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Synthesis and evaluation of swelling characteristics of fullerene (C_{60}) containing cross-linked poly(2-hydroxyethyl methacrylate) hydrogels

Rashmi Katiyar[1], Dibyendu S Bag[2*], Indira Nigam[1]

[1]*Department of Plastic Technology, H.B. Technological Institute, Kanpur 208002, India*
[2]*Defence Materials and Stores Research and Development Establishment (DMSRDE), Kanpur 208013, India*

[*]Corresponding author. E-mail: ds_bag@rediffmail.com

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ABSTRACT

Fullerene (C_{60}) containing cross-linked poly (2-hydroxyethyl methacrylate) polymers (CFPH) with varying C_{60} content were synthesized by free radical polymerization. The fullerene content in the cross-linked polymers was determined by TGA analysis. The swelling properties of these fullerene containing hydrogels (CFPH) were studied in distilled water (pH=7.2) at room temperature (25^{o}C) and compared to the corresponding hydrogel without fullerene (CPHEMA). The equilibrium swelling ratio is lower for the fullerene containing hydrogels (54.68% and 40.0% for hydrogels having 6.0 wt% and 18.0 wt% fullerene respectively) due to the presence of hydrophobic fullerene moieties inside the hydrogels than that of the hydrogel (68.75%) without fullerene. The hydrophobic fullerene nanomaterials acting as inherent nanofillers obstruct the path of water permeation inside the polymers thereby taking more time to achieve equilibrium swelling for fullerene containing hydrogels than that of the hydrogel without fullerene. The kinetics of swelling behavior of such fullerene containing cross-linked hydrogels (CFPH) was observed to follow Fickian behavior. Increase of temperature and ionic strength of the medium decrease the water uptake capacity of the fullerene containing cross-linked hydrogels. Fullerene containing hydrogels may be useful in drug delivery system and other biomedical applications. Copyright © 2014 VBRI press.

Keywords: Fullerene (C_{60}) containing cross-linked polymers; C_{60} containing hydrogels; poly(2-hydroxyethyl methacrylate) hydrogels; swelling ratio.

Rashmi Katiyar is a research scholar at Harcourt Butler Technological Institute, Kanpur, India. She received her Master Degree in Chemistry from C. C. S. University, Meerut. She has been working in the field of fullerene containing polymers for the past 5 years. and published 6 papers in the journals of international repute. She was also awarded Dr. Santhi Nath Ghosh Memorial Award for best paper presentation in the National Seminar on *"Current trends in Polymer Science and Technology (POLY-2011)"* held at Jadavpur University, Kolkata.

Dibyendu Sekhar Bag is a scientist of polymer materials since 2000 in Defence Materials and Stores Research and Development Establishment (DMSRDE), Kanpur, a Laboratory under the Defence Research and Development Organization (DRDO), Govt. of India. He obtained his M. Sc. degree in Chemistry and Ph. D. degree in Polymer Science both from Indian Institute of Technology, Kharagpur. He worked as a Senior Scientific Officer at Ahmedabad Textile Industry's Research Association (ATIRA) for two years. Later he also served for two years as an Assistant Professor at the Department of Polymer Engineering, Birla Institute of Technology, Mesra, Ranchi. He was one of the core members in a team of DRDO visiting scientists to Pennsylvania State University, USA. He contributed significantly in various research projects, industrial and defence R&D programs. Dr. Bag is recipient of several awards. He is the author/coauthor of about 50 scientific research papers in reputed journals including a book chapter and inventor of 6 patents. He is also the author of a book: "Principles of Polymers-An Advanced Book", recently published by Nova Science Publisher Inc., New York, USA. He is the co-editor of Journal of Polymer Materials-An International Journal.

Indira Nigam is an Associate Professor in the Department of Plastic Technology, Harcourt Butler Technological Institute, Kanpur, India. She did her B. Tech., M.Tech. and Ph.D. degree in Chemical Technology (Plastic Technology) from the same Institute. She is having 2 years of industrial experience and 18 years of teaching and research experience. She has published more than 20 research papers in various reputed journals and guided students for their M. Tech. and Ph. D. thesis.

Introduction

Fullerene (C_{60}) containing polymers have attracted a lot of attention to the researchers for the potential technological applications of such materials in the field of nanotechnology, supramolecular chemistry and material science especially for optical, non-linear optical and electroactive materials **[1-3]**. Various kinds of functionalization strategies have been explored to synthesize fullerene containing polymers **[4]**. Radical polymerization of vinyl monomers (e.g., methyl methacrylate, n-butyl methacrylate etc.) in the presence of fullerene is the easiest method for synthesizing fullerene containing polymers **[5-7]**.

On the other hand, a hydrogel is a three-dimensionally cross-linked hydrophilic polymer network swollen in aqueous medium **[8-12]**. It does not dissolve in water due to the presence of the chemical or physical cross-links in the polymer network. But it absorbs and retains a large amount of water, in some cases up to a thousand times of their dry weight **[10]**. Hydrogels capable of absorbing large amount of water may also adopt various shape and morphologies when subjected to external stimuli such as temperature, pH and ionic strength of the medium, pressure, electric and magnetic field. The change in shape or any other property may be reversible and such gels are called smart hydrogels **[11-12]**.

Hydrogels have been studied intensively as promising biomaterials used for medical and pharmaceutical applications viz. baby diapers, feminine napkins, drug delivery systems and tissue engineering **[13-17]**. Poly (2-hydroxyethyl methacrylate) (PHEMA) is one of the most important synthetic hydrogels which was reported in 1960s **[18]**. It has been extensively exploited for contact lenses, drug delivery systems and other biomedical applications **[19-23]**. PHEMA presents high hydrophillicity and its hydration properties are attributed to the hydroxyl (-OH) groups in the pendant of the polymer. However, this hydrogel suffers from poor mechanical and thermal properties **[24]**. A lot of attention has, therefore, been paid in combining the attractive high hydrophilicity of PHEMA with the simultaneous improvement of its mechanical and thermal stability **[25-26]**.

