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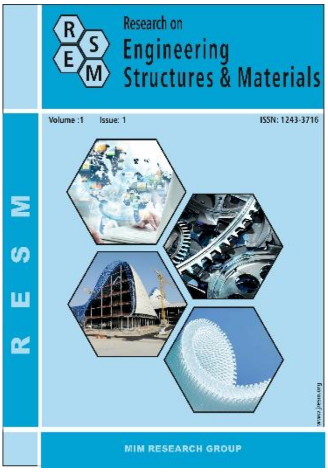

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Inclusion compound formation between hazelnut oil and gamma cyclodextrin

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Abstract

Research in macromolecular self-assembly has been progressively developed since the 1970s and in recent years, more factors and concepts in supramolecular chemistry have been introduced into studies of the self-assembly of polymers. In this respect, inclusion complexation based on cyclodextrins plays a significant role. Hazelnut oil has been used in food and pharmaceutical industry due to its unique properties. Due to its high vitamin-E content, hazelnut oil can slow down the oxidation process; therefore, hazelnut oil can be used as an effective antioxidant. In this study, inclusion complexation between cyclodextrin and hazelnut oil was investigated in detail. In order to form an inclusion compound excess amount of cyclodextrin (CD) and hazelnut oil (H-oil) was used in the experimental part and it was successfully demonstrated that hazelnut oil formed an inclusion compound with gamma cyclodextrin. This inclusion compound could be used either in food products or specific applications used with textile materials since the components performed in this research were both biodegradable and bioabsorbable. Cyclodextrin, inclusion compound, physical mixture of it and hazelnut oil pure state were characterized by FTIR-ATR (Fourier Transform Infrared Spectroscopy-Attenuated Total Reflection), TGA (Thermal Gravimetric Analysis) and XRD (X-Ray Diffraction) analyses. According to the results, hazelnut oil as a guest material was successfully encapsulated in the cavities of host gamma cyclodextrin (g-CD) and FTIR studies indicated that both guest and host molecules were present in the precipitated inclusion complexes (ICs).

1. Introduction

Macromolecular self-assembly includes two major fields, i.e. supramolecular polymers, which are formed from small molecules driven by non-covalent interactions, and self-assembly of multicomponent systems in which macromolecules serve as at least one of the components. Inclusion complexation, normally involves the interactions of two components, so called ‘‘host’’ and ‘‘guest’’ molecules. It is not generally recognized as one kind of the basic non-covalent interactions, because of its combination nature of several elemental supramolecular interactions. The inclusion complexation between CDs and various guests has been extensively investigated in supramolecular chemistry resulting in a broad scope of guest molecules available under different conditions [1].

Cyclodextrins are truncated cone structures compose of 1, 4 linked alpha glucose units. Number of glucose units determines the diameter of inner cavity of cyclodextrins. Since

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alpha cyclodextrin compose of 6 glucose units, it has the smallest cavity with a diameter of 0,49 nm. Beta cyclodextrin and gamma cyclodextrins compose of 7 and 8 glucose units and their cavity sizes are 0.62 and 0.79 nm, respectively [2]. Cavity size is the most critical parameter on inclusion compound formation because it determines the maximum possible size of the guest molecule that can be host inside the cyclodextrin molecule. Basic structure of gamma CD and mode of complexation with guest compounds are schematically indicated in Fig.1. Hydrophobicity of the molecule is another factor playing a role in the inclusion compound formation. Hydroxyl groups of cyclodextrins are located on the outer surface of the molecules, resulting a hydrophilic surface and hydrophobic inner cavity. Thus, hydrophobic molecules, such as oil molecules, can conveniently form inclusion compounds with cyclodextrins. Hydrophobic guest molecules are thermodynamically more stable inside the cavity of cyclodextrin rather than in aqueous solution and therefore they form a non-covalently bonded complex, called an inclusion complex (IC) [3].There are several studies on inclusion compound formation between cyclodextrin and essentional oils such as *Ocimum basilicum* [4], garlic [5], lemon [6], cinnamon [7,8], citronella [9], crude [10], thyme [11], *Lippiasidoides Cham* [12], *Litsea cubeba* [13], soybean, sweet almond [14], eucalyptus [15], black pepper [16], yarrow [17], fish, tarragon, mustard, peppermint, marjoram [18], tea tree [19] oils.

