ISSN : 0974 - 7478 Volume 6 Issue 2

Trade Science Inc.

Macromolecules

An Indian Journal

Full Paper

MMAIJ, 6(2), 2010 [82-85]

Inclusion complex compounds of poly (ethylene glycol)-cyclodextrin in poly (Vinyl alcohol)

Mohammad Ali Semsarzadeh[1]*, Sahar Amiri[2]

[1]Modares University, Jalal Al Ahmad Highway, P.O. Box 14115-143, Tehran, (IRAN)

[2]Polymer Engineering Group, Chemical Engineering Department, Faculty of Engineering, Tarbiat, Tehran, (IRAN)

Received: 13th July, 2010 ; Accepted: 23rd July, 2010

ABSTRACT

Poly (ethylene glycol) (PEG) reacts with cyclodextrins. The inclusion compound formed from α-cyclodextrin strongly depends on the structure, molecular weight and geometry of the polymer. The formation of a dicomponent inclusion complexe (DIC) of poly (ethylene glycol) and α-cyclodextrin in the presence of poly (vinyl alcohol) (PVA) and formation of hexagonal crystals upon sonification indicated different microstructures. The formation of the new inclusion complex in PVA is strongly dependent on concentration of PVA, temperature and sonification time. The morphology of the stable complexes with hexagonal structures identified with XRD are reported.

KEYWORDS

Cyclodextrin;
Poly (ethylene glycol);
Poly (vinyl alcohol);
Sonification;
Hexagonal microstructures.

INTRODUCTION

Poly (ethylene glycol) and cyclodextrins are soluble in water, making a thermodynamically homogeneous solution. Kinetically, poly (ethylene glycol) forms a reversible complex inclusion compound with α – cyclodextrins[1,2]. The complex inclusion of polymers with cyclodextrins has been reviewed by Harada[1]. But there is not much available on the reactions of cyclodextrin with PVA.

In this paper the regularly shaped, hexagonal complex of α-CD with PEG in the presence of PVA were prepared and studied.

In this work, the sonic energy was found to have a major effect on the formation of discrete size micro-hexagonal crystals of the complex inclusion compounds of PEG- α-CD in PVA solution. At room temperature (25°C) the sonic energy and time were determining factors in this process. The right concentration of PVA facilitated the formation of the discrete hexagonal micro crystals. The effect of PVA, and its solution viscosity on the reaction and its effect on the ionic environment, contributes to the new morphology and control the size of the hexagonal crystalline microstructures. At longer times of sonification micro crystals may form. In the absence of sonification or PVA, the inclusion compounds tend to become random and discrete hexagonal crystals did not form. The preparations of discrete crystals in PVA have not been reported previously. Complex crystals may be used in drug delivery system because of their ability to enhance drug delivery through biological membranes and also in the separation process, HPLC in or gas chromatography (GC).

Cyclodextrins are capable to form inclusion complexes in pharmacy, analytical sciences, separation processes (e.g., for environmental protection), and cataly-

sis, as well as in the cosmetic, textile, food and packaging industry. In the pharmaceutical field, CDs have primarily been applied as solubilizers for lipophilic drugs to enhance their bioavailability and/or reduce adverse effects after oral, parenteral or other routes of administration. After administration of a drug/CD complex, its dissociation leads to drug release in relevant body compartments, which is mediated by dilution effects, competitive replacement by tissue/serum components (e.g., lipids or cholesterol), therefore the research in this area is extremely important.

EXPERIMENTAL

Material

Polies (ethylene glycol), PEG, with molecular weight of 1000, poly (vinyl alcohol), PVA, with molecular weight of 72000, and α-cyclodextrin with molecular weight of 978.2 with high purity (> 98%) were from Merck. Phosphate buffers were also from Merck.

Equipment

Wide- angle X- ray diffraction (WAXD) was used to study the diffraction patterns of PVA/ αD/PEG crystals at ambient conditions; a Xpert Philips diffractmeter (USA) with nickel filtered Cu Kα radiation was used in this work. Data were collected at a rate of °2θ min over the 5°≈60° range of 2θ[3-6]. Scanning electron microscopy (SEM), Philips XL30 (Poland), was used to study the Au coated microstructures of complexes. Chemical structures were studied by FTIR on a FTS-7 –BIO-RAD (USA) instrument in KBr.