Fullerene (C_{60}) possesses a wide range of exotic properties such as mechanical strength, thermal stability, optical non-linearity, excellent drug delivery characteristics etc **[27-30]**. The drug delivery properties of fullerene are attributed to the fact that fullerene cores are ideal environment for encapsulating drug molecules **[30-32]**. By proper designing fullerene containing cross-linked poly (2-hydroxyethyl methacrylate)s (CFPH), these can be used as drug carriers in future, where the drugs can be released in a controlled manner by manipulating the external environment.

There has been increasing recent interest in combining the unique properties of fullerene with stimuli responsive polymers and hydrogels by incorporating fullerene into the polymeric structures/systems **[33-34]**. However, reports in this field are scanty. Hence, the objectives of the present investigation are (i) to synthesize fullerene containing cross-linked poly (2-hydroxyethyl methacrylate) hydrogels (CFPH), (ii) to study the effect of fullerene on the swelling properties including swelling kinetics of such fullerene containing hydrogels, (iii) to study the effect of temperature and ionic strength of the medium on the swelling characteristics of C_{60} containing hydrogels and (iv) to study the thermal properties of fullerene containing cross-linked poly (2-hydroxyethyl methacrylate)s.

Experimental

Materials

Fullerene (99+%, Lancaster, U. K.) and *o*-dichlorobenzene (99%, Lancaster, U.K.) were used directly as received. 2-Hydroxyethyl methacrylate (HEMA) (97%, Lancaster, U.K.) was purified prior to use by the standard method **[35]**. Propylene glycol dimethacrylate (PGDMA) (Aldrich, USA) was synthesized at laboratory. Benzoyl peroxide (BPO) (≥ 98%, Aldrich, USA) was recrystallized using chloroform and stored at 5°C before use.

Synthesis of fullerene (C_{60}) containing cross-linked polymers

The fullerene containing cross-linked poly (2-hydroxyethyl methacrylate) (CFPH) polymers were synthesized by polymerization of 2-hydroxyethyl methacrylate (HEMA) in the presence of fullerene using benzoyl peroxide (BPO) (1 wt% of monomer) as an initiator and propylene glycol dimethacrylate (PGDMA) (2 wt% of monomer) as a cross-linker in *o*-dichlorobenzene in a temperature controlled water-bath for 24 hrs at 70°C under nitrogen atmosphere. The amount of fullerene was varied from batch to batch in order to obtain three polymer samples (CPHEMA, CFPH-1 and CFPH-2) with varying C_{60} content (**Table 1**). The polymers thus formed were purified by washing these with distilled water in a soxhlet extractor and followed by 1-methyl naphthalene to remove unreacted fullerene and acetone to remove unreacted HEMA and other chemicals. These purified fullerene containing cross-linked polymers (CFPH) become hydrogels after soaking water. The hydrogels were then dried to constant weight. The fullerene containing hydrogels were studied for their swelling characteristics.

Table 1. Feed composition for the synthesis of fullerene containing cross-linked poly(2-hydroxyethyl methacrylate) polymers.

Sl. No.	Sample code	Conc. of fullerene (mg)	Conc. of HEMA (gm)	Initiator (BPO) (mg)	Cross-linker (PGDMA) (mg)	Appearance of samples after purification
1.	CPHEMA	0.0	1.0	10.0	20.0	White
2.	CFPH-1	100	1.0	10.0	20.0	Brown
3.	CFPH-2	250	1.0	10.0	20.0	Dark brown

Solvent = o-diclorobenzene, Temperature = 70°C, Time = 24 hrs

Characterization

The fullerene containing cross-linked polymers (CFPH) were characterized by FTIR and thermal analyses. FTIR spectra of the samples were recorded on a Perkin Elmer (Spectrum 100 Series) spectrophotometer using KBr pellets. TGA and DTGA thermograms of the samples were taken from a TGA 851 Thermogravimetric Analyzer (Mettler Toledo) at a heating rate of 20°C/min under argon. DSC curves of the samples were obtained using a DSC

Q100 differential scanning calorimeter (TA Instruments) with a scanning rate of 10°C/min under argon atmosphere.

Determination of fullerene content from TGA analysis

The fullerene (C_{60}) content in the fullerene containing polymers was calculated from the TGA analysis using the following equation;

$$C_f\,(wt\%) = CR_f - CR_p \qquad ---(1)$$

where, C_f = Concentration of fullerene (wt %)/Q incorporated in the crosslinked polymers' CR_f = Char residue (wt%) of fullerene containing polymers at 600°C, CR_p= Char residue (wt%) of the controlled polymer without fullerene at 600°C.

Study of swelling behavior

In order to study the swelling behavior of fullerene containing hydrogels, an accurate weight of each CFPH dry sample was immersed in distilled water at room temperature (25°C). The sample started swelling (pH = 7.2) due to uptake of water. After a fixed interval of an hour, hydrogel samples were taken out from water, blotted with filter paper to eliminate excess of water and weighed. The swelling ratio was calculated using the following equation;

$$Swelling\ Ratio\ (SR)\% = \frac{W_t - W_0}{W_0} \times 100 \qquad ---(2)$$

where, W_t = weight of a swollen hydrogel at time, t and W_0 = weight of the dry hydrogel sample.

Determination of equilibrium water content

The equilibrium water content is the maximum amount of water absorbed by a hydrogel. It was calculated with the help of the following equation;

$$Equilibrium\ Water\ Content\ (EWC)\% = \frac{W_e - W_0}{W_e} \times 100 \qquad ---(3)$$

where, W_e = weight of a hydrogel at equilibrium swelling and W_0 = weight of the dry hydrogel sample.

