1(A)], parent epoxy resin (CY-230) [1(B)], reaction product of fulleranol with CY-230 in 1:10 ratio [1(C)], and the reaction product of fulleranol with CY-230 in 1:1 ratio [1(D)] were shown in Fig. 1. Disappearance of the characteristic FTIR bands of fulleranol at 1593.2, 1381.2, and 1068 cm⁻¹ and changes of broad hydroxy band of fulleranol into a sharp band (indicating reduced hydrophilicity) in the reaction product clearly demonstrate that the epoxy units were covalently attached to the C₆₀(OH)_x core, which may lead to greater encapsulation. The main bands in the FT-IR spectra [1(B)] of unreacted epoxy (pure CY-230) occurs at 3056, 2964, 2929, 2880, 1725, 1607, 1509, 1459, 1395, 1289.7, 1247, 1184, 1120, 1097, 1034, 912, 832, 796 cm⁻¹, whereas FTIR spectra [1(C)] showed the main band of the reaction product of fulleranol with CY-230 (in 1:10 ratio) at 3396.6, 2961, 2926, 2880, 1607, 1509, 1459, 1408, 1297, 1258, 1182, 1097, 1028, 873, 805 cm⁻¹. Comparison of FT-IR spectra of [1(B)] with [1(C)] clearly demonstrated that the reaction product differs from parent epoxy (CY-230) at few main bands. The appearance of new peaks at 3396.6 and 805 cm⁻¹ in [1(C)] and disappearance of 3056 and 1725 cm⁻¹ peaks due to parent epoxy were the important and the most significant observations. Also, in some cases the peak positions were shifted and intensity differs. From the analysis of FT-IR spectra of [1(A)], [1(B)], and [1(C)] two significant conclusions could be drawn. Firstly, the epoxy units were covalently attached to fulleranol core moiety and secondly, the covalent attachment occurred through the selective chemical reaction of hydroxy groups of fulleranol with the carbonyl groups of epoxy resin only with the formation of hemiketal (appearance of 3396.6 cm⁻¹ peaks and disappearance of 1725 cm⁻¹ peak in the product with respect to unfunctionalized epoxy). The structure of the product formed can be easily explained when an epoxy resin containing single carbonyl group is reacted with hydroxy group of fullerene. However, in case of epoxy resin containing two carbonyl groups, two competitive reactions can occur simultaneously. Firstly, the two hydroxy groups of same fullerene core can react with the two carbonyl groups of the same epoxy molecule leading to the formation of a stable star like cyclic structure. And secondly, the two hydroxy groups of different fullerene cores may react with two carbonyl groups of the same epoxy molecule resulting in the formation of a highly crowded structure because of bulky cyclohexane epoxide ring



Scheme 1.

attached to the carbonyl group, which will be pushed closer to the fullerene moiety. Considering the same reactivity for both the hydroxy groups towards the carbonyl groups, which are separated by small distance (usually four carbon), as in the present case, the second path is highly unlikely because of the steric hindrance offered by both fullerene and the cyclohexane epoxide ring, leaving only the possibility of formation of a star-like cyclic structure. Further, as will be discussed subsequently, it has been observed that the reaction rate and the nature of the product formed are independent of the concentration of parent epoxy resin used, which definitely rule out the possibility of attachment of second fullerene core. If the reaction had proceeded through the second path the concentration of parent epoxy resin

taken should have played a vital role on the nature of the product formed [9,10]. The disappearance of aromatic peak (3056 cm^{-1}) in the product indicate that small amount of aromatic compounds might have been added as plasticizer/modifying agent in commercial grade epoxy formulation which was finally washed out after reaction with fullerene. Another significant observation was that the epoxy peak (1247 cm^{-1}) of parent epoxy resin (CY-230) was retained in the product, which also clearly demonstrated that hydroxy groups of fullerene did not react with epoxy groups under such conditions. To substantiate our finding two more chemical reactions of fullerene were carried out under similar alkaline condition; (i) with CY-230 in 1:1 ratio of fullerene to epoxy and (ii) with a DGEBA epoxy resin (LY-