Complex formation of α-CD / PEG without sonic energy

The inclusion complex of α-CD and PEG was prepared by adding an aqueous solution of PEG (5.0 mL of 5.0 wt %) to the aqueous solution (5.0 mL of 14.5 wt %) of α-CD continued with mixing for 1, 2, 4 and 6 hours at 0°C, 25°C, 40°C and 50°C (TABLE 1). The inclusion complexes were then separated and redissolved in phosphate buffers at pH (7- 9) at room temperature[1,2,7-9].

Preparation of PEG/ α-CD in PVA

The new complex of α-CD/ PEG in PVA was first prepared from PEG and α-CD (TABLE 1). The sonificated complex was then dissolved in the aqueous solution of PVA (5.0, 10, 15 and 20 wt %) at room temperature and allowed to stand for one day. The solution was then stirred for one hour at 50°C and it was allowed to stand to form the new complex. The solid complex was easily separated and dissolves in water to cast films.

RESULTS AND DISCUSSION

The crystalline morphologies of α-CD and α-CD/ PEG are shown in figure 1 and 2. The reaction conversion or complex formed at 0°C, 25°C, 40°C and 50°C from 1 to 6 hours is shown in TABLE 1. The conversion of the complex at 0°C increased from 46 % to 55% after 4 hours. The hexagonal crystal lattice of α-CD and poly (ethylene glycol) with crystalline dimensions of a=b=1.323mm and γ=120° has been reported[6,10-12]. The effect of PVA on the crystal lattice of α-CD and poly (ethylene glycol) has not been reported. In this work the effect of sonification on the crystal formation indicated that a longer sonification time of at least 30 min. is needed for crystallization. Under this condition, the discrete hexagonal crystals are formed under PVA concentration of (5wt %) in 20 wt% of α-CD/ PEG. The formations of new crystals are shown in figure 4.

The major XRD peaks of the complex of α-CD/ PEG in PVA at different sonification times are reported in TABLE 3. The effect of sonification time on the microstructure of the complex is shown in figure 7 and 8.

The crystalline morphologies of α-CD and α-CD/ PEG are shown in figure 1 and 2. The reaction conversion or complex formed at 0°C, 25°C, 40°C and 50°C from 1 to 6 hours is shown in TABLE 1. The conversion of the complex at 0°C increased from 46 % to 55% after 4 hours. This figure indicated that apart from sonification time (30 min) or temperature (25°C), PVA concentration has played a critical role in formation of discrete and stable microcrystals of the complex of α-CD with PEG in PVA. The absence of crystals observed at higher concentration of PVA solution PVA/ (α-CD/ PEG) = 2/1 wt% in figure 7 or 1/1 in figure 3 may indicate that a dissolution of the complex has taken place (Figure 7a & 7b).

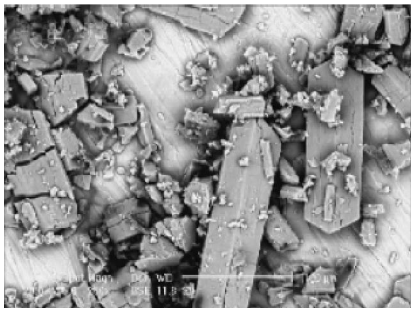
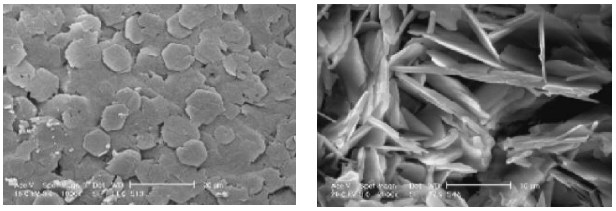
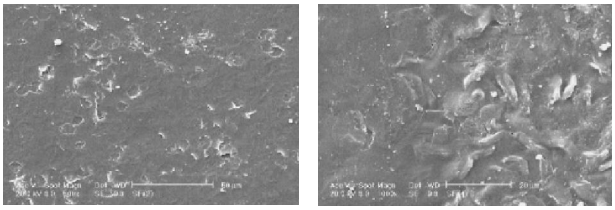


Figure 1 : SEM of α-CD



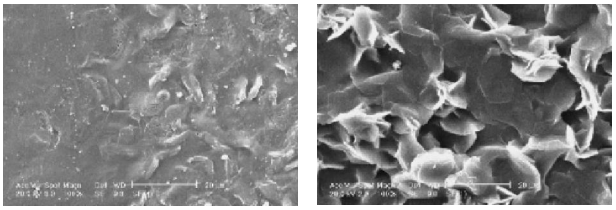
(a) (b)