The minimum time taken to attain maximum swelling for a fullerene containing poly (2-hydroxyethyl methacrylate) (CFPH) sample is considered as the time of equilibrium swelling. It is evaluated from the plot of swelling ratio versus time (**Fig. 5**). The time is 9 hrs for CFPH-2 and less for the other two samples studied here (**Table 3**). Hence, all the samples were allowed to swell for 12 hrs to achieve equilibrium swelling for further swelling study. The samples were taken out from water after 12 hrs, blotted with filter paper and then weighed. This weight is taken as W_e.

Determination of swelling kinetics

The amount of water absorbed by a hydrogel at a particular time, t is designated as M_t which is equal to (W_t–W_0). The water uptake, S_w (=M_t /W_0) is an exponential function of time, t. Hence, the following power law relation is commonly used to determine the mechanism of diffusion of solvent in polymeric networks for swelling **[36-38]**.

$$Sw = \frac{M_t}{W_0} = kt^n \qquad ---(4)$$

The swelling characteristic constant (k) and diffusional (or transport) exponent (n) depend on the solvent-polymer system. The swelling process is considered as;

(a) *Fickian or diffusion controlled* when the value of diffusional exponent, 'n' = 0.5. This means that the rate of solvent diffusion is slower than rate of relaxation of the polymer chains.

(b) *Non-Fickian* swelling behavior which is of two types: relaxation-controlled and anomalous transport.

- Relaxation-controlled occurs when the value of diffusional exponent, 'n' = 1 which indicates that the rate of diffusion is more than the rate of relaxation.
- Anomalous diffusion/transport is observed when the value of diffusional exponent, 'n' is between 0.5 and 1.0. This means that the rates of diffusion of solvent and relaxation of chains are comparable.

The value of 'k' and 'n' are determined from the logarithm plot of M_t/W_0 versus time (t) where the value of slope is 'n' and intercept is 'k'.

Determination of enthalpy of swelling/mixing

In order to study the effect of temperature on the swelling properties, the logarithm of equilibrium water uptake (S_∞) is plotted against the reciprocal of swelling temperature. The relationship between ln S_∞ and 1/T follows Gibbs-Helmholtz equation **[36, 39].**

$$\frac{dln(S_\infty)}{d(\frac{1}{T})} = -\frac{\Delta H_m}{R} \qquad ---(5)$$

where, S_∞ = equilibrium water uptake which is equal to (W_e – W_0)/W_0, ΔH_m = enthalpy of swelling/mixing between polymer and water, R= gas constant (8.314 J K^{-1} mol^{-1}) and T = temperature of the swelling medium in °K. The enthalpy of swelling/mixing (ΔH_m) was calculated from the slope of plot of ln S_∞ versus (1/T).

Study of effect of temperature and ionic strength of the medium on swelling

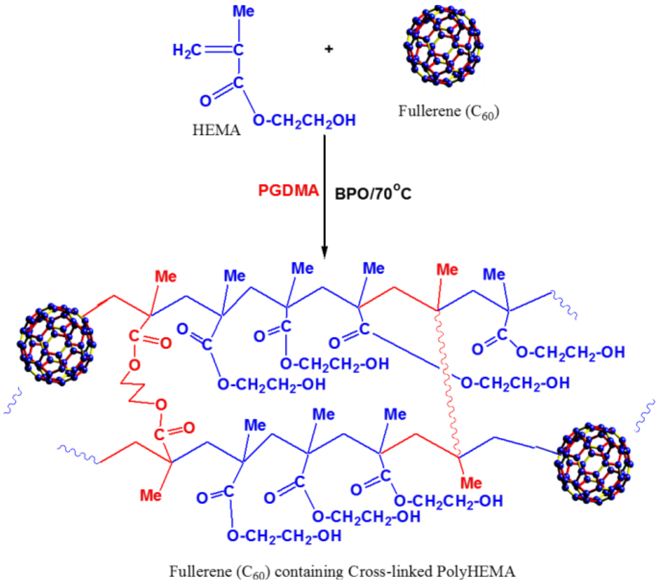
The effect of temperature on the swelling properties of fullerene containing hydrogels was studied by allowing the samples to swell equilibrium for 12 hrs in a temperature controlled water bath at different temperatures from 25°C to 40°C and measuring the water content of the each hydrogel sample.

Effect of ionic strength of the medium on the swelling behavior of such fullerene containing hydrogels was studied by swelling the samples in aqueous solution with varying NaCl concentration (e.g., 1wt%, 3wt% and 5 wt%) and determining the equilibrium water content in each case.

Results and discussion

Synthesis of C_{60} containing cross-linked polymers

The cross-linked poly (2-hydroxyethyl methacrylate) hydrogels with different fullerene content were synthesized as described in the experimental section. It is represented in **Scheme 1**. A crosslinked poly (2-hydroxyethyl methacrylate) hydrogel (CPHEMA) without fullerene was also synthesized as a control sample under similar polymerization condition. The synthesized hydrogels with and without fullerene were characterized by FTIR and thermal analyses. The fullerene content in the cross-linked polymers was determined by TGA analysis. The glass transition temperatures (T_g) of the samples were measured from DSC analysis. Swelling behavior of the fullerene containing cross-linked poly (2-hydroxyethyl methacrylate) (CFPH) hydrogels was also studied.



Scheme 1. Schematic representation of synthesis of fullerene containing cross-linked polymers (CFPH).