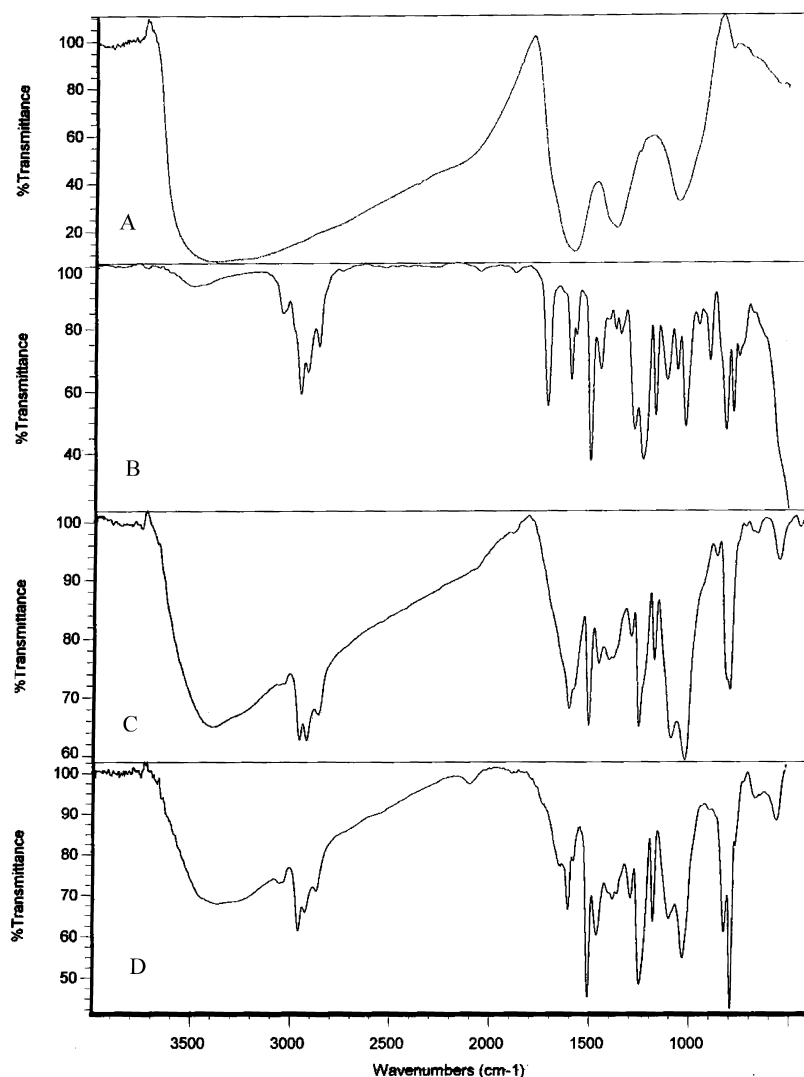


Fig. 1. FTIR spectra of the samples: (A) fullerenol, (B) parent cycloaliphatic epoxy (CY-230), (C) the reaction product of fullerenol and epoxy in 1:10 ratio, and (D) the reaction product of fullerenol and epoxy in 1:1 ratio.

556), where there was no carbonyl group present. Whereas no reaction was observed in the second case, the reaction product of the first case gave same product as that of previous one in similar yield [1(D)]. These two reactions clearly demonstrated that the reaction of fullerenol with cycloaliphatic epoxy (CY-230) was independent of concentration of epoxy used and always proceed through carbonyl group reaction only.