Figure 2 : SEM images of the prepared α-CD/ PEG inclusion compounds, (a)2hours at 0°C at PH=7 (b) 4 hour at 25°C at PH=7



(a) (b)

Figure 3 : SEM images of the effect of concentration of α-CD/ PEG in at fixed concentration of PVA. (a) PVA (5%), [α-CD/ PEG](5 %) (b)PVA(5%), [α-CD/PEG](20 %)



(a) (b)

Figure 4 : SEM of the effect of sonification on the shape of crystals. (a) PVA (5%), [α-CD/ PEG] (20 %) sonification time: 15 min (b) PVA (5%),[α-CD/ PEG] (20 %) sonification time: 30 min

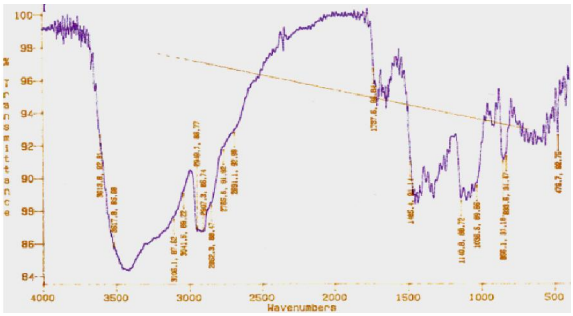


Figure 5 : IR peaks of α-CD in PVA

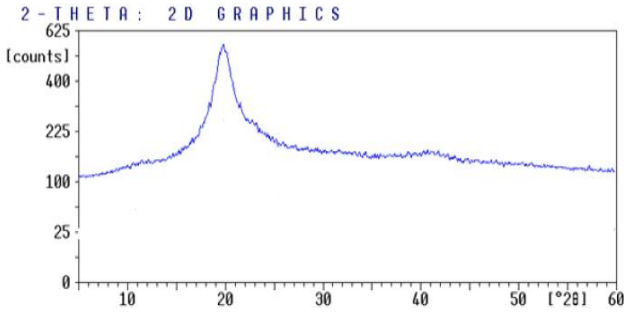
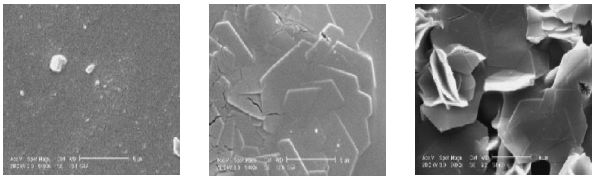


Figure 6 : XRD peaks of α-CD in PVA



(a) (b) (c)

Figure 7 : SEM of complex of (α-CD/ PEG), The effect of concentration of PVA on [α-CD/ PEG] at 30 min Sonification. (a)PVA(10%), [α-CD/ PEG](5 %) (b) PVA(15%), [α-CD/ PEG](20%) (c) PVA (5%), [α-CD/ PEG](20%)

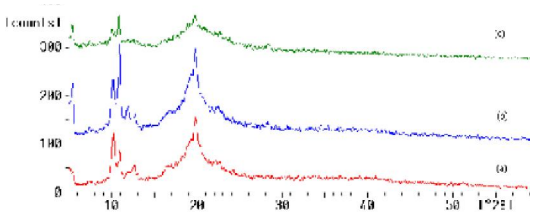


Figure 8 : XRD of the complex inclusions of CD/ PEG with PVA. (a) PVA:5%, [α-CD/ PEG]:20% sonification time:15min (b) PVA:5%, [α-CD/ PEG]:5% sonification time:15min (c) PVA:5%, [α-CD/ PEG]:20% sonification time:30 min

The microstructure of the stable complex crystals shown in figure 7c indicated the effect of sonification at longer time or 30 min on PVA/ (α-CD/ PEG) =1/4 wt %. Where there is no excess of PVA in the solution.