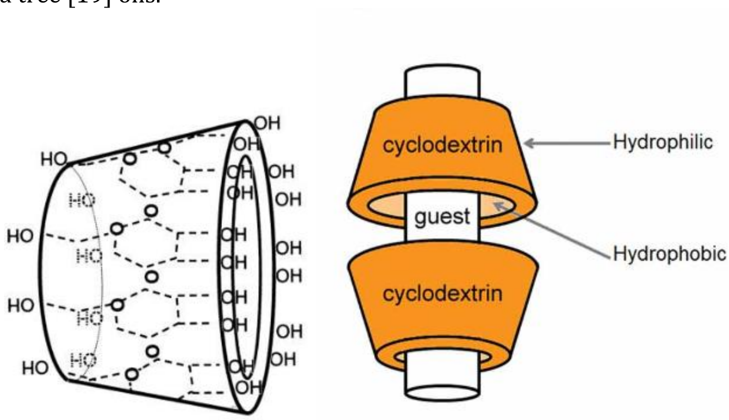
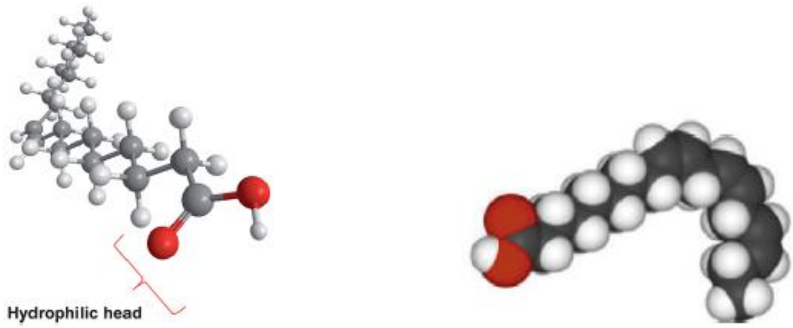


Fig. 1 Basic structure of a g-cyclodextrin and mode of complexation with guest compounds [20]

Hazelnuts (*Corylus avellana L.*) are mainly cultivated in Turkey and Italy which belong to the *Betulaceae* family and they are particularly valuable for their lipids, which account for 60% of the hazelnut kernel. Recently, hazelnut oil (H-oil) has been gaining recognition as a high-quality food product because of its fatty acid composition, which includes oleic and linoleic acids as well as vitamin E (a-tocopherol) and sterols. Monounsaturated and polyunsaturated fatty acids, as well as minor lipid components, play an important role in human nutrition and health such as lowering cholesterol levels [21,22]. It is also a good source of vitamin-E which is fat soluble and an antioxidant material in the human body that protects against free radical damage [23]. Turkey is the world's largest hazelnut producer, contributing approximately 70 % to the total global production. [24,25].

In hazelnut oil chemical structure, oleic acid (Fig.2.a) is the dominant fatty acid (74.2–82.8%) in all varieties while linoleic acid (Fig. 2.b) is the second most abundant fatty acid in the samples and its range is between 9.82% and 18.7%. Palmitic, stearic and palmitoleic acids follows this [26].



a) Chemical structure of oleic acid b) Chemical structure of linoleic acid

Fig. 2 Chemical structure of oleic acid (a) [27] and linoleic acid (b) [28]

Due to its high vitamin-E content, hazelnut oil can slow down the oxidation process. Moreover, most of it oil content composes of unsaturated oil, which also minimize the oil oxidation. Because of these aforementioned properties, hazelnut oil is an effective antioxidant [29].

According to the best knowledge we have, hazelnut oil/gamma-cyclodextrin inclusion compound formation has not been studied. In this study, hazelnut oil was employed as a guest molecule while alpha, beta, and gamma cyclodextrins acted as host molecules. Our results indicated that only gamma cyclodextrin molecules were able to form inclusion compound with the hazelnut oil. While inclusion compound formation process between alpha and beta cyclodextrin and hazelnut oil resulted in phase separated transparent solutions, gamma cyclodextrin and hazelnut oil formed a homogenous white colored solution and then precipitated down. This precipitation was characterized with FTIR, Wide Angle X-Ray, and Thermogravimetric Analyzer to confirm the inclusion compound formation.