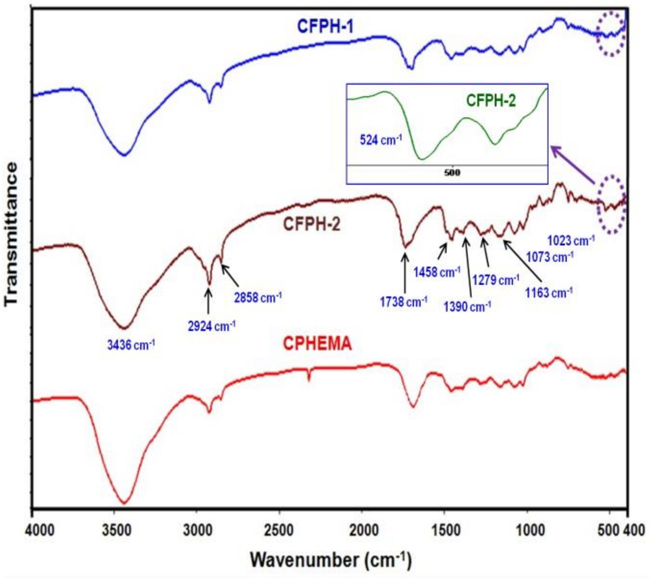


Fig. 1. FTIR spectra of C_{60} containing cross-linked polymers.

FTIR analysis

FTIR spectra of fullerene (C_{60}) containing cross-linked poly(2-hydroxyethyl methacrylate) polymers (CFPH-1 and CFPH-2) and similar cross-linked polymer without fullerene (CPHEMA) are shown in **Fig. 1**. A wide absorption peak at 3436 cm^{-1} is due to the hydroxyl (-OH) group of HEMA unit. The sharp peak at 1738 cm^{-1} is due to C=O group of ester of HEMA unit. The OC-O appears at 1279 cm^{-1}. The C-H asymmetric stretching of the methyl (CH_3) group, alkyl side chain and alkyl main chain ($--CH_2--$) all merge together and appear at 2924 cm^{-1}. The peak at 2858 cm^{-1} is due to symmetric stretching of CH_3 and CH_2 groups. On the other hand, C-H asymmetric bending of CH_3 and CH_2 appears at 1458 cm^{-1} and the symmetric bending at 1390 cm^{-1}. The C-O stretching vibration of $–CH_2OH$ of HEMA unit appears at 1163 cm^{-1}. The peaks at 1063 and 1023 cm^{-1} may be due to CH_3 and CH_2 rocking respectively.

The infrared spectrum of C_{60} is generally consisting of four modes observed at frequencies of 527, 576, 1182 and 1427 cm^{-1}. The 1427and 1182 cm^{-1} modes are essentially associated with a tangential motion of the carbon atoms while the 576 and 527cm^{-1} modes are associated with a primarilyradial motion of the carbon atoms **[40-41]**. The functionalized C_{60} cage is identified by the distinct peak at 527 cm^{-1} **[5-6, 42]**. Here the peak 1427 cm^{-1} is not observed as it may be merged with the asymmetric bending of CH_3 and CH_2 which appears at 1458 cm^{-1}. The other characteristic peak due to fullerene at 1182 cm^{-1} may be again merged with peak 1163 cm^{-1}. However, the prominent peaks at 524 cm^{-1} reveals the presence of functionalized C_{60} cages in the fullerene containing cross-linked polymers.

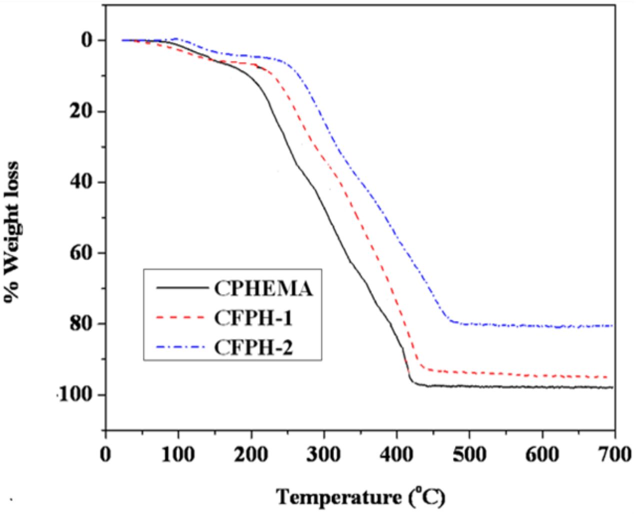


Fig. 2. TGA thermograms of cross-linked polymers with (CFPH-1 and CFPH-2) and without fullerene (CPHEMA).

TGA analysis

Thermal properties of C_{60} containing cross-linked poly (2-hydroxyethyl methacrylate) (CFPH) polymers were studied using TGA analysis. The C_{60} content in such polymers was also estimated from the char residue in the TGA thermograms.

Thermal properties of C_{60} containing cross-linked polymers

The fullerene (C_{60}) containing polymers (CFPH) were characterized by TGA analysis in order to understand the effect of fullerene on the thermal degradation behavior of these cross-linked polymers. **Fig. 2** represents the TGA curves of such C_{60} containing cross-linked polymers. The results are given in **Table 2**. The onset of thermal degradation of fullerene containing cross-linked polymers (CFPH) is higher than that of the same polymer without fullerene (**Table 2**). Onset of thermal degradation increases from 210^{o}C to 260^{o}C with increasing fullerene content in the polymer. The char residue at 600^{o}C is observed to be more in fullerene containing cross-linked poly (2-hydroxyethyl methacrylate) (CFPH) than that of the cross-linked poly (2-hydroxyethyl methacrylate) (CPHEMA) without fullerene.

Table 2. Effect of fullerene on thermal properties of C_{60} containing cross-linked polymers.