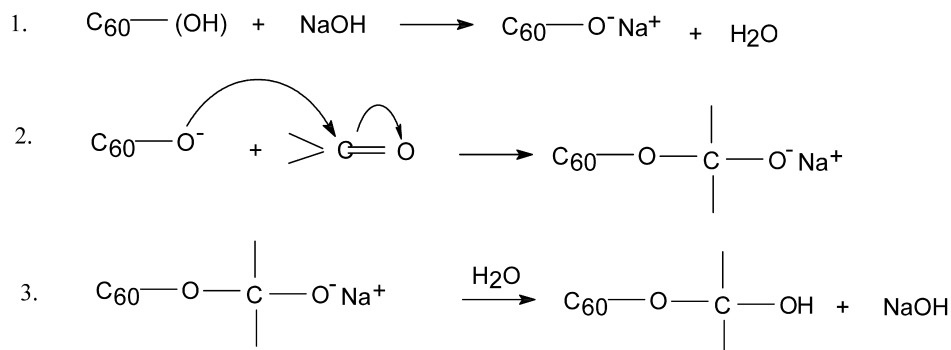
3.2. Mechanism of reaction

The hydroxy groups attached to fullerene, which was considered to be a strain aromatic organic molecule (nonplanar pyramidal polyalkene structure) [20], were sufficiently acidic to be ionized by sodium hydroxide to fulloroxide ($C_{60}O^-$) anions. The nucleophiles thus formed, underwent nucleophilic addition reactions with the polar carbonyl groups of the cycloaliphatic epoxides with the

formation of hemiketals. The mechanism may be depicted as follows (Scheme 2).

3.3. Thermal properties

The thermal stability of the samples was measured using thermogravimetric analysis. The degradation pattern, for the various samples, so obtained is shown in Fig. 2. The initial weight loss observed below 100 °C in all the samples were because of the residual moisture inherently present in the samples, which remains even after vacuum drying. In pure hydroxy fullerene [2(A)], a continuous but slow weight loss was observed from 150 to 550 °C, after which it degrades rapidly. Neat epoxy resin [2(B)] degrades mainly in two stages; one between 150 and 225 °C and other between 225 and 325 °C, which is the main degradation stage. It is interesting to observe that the thermal behaviour of the product was significantly influenced by the presence of fullerene molecule [2(C)]. It can be observed from the figure



Scheme 2.

that the thermal stability of the product shows an appreciable increase, with significant weight loss occurring only after 300 °C. This supports the covalent attachment of epoxy chain to fullerene with the formation of a stable star-like cyclic molecule. Further the thermal degradation behaviour of 1:1 epoxy-fullerene and 1:10 epoxy-fullerene was almost the same.

4. Conclusion

The hydroxy groups of fullerene selectively undergo nucleophilic addition reaction with carbonyl groups of a cycloaliphatic epoxy resin with the formation of star like polymers. The thermal stability of the product was significantly influenced by the presence of fullerene molecules. It will be interesting to see how the same reaction system behaves in acidic condition, which is currently under progress, and we will be reporting the results shortly.

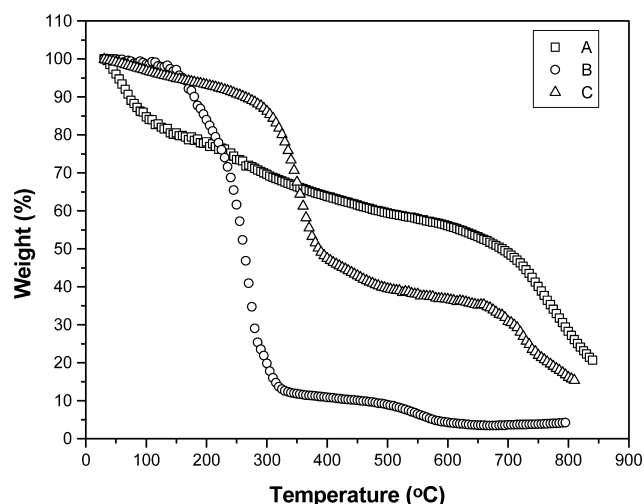


Fig. 2. TGA profiles of the samples: (A) fulleranol, (B) parent cycloaliphatic epoxy (CY-230), and (C) the reaction product of fulleranol and epoxy in 1:10 ratio, obtained in nitrogen atmosphere at a heating rate of 10 °C/min.

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