2. Experimental: Co-precipitation method

Gamma cyclodextrin was obtained from Cerestar, USA. Hazelnut oil was purchased from Zade Vital, Turkey. All chemicals were used without further purification. Cyclodextrin was dissolved in deionized water. In order to form a stoichiometric inclusion compound excess amount of cyclodextrin dissolved in water and due to the 15:1 host/guest material ratio, guest material was added drop by drop, first they were sonicated in an ultrasonic bath for 10 mins and then stirred on a hot plate for 2 hours in a flask. After this process, samples were left undisturbed two hours and then filtered using a vacuum pump and filter paper. Precipitated inclusion compound were oven dried for 24 hours at 50 °C before conducting any instrumental characterization.

FTIR-ATR (Fourier Transform Infrared Spectroscopy-Attenuated Total Reflection), spectrum of samples was collected using a Nicolet 510P in the range of 4000-400 cm^{-1}. Each sample was scanned 64 times and analyzed by using the Omnic software.

Thermal decomposition of samples was analyzed using Perkin Elmer (TGA) Thermogravimetric analyzer. During these experiments nitrogen gas was used to purge the furnace. Samples were heated from 25 to 900 °C.

Crystal structures of samples were characterized via using a Siemens type-F X-Ray Diffractometer (XRD) equipped with a Ni-FILTERED CuK_a radiation source (k= 1.54 Å). The supplied current and voltage were 30 kV and 20 mA, respectively, and diffraction intensities were collected every 0.1° from 2θ=5° to 30° at a rate of 2θ=3°/min.

3. Results and Discussions

According to the test results, gamma cyclodextrin (g-CD) molecules were able to form inclusion compound with the hazelnut oil. Therefore, further characterization was conducted only for the hazelnut oil and gamma CD inclusion compound which was coded as hazelnut oil-g-CD (H-g-IC). While inclusion compound formation process between alpha and beta cyclodextrin and hazelnut oil resulted in phase separated transparent solutions, gamma cyclodextrin and hazelnut oil formed a homogenous white colored solution and then precipitated down. It was explained in the literature [2] that the first indication of inclusion complex formation was the columnar crystal structure of cyclodextrin and columnar structures improved when CDs stacked on top of one another and produced endless channels in which guest molecules resided. These channels were stabilized by guest molecules and hydrogen bonds between the hydroxyl groups of cyclodextrin yielding a head to head or head to tail arrangement.

As seen in Fig. 3, Wide-angle X-ray diffraction (WAXD) scattering patterns substantially differed after the inclusion of guest hazelnut oil molecules. The reported WAXD pattern for neat cage g-CD had characteristic diffraction peaks at 2h = 12.4^0, 16.5^0, 18.8^0 and 23.4^0 and as reported in Fig. 3, these peaks were also observed in as-received g-CD. After the formation of H-g-IC, a new peak appeared at 2h = 7.5^0, seen in Fig. 4, which corresponded to (200) planes of the hydrated crystals [2]. XRD scattering of physical mixture of hazelnut oil and gamma CD (H-g-mix) was clearly seen in Fig. 5 which had footprints of g-CD in some parts of scattering patterns due to the fact that physical mixture of two compounds did not indicate an inclusion compound.

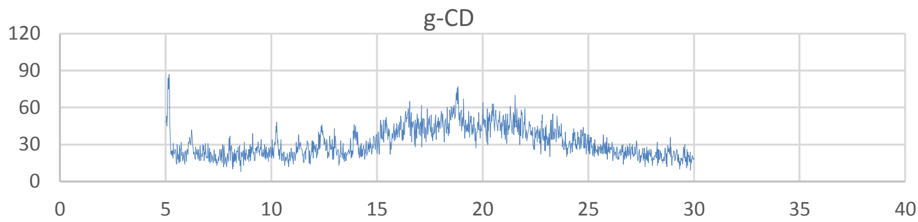


Fig. 3 XRD scattering of gamma CD (g-CD)

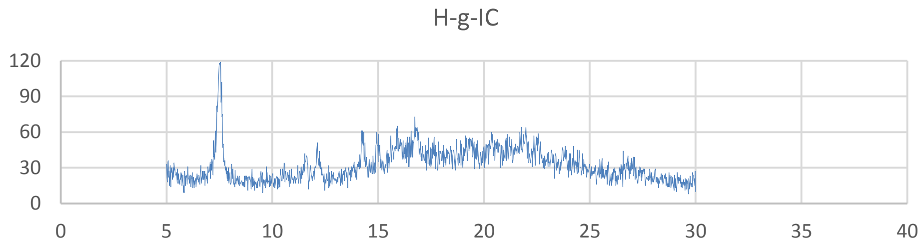


Fig. 4 XRD scattering of hazelnut oil and gamma CD inclusion compound (H-g-IC)