Sl. No.	Sample code	Fullerene content^{a} (wt %)	Onset temperature (^{o}C)	Char residue at 600^{o}C (wt %)	$T_{1(max)}$ (^{o}C)	$T_{2(max)}$ (^{o}C)	Glass transition temperature^{b} (T_g) (^{o}C)
1.	CPHEMA	0.0	210	02	-	410	110
2.	CFPH-1	6.0	230	08	274	415	120
3.	CFPH-2	18.0	260	20	303	448	135

^{a}*Obtained from TGA;* ^{b}*Obtained from DSC analysis*

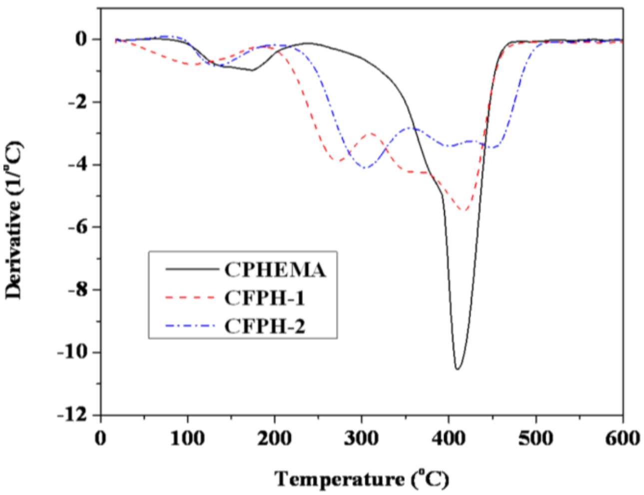


Fig. 3. DTGA curves of cross-linked polymers with (CFPH-1 and CFPH-2) and without fullerene (CPHEMA).

DTGA curves of the cross-linked poly (2-hydroxyethyl methacrylate) with and without fullerene are shown in **Fig. 3**. Poly (2-hydroxyethyl methacrylate) has been reported to undergo two-staged degradation **[43-44]**. However, in the present system, cross-linked poly(2-hydroxyethyl methacrylate) (CPHEMA) where the first stage of degradation is not prominent while both the stages of degradation are clear in fullerene containing cross-linked polymers (CFPH) . The two-staged degradation in CFPH is evidenced by the appearance of two peaks in the DTGA thermograms. The first stage of degradation is due to the unzipping of the poly (HEMA) chain to yield the monomer (HEMA) and the second stage of degradation is due to the scission of the cross-linked poly (2-hydroxyethyl methacrylate) structure **[44-45]**. Fullerene in the cross-linked poly (2-hydroxyethyl methacrylate) inhibits the unzipping process as it captures the radicals formed during the early degradation process **[45]**. Hence thermal properties of fullerene containing polymers are better than that of the corresponding polymers without fullerene.

Determination of fullerene content in C_{60} containing cross-linked polymers

Generally, the thermal degradation of virgin poly(HEMA) leaves a char residue of 5-6% at 400^{o}C and above 600^{o} C there is almost no char residue **[46]**. However, in this case of cross-linked polymer i.e., CPHEMA polymer less than 2% char residue is observed at 600^{o}C in the TGA analysis. At this temperature (600^{o}C), poly (HEMA) almost completely degrades leaving only fullerene (C_{60}). On the other hand, fullerene undergoes a minor or no weight loss at 600^{o}C **[47-48]**. Hence the weight percent of C_{60} incorporated in cross-linked poly(2-hydroxyethyl methacrylate) was determined from the remaining char residue data at 600^{o}C obtained after eliminating the char residue of cross-linked poly (2-hydroxyethyl methacrylate) (CPHEMA) (Eq.1). The amount of fullerene content in the cross-linked polymers thus calculated from TGA analysis is given in **Table 2**.

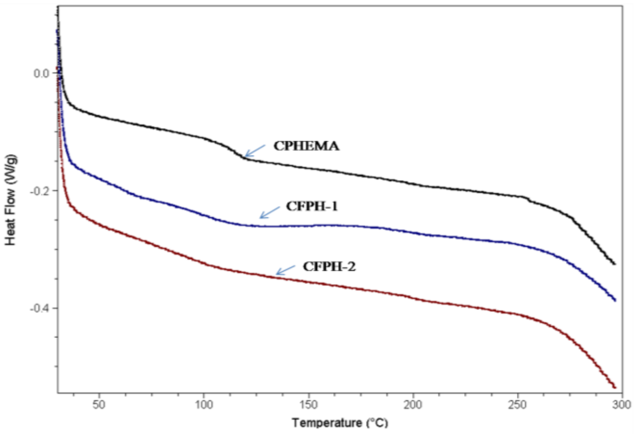


Fig. 4. DSC thermograms of fullerene containing cross-linked polymers (CFPH-1 and CFPH-2) and the control polymer without fullerene (CPHEMA).

DSC analysis and glass transition temperature

The glass transition temperatures (T_g) of C_{60} containing cross-linked poly (2-hydroxyethyl methacrylate) polymers were determined using DSC analysis. The DSC curves are shown in **Fig. 4**. The T_g values of fullerene containing polymers (CFPH) are more than that of virgin cross-linked poly (2-hydroxyethyl methacrylate) (CPHEMA) (**Table 2**). The glass transition of poly (HEMA) is reported to be 87^{o}C **[49]**. It is also well known that cross-links increase the glass transition temperature of polymers because it restricts the segmental motion of polymers. Here, we observe the T_g of the cross-linked poly (2-hydroxyethyl methacrylate) (CPHEMA) to be 110^{o}C which is much higher than the usually observed T_g of linear poly (HEMA). Again, incorporation of bulky fullerene in the cross-linked poly (2-

hydroxyethyl methacrylate) increases the glass transition temperature which continues to increase further with increasing fullerene content (**Table 2**). This is because of the presence of bulky fullerene moiety in the cross-linked structures which restricts the segmental motion of polymers chains **[50]**.