Figure 8 indicated the characteristic peaks of the new complex formed under this condition at different times and PVA concentrations. The broad peak at 2θ = 19.260 and a narrower one at 2θ =10.85 (of the film) indicated that PVA solution may act like phosphate buffer to facilitate the formation of a stable and hexago-

TABLE 1 : Conversion of (α-CD/PEG) without sonification at different times and temperatures

Conversion of α-CD+PEG without sonification(%)				
Time of reaction	Temperature			
	0°C	25°C	40°C	50°C
1 hour	46	32	30	-
2 hour	49	43	39	-
3 hour	51	48	42	41
4 hour	55	52	42	51

TABLE 2 : Conversion of) α-CD/PEG) with sonification at room temperature

Concentration of (α-CD+PEG)	Sonification time	
	15 min	30 min
5 %	21 %	51 %
15 %	23 %	64 %
20 %	32 %	82 %

TABLE 3 : The major XRD peaks for PEG/α-CD in PVA complex inclusion compounds

Sample	2θ
5% PVA 20% (α-CD/PEG) Sonic time:30 min	5.385, 9.970, 10.855, 17.265, 19.760, 28.375
5% PVA 20% (α-CD/PEG) Sonic time:15min	5.120, 5.460, 7.655, 10.220, 10.970, 44.235
5% PVA 5% (α-CD/PEG) Sonic time:15min	5.445, 7.540, 10.195, 11.005, 11.885, 12.710, 16.530, 19.840, 22.415, 41.625
(α-CD in PVA)	13.230, 17.660, 19.875, 22.470

nal microcrystalline complex of about 10μm dimension. The concentration and molecular weight of PVA has contributed to provide the right ionic environment for this reaction stabilized by hydrogen bonding. The higher molecular weight of PVA compared to phosphate buffers, may control the reaction in formation of the complex with higher degree of uniformity and size. The sonification has provided enough energy to overcome the viscosity effect of PVA solution in this reaction, but at higher concentration of PVA the chemical potential may provide enough energy to assist the dissolution of the complex crystals (Figure 7a). Furthermore, the effect of sonification time on the concentration ratio of PVA indicates different microstructures (Figure 8). At equal PVA/complex ratio new complex with different characteristics peaks are reported (TABLE 3). At 30 min. of sonification, PVA ratio is far less 1 or about 1/4, under this condition different inclusion complexes might have been formed. (Figure 7 and TABLE 3).

CONCLUSION

The inclusion compounds of PEG/ α-CD have not been reported in PVA. The sonification of the reaction in poly (vinyl alcohol) solution with different ratios of PVA/complex was used to provide the hydroxyl groups with right ionic strength and the chain mobilities needed for the formation of the new inclusion complex with α-CD with PEG. At equal ratio it is possible to have a tricomponent inclusion compound or (TIC). The size and geometry of its microcrystal are almost uniform and about 10 micron. In this process the chain mobility and presence of -OH groups, have contributed to the formation of the crystals with specific geometry.

REFERENCES

[1] A.Harada, J.Li, M.Kamachi; Macromolecules, **26**, 5698-5703 **(1993)**.

[2] T.Ooya, T.Ichi, T.Furubayashi, M.Katoh, N.Yui; Reactive and Functional Polymers, **6**, 2-13 **(2007)**.

[3] H.S.Choi, S.C.Lee, Y.Yamamoto, N.Ylli; Macromolecules, **38**, 2878-91 **(2005)**.

[4] J.Kawasaki, D.Satou, T.Takagaki, T.Nemoto, A.Kawaguchi; Polymer Science, **48**, 1127-1138 **(2007)**.

[5] M.Ohmura, Y.Kawahara, K.Okude, Y.Hasegawa, M.Hayashida, R.Kurimoto, A.Kawaguchi; Polymers, **45**, 6967-6975 **(2004)**.

[6] T.Loftsson, D.Duchene; Journal of Pharmaceutiscs, **329**, 1-11 **(2007)**.

[7] G.Crini, M.Morcellet; Journal Of Separation Science, **25**, 789-813 **(2003)**.

[8] J.Araki, C.Zhao, Kohzoit; Macromolecules, **38**, 7524-7527 **(2004)**.

[9] J.H.Son, Y.Kang, J.Won; Journal of Membrane Science, **281**, 345-350 **(2006)**.

[10] Y.Hirose, Y.Otsubo; Colloids and Surfaces, **317**, 38-442 **(2008)**.

[11] F.Peng, C.Hu, Z.Jiang; Journal of Membrane Science, **297**, 236-242 **(2007)**.

[12] M.A.Semsarzadeh, S.Farhangi, M.Bagheri; ISPST 8th International Seminar on Polymer Science and Technology, Tehran, Iran, **(2007)**.