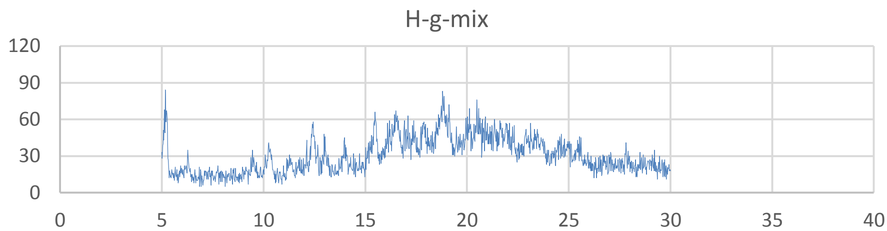


Fig. 5 XRD scattering of physical mixture of hazelnut oil and gamma CD (H-g-mix)

Another proof of successful encapsulation of hazelnut oil molecules in g-cyclodextrin was obtained from FTIR-ATR analysis. In Fig. 6, FTIR-ATR analysis between 4000-700 cm^{-1} of a) H-g-IC b) H-oil and c) g-CD were showed, respectively. The FTIR spectra of gamma CD showed characteristic bands at 3388 and 2926 cm^{-1} which corresponded to O–H and C–H stretching, respectively. However, in H-oil FTIR spectra, strong characteristic peaks could be clearly seen at 2922, 2852 and 1743 cm^{-1}, including the fingerprint region. When the spectra of H-g-IC was examined, it could be determined that these characteristic strong peaks that belonged to H-oil, showed themselves within weaker peaks for H-oil appear at 2918, 2850 and 1740 cm^{-1} which attributed to the formation of inclusion compound of H-oil and gamma CD. Therefore the coexistence of P and CD was confirmed in FTIR-ATR analysis of H-g-IC. The fact that the guest H-oil peaks were very weak when compared to CD vibrational bands in the IC was not surprising considering the expected weight ratio of guest/host molecules was around 1:15.

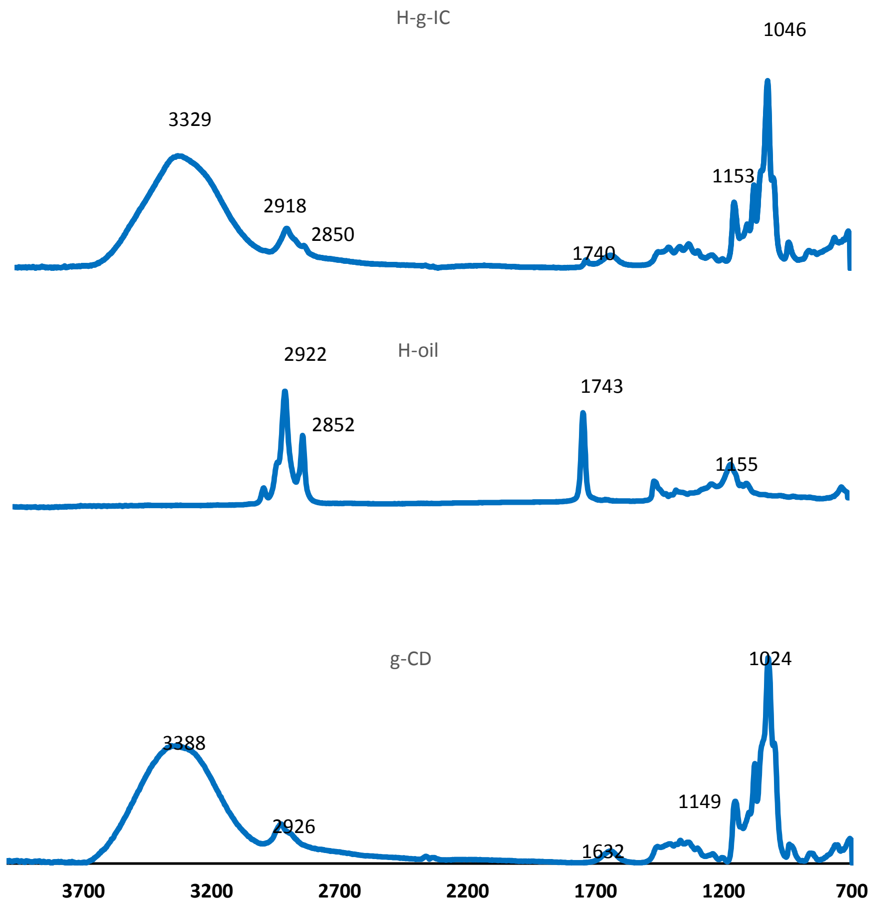


Fig. 6 FTIR-ATR analysis between 4000-700 cm^{-1} of a) H-g-IC b) H-oil c) g-CD, respectively