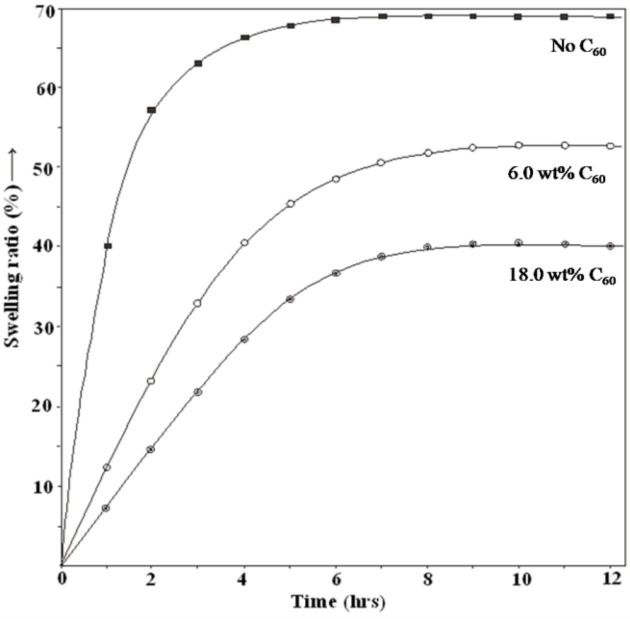


Fig. 5. Plot of swelling ratio versus time for C_{60} containing hydrogels.

Table 3. Effect of C_{60} on swelling characteristics of C_{60} containing cross-linked poly(2-hydroxyethyl methacrylate) hydrogels.

Sl. No.	Sample Code	Conc. of fullerene (C_{60}) (wt%) obtained by TGA	Time of equilibrium swelling (hrs)	Equilibrium swelling ratio (%)	Swelling character-istic ‘k’	Diffusional Exponent ‘n’	EWC (%)	Enthalpy of swelling/mixing (H_m) (kJ mol^{-1})
1.	CPHEMA	0	5	68.75%	0.244	0.48±0.01	40.74	-20.62
2.	CFPH-1	6.0	6	54.68%	0.234	0.46±0.01	35.29	-15.56
3.	CFPH-2	18.0	9	40.00%	0.174	0.40±0.01	28.57	-13.76

Equilibrium swelling ratio

The swelling properties of the fullerene containing cross-linked poly (2-hydroxyethyl methacrylate) polymers (CFPH) were studied in aqueous medium at room temperature (25^{o}C). The swelling values of fullerene containing gels were compared with that of the gel without fullerene. The plot of swelling ratio versus time is shown in **Fig. 5**. The minimum time taken to attain optimum swelling for a sample is considered as the time of equilibrium swelling and the optimum swelling is considered as the equilibrium swelling as no further increase in swelling is observed. The values are estimated from the plot (**Fig. 5**). The time taken to achieve equilibrium swelling is higher for the fullerene containing hydrogels than that of the hydrogel without fullerene (**Table 3**). Again, the time required to attain equilibrium swelling increases with increasing concentration of fullerene in the hydrogels. The maximum swelling ratio of cross-linked poly (2-hydroxyethyl methacrylate) (CPHEMA) gel was estimated to be 68.75% whereas the values are 54.68% and 40.0% for the fullerene containing hydrogels (CFPH-1 and CFPH-2) having 6.0 wt% and 18.0 wt% fullerene respectively. Thus the equilibrium swelling ratio is less in C_{60} containing hydrogels than that of the hydrogel without C_{60}. We also observed similar results in case of C_{60} containing poly(N-isopropyl acrylamide) hydrogels **[51]**.

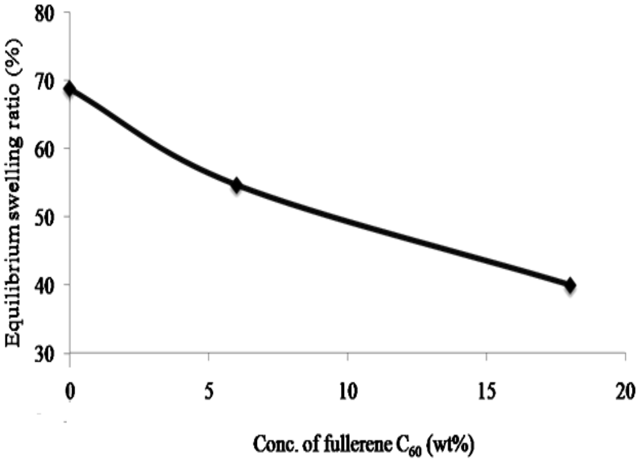


Fig. 6. Variation of equilibrium swelling ratio with fullerene concentration in hydrogels.

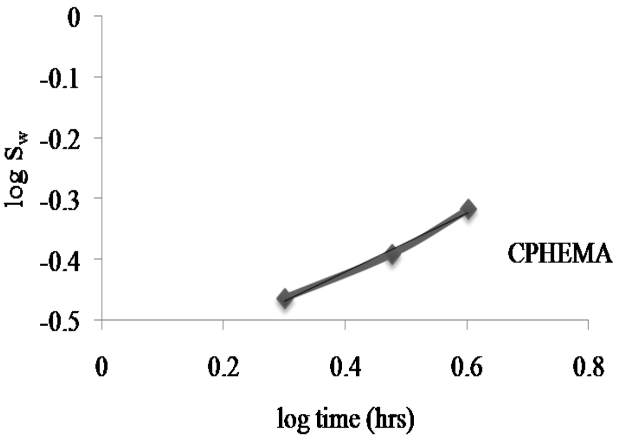


Fig. 7. Log plot of S_w versus time for cross-linked poly (2-hydroxyethyl methacrylate)(CPHEMA).