In Fig. 7, thermogravimetric analyses of gamma CD, H-oil, their physical mixture H-g-Mix and their inclusion compound H-g-IC could be seen clearly. Decomposition experiments were performed by TGA using N_2 as an inert carrier gas with heating rate of 10 °C/min, from 25 to 900 °C. According to TGA results seen in Fig. 7, hazelnut oil showed that it was thermally stable up to 300°C and the decomposition range of hazelnut oil was 302-445°C. The stability could be attributed to an expressive quantity of unsaturated fatty acids in the hazelnut oil, because it was reported in the literature that oil with high concentrations of unsaturated fatty acids was more susceptible to thermal deterioration however it was also explained that several other vegetable oils that contained a high concentration of unsaturated fatty acids possessed stability equivalent to other oils with lesser instauration showing that there were other factors which influence the thermal stability of vegetable oils. Moreover, it was also indicated that the presence of antioxidants also improved oil stability which attributed to the antioxidant material especially to the a-tocopherol existing in hazelnut oil [30]. It was considered that all these parameters could provide a high thermal stability of H-oil. When thermograph of g-CD was examined, it could be seen that the main weight loss due to degradation occurred between 300 and 350°C. Successful encapsulation of hazelnut oil in g-cyclodextrin could be obtained from H-g-IC thermographs which showed a gradual weight loss between 291-341°C. Since there was a physical mixture in H-g-Mix, not a synthesized compound, TGA thermograph of its physical mixture showed a two-step weight loss, between 258-340 °C and 366-404 °C.

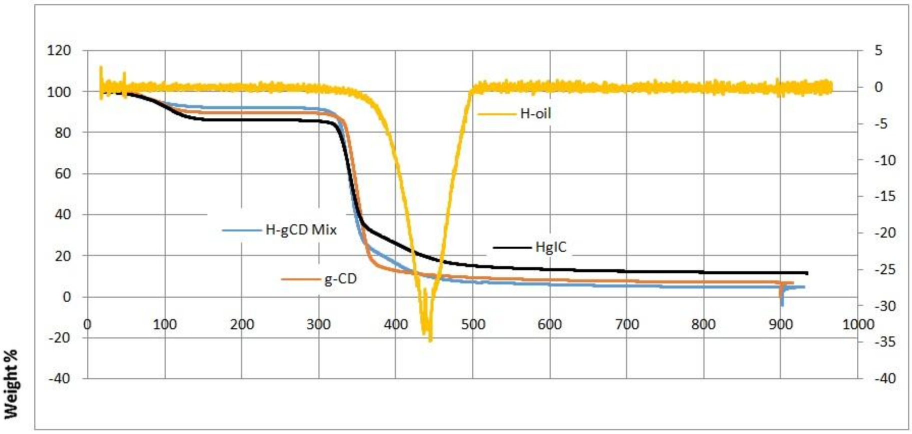


Fig. 7. TGA thermograph of g-CD, H-oil, their physical mixture H-g-CD Mix and their inclusion compound H-g-IC

4. Conclusion

Hazelnut oil was used as a high-quality food product because of its fatty acid composition, which included oleic and linoleic acids as well as vitamin E (a-tocopherol). In this study, differently from the literature, hazelnut oil as a guest material was encapsulated in the cavities of host gamma CD-IC. XRD patterns scattering patterns substantially differed after the inclusion of guest hazelnut oil molecules. FTIR studies also indicated that both guest and host molecules were present in the precipitated inclusion compounds. As a result of thermogravimetric analyses, decomposition range of hazelnut oil was indicated as 302-445°C and it was determined that it had a high thermal stability because of expressive quantity of unsaturated fatty acids and antioxidants such as a-tocopherol existing in the structure of it. It was considered that this successfully performed inclusion compound could be used either in food products or specific applications used with textile materials such as cosmototextiles in further studies.

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