The hydrophobic fullerene nanomaterials acting as inherent nanofillers obstruct the path of water permeation inside the polymers thereby taking more time to achieve equilibrium swelling for fullerene containing hydrogels than that of the hydrogel without fullerene. In other words, the hydrophilic hydroxyl groups (-OH) of HEMA unit easily form H-bonding with the water molecules resulting fast water uptake (less time taken to attain equilibrium swelling) by the hydrogel and also uniform distribution of water molecules inside the gel matrix providing high equilibrium swelling ratio value in case of the hydrogel without fullerene as compared to the fullerene containing hydrogels. In the C_{60} containing cross-linked polymers the amount of hydrophilic hydroxyl groups (-OH) are reduced as hydrophobic C_{60} is incorporated in it as compared to the same amount of cross-linked polymer without C_{60}. Moreover, presence of hydrophobic C_{60} leads to the hydrophobic zone in a gel matrix which is not a favorable situation for gel swelling. The lower value of swelling ratio in C_{60} containing hydrogels than that of the hydrogel without C_{60} is due to the presence of such hydrophobic C_{60} moieties inside the hydrogels. The equilibrium swelling ratio was also observed to decrease with increasing C_{60} content in hydrogels (**Fig. 6**). This further ensures that the hydrophobic nature of fullerene causes to lowering of hydrogel swelling in C_{60} containing cross-linked polymers.

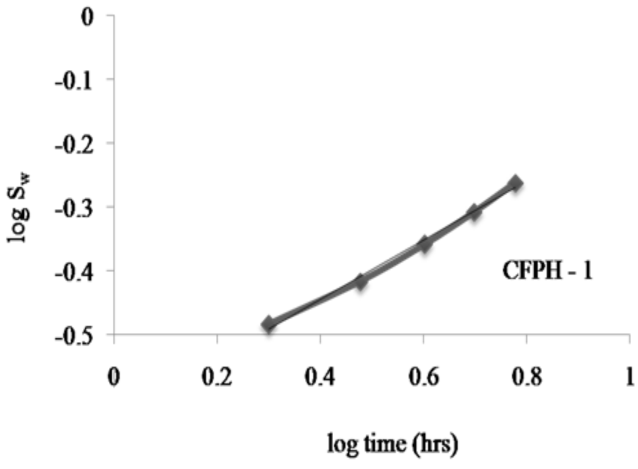


Fig. 8. Log plot of S_w versus time for fullerene containing cross-linked polymer (CFPH-1).

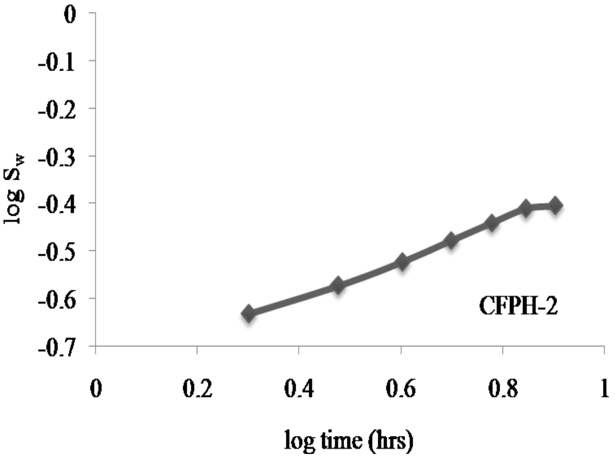


Fig. 9. Log plot of S_w versus time for fullerene containing cross-linked polymer (CFPH-2).

Swelling kinetics

The swelling behavior of the cross-linked poly (2-hydroxyethyl methacrylate) gels with and without fullerene was studied with the help of Eq. 4. The value of swelling characteristic constant ‘k’, and diffusional exponent, ‘n’ were determined from the intercept and slope of the logarithm plot of S_w versus time (**Figs. 7, 8** and **9**). The absolute values of ‘k’ and ‘n’ decrease with increasing the concentration of fullerene (**Table 3**). This indicates that the rate of diffusion decreases with increasing fullerene content which may be obvious due to the hydrophobic nature of fullerene. The values of ‘n’ are approximately equal to 0.5 which means that the swelling behavior of the cross-linked poly (2-hydroxyethyl methacrylate) gel with and without fullerene follow Fickian behavior **[36-37]**.

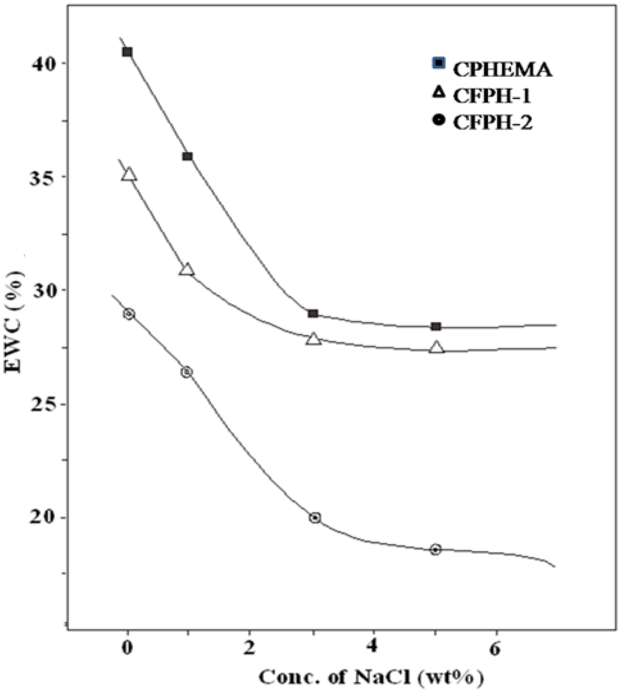


Fig. 10. Variation of equilibrium water content (EWC) of C_{60} containing hydrogels with ionic strength of the medium at 25°C.

Equilibrium water content and effect of ionic strength on swelling behavior

The effect of ionic strength on the swelling properties of C_{60} containing hydrogels was also studied. The cross-linked polymers with and without fullerene were swollen in aqueous Q solutions with various NaCl concentrations (1wt%, 3wt% and 5wt %). Then equilibrium water content was determined in each case using Eq. 3. **Fig. 10** shows the variation of equilibrium water content with the ionic strength of the medium for various hydrogels. As the ionic strength (NaCl concentration) of the swelling medium increases, the equilibrium water content of the hydrogels decreases. It is also observed that it decreases exponentially. Increase in the ionic strength of the medium results in an increase in the polarity of the medium thereby decreasing water-polymer association/interaction and increasing polymer-polymer interaction (strengthening hydrophobic interaction) which results in decreased swelling properties and decreased equilibrium water content (EWC).

Effect of temperature on swelling properties of C_{60} containing hydrogels

The effect of temperature on the swelling behavior of C_{60} containing cross-linked poly (2-hydroxyethyl methacrylate) hydrogels was studied by allowing the hydrogel samples to swell in a temperature controlled water bath at different temperatures from 25°C to 40°C for 12 hrs. The equilibrium water content was then determined with the help of Eq. 3. **Fig. 11** shows the variation of equilibrium water content in hydrogels with temperature. It decreases with increasing temperature which is obvious. Increase in the temperature of the swelling medium ruptures the weak H-bonds between the water molecules and hydrophillic hydroxyl group (OH) of cross-linked poly (2-hydroxyethyl mathacrylate) resulting in a decrease in the equilibrium water content. In other words, water molecules are squeezed out of hydrogels due to decrease of water association with the polar polymers because of the dissociation of H-bonding with increasing temperature.

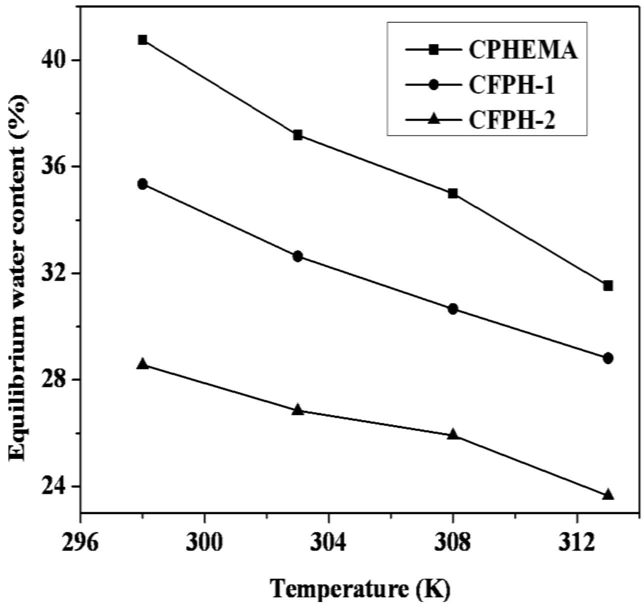


Fig. 11. Variation of equilibrium water content with temperature.

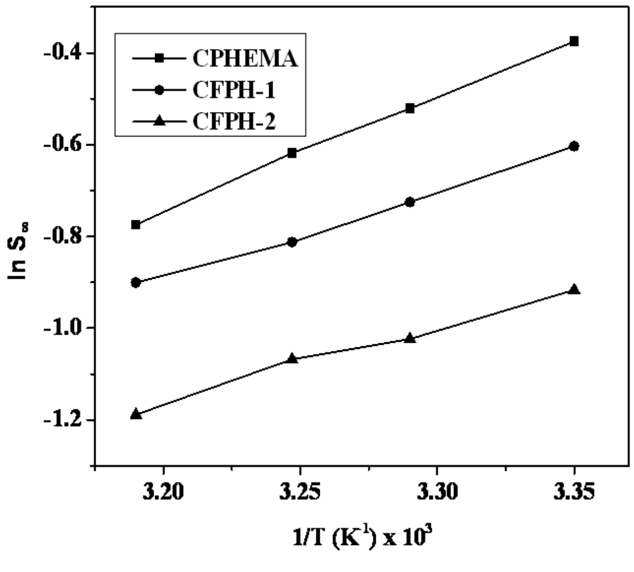


Fig. 12. Plot of ln S_∞ versus temperature inverse.

Determination of enthalpy of swelling/mixing of C_{60} containing hydrogels

The enthalpy of swelling /mixing between polymer and water (ΔH_m) was determined with the help of Gibbs-Helmholtz equation (Eq. 5). It was calculated from the slope of plot of logarithm of equilibrium water uptake versus temperature inverse i.e., ln S_∞ versus (1/T) (**Fig.12**). The absolute value of ΔH_m is higher for hydrogel without fullerene than that of the hydrogels with fullerene (**Table 3**). Again, it decreases with increasing fullerene content. This behavior might be due to the presence of hydrophobic nature of fullerene inside the hydrogels. And the enthalpy of swelling (value of ΔH_m) is dependent on the hydrophobic (here, C_{60} moiety) inclusion of the hydrogels.

Conclusion

Fullerene (C_{60}) containing cross-linked poly (2-hydroxyethyl methacrylate) hydrogels (CFPH) were synthesized. The C_{60} content in such hydrogels was determined by TGA analysis. The glass transition temperature (T_g) increases with increasing fullerene content in fullerene containing cross-linked polymers. The onset of thermal degradation is also observed to increase with increasing fullerene content. Incorporation of fullerene in the cross-linked polymers inhibits the unzipping process of degradation as it captures the radicals formed during the early degradation process and provides thermal stability to the polymers. The swelling behavior of cross-linked poly (2-hydroxyethyl methacrylate) hydrogels is observed to decrease by the incorporation of fullerene in the cross-linked structures. The time taken to attain equilibrium swelling increases in C_{60} containing cross-linked poly (2-hydroxyethyl methacrylate) gels than that of hydrogel without C_{60}. The equilibrium swelling ratio is observed to lower in fullerene containing hydrogels than that of the hydrogels without fullerene due to the hydrophobic nature of fullerene. The equilibrium water content (EWC) of the hydrogels decreases with increasing temperature and also with increasing ionic strength of the medium. The absolute value of enthalpy of swelling / mixing (ΔH_m) decreases with increasing fullerene content in the hydrogels due to the presence of hydrophobic fullerene in the hydrogels.

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