Application of cyclodextrins in thermosetting polymers: cyclodextrin-polyhemiaminal composite polymers and inclusion complex formation of [aromatic diamines@cyclodextrin]

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Doctoral Thesis

Application of cyclodextrins in thermosetting polymers: cyclodextrinpolyhemiaminal composite polymers and inclusion complex formation of [aromatic diamines@cyclodextrin]

(熱硬化性ポリマーにおけるシクロデキストリンの応用:
 ポリヘミアミナール架橋ポリマーと
 [芳香族ジアミン@シクロデキストリン]包接錯体)

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উৎসৰ্গ (Dedicated to my parents)

আমার আব্বা এবং আম্মার প্রতি যাদের জ্ঞ্যানের আলোয় আমি আলোকিত। যাদের অনুপ্রেরণায় আমার এই পথ চলা।

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Chapter 1

Title: Synthesis and characterization of composite polyhemiaminal cross-linked polymers with cyclodextrins

Abstract: Typical thermosetting polymers containing high cross-link density are challenging to recycle, reprocess and solubilize in organic solvents causing serious environmental and waste management problems. Numerous thermosetting polymers have been designed by incorporating either dynamic covalent bonds or blending with thermoplastics to improve solubility, thermal stability, and recyclability. The most reliable method is to incorporate dynamic covalent bonds into a cross-linked knot or in the monomer. The incorporation of dynamic bonds is a useful method to prepare stimuli-responsive materials. Polyhemiaminal (PHA) cross-linked polymer is a new class of thermosetting polymer containing hemiaminal dynamic covalent bonds in the cross-link knot. PHA polymers are prepared by polycondensation of diamines and formaldehyde at 50 °C and cyclize to polyhexahydrotriazine (PHT) by the removal of water at high temperature (180–200 °C). Despite the promise of PHA and PHT polymers, low thermal stability is observed due to thermally labile hexahydro triazine knot. To solve this issue, we synthesize composite polyhemiaminal (PHA) cross-linked polymers by reacting formaldehyde with sonicated precursor solution of 4,4'-oxydianiline (ODA) and Cyclodextrins (α -, β -, and γ -) (CDs), demonstrating that the material obtained under optimal conditions (ODA:CD molar ratio of 1:0.5, saturated (37%) aqueous formaldehyde solution (100% formalin)) exhibits good film formability and high thermal stability with two characteristic decomposition phenomena and high charcoal yield. In such a way, CDs improve the thermal stability of the CDs/PHA composites. Notably, the deposited layer of CD was found soluble in a solution of N-methyl-2-pyrrolidinone and 8-9 wt% LiBr at 80 °C, whereas the remaining PHA matrix was unchanged over time. CDs-based composites and hemiaminal core formation were confirmed by various spectroscopic techniques, and polymer recyclability was checked by pH resolution. Hemiaminal core formation of both PHA polymer and CDs/PHA composites was studied by real-time nuclear magnetic resonance (NMR) analysis in deuterated dimethyl sulfoxide (DMSO-d₆) at 55 °C NMR probe temperature in the direct method. Further, paraformaldehyde reaction with CDs and some other alcohols was assessed to evaluate the composite behavior of CDs.

Keywords: Thermoplastic; Thermosetting plastic; Dynamic covalent bonds; Polyhemiaminal polymer; Laser-engravable materials; Cyclodextrins, Polyoxymethylene.

1.1 Introduction

Typical thermosetting polymers are covalently cross-linked polymers intended to various applications such as adhesive, coating, electronic devices, automotive and aerospace parts due to high mechanical strength, solvent resistance, low density, and load-carrying capacity [1–5]. However, conventional thermosetting polymers are challenging to recycle, reprocess and remold once cured due to three-dimensional covalently cross-linked network, which causes serious waste management and environmental problems [1,6]. An example of conventional thermoset containing a carbon-carbon covalent backbone is Bakelite thermosetting polymer [5]. In contrast, thermoplastics are covalently bonded large macromolecules held together by polymer entanglement, which are widely used as commodity plastics. Thermoplastics are recyclable and remold able up too many cycles, but mechanical properties are inferior compared to thermosetting plastics to be useful for high-performance applications [1-3]. Recent attention has been growing on the incorporation of dynamic covalent bonds into thermosetting polymers intended to various applications such as drug delivery, smart coating, and self-healing materials [2–4,6–10]. Dynamic covalent bonds are stable covalent bonds that exhibit reversible behavior exposure to specific external stimuli such as pH, light, temperature, and redox change [7,10]. Dynamic covalent bonds typically used to prepare reversible thermosets are disulfide bridge, transesterification, Diels-Alder linkage, boronic ester exchange, olefin metathesis exchange, and so on [7,10,11].

Hemiaminal dynamic covalent bond (HDCN) is a dynamic covalent bond used to prepare polyhemiaminal (PHA) thermosetting polymers [7,10]. HDCN is the intermediate core structure formed by the condensation reaction of diamine and formaldehyde in the polar aprotic solvent during the synthesis of poly(hexahydrotriazine) (PHT) polymer. PHT polymers feature the advantages of high mechanical strength, chemical resistivity, low density, and pH responsiveness, consequently attracting increased attention and being potentially suited for the fabrication of adhesives, coatings, printing materials, and electronic sensors [7,10,12–23]. Polymers with photosensitive triazine- or thermally labile hexahydrotriazine (HT) cores are typically used as photopolymers in laser ablation applications [13–15,18]. Spacer chain variation and doping of the thermally labile HT core with conventional polymers and have been employed to design polymers for laser engraving applications (Scheme 1) [13–15,19]. Moreover, much effort has been directed at the ultra-sonication-assisted catalyst-free simple synthesis of aromatic residue-substituted HT derivatives [20]. Recently, the generation of PHT cross-links via PHA intermediate formation at 50 °C and cyclization to PHT at 200 °C were used to prepare novel thermosetting polymers intended for automotive and adhesive coating applications. Those PHA and PHT polymers are associated with high mechanical strength (Young's moduli ~6.3 and ~14 GPa) exceeding those of known thermosets and acid-triggered recyclability (Scheme 1) [12]. Further, the self-healing properties of organogels intended for adhesive material applications have been probed computationally and experimentally in terms of supramolecular interactions and model core analysis [7,21]. Numerous thermosets have been studied by copolymerizing reactive species such as maleimide, epoxides, and acrylates with PHT and are characterized in terms of mechanical properties and processability for large-scale applications [22]. Moreover, recent interest has been growing in the PHA-based fibre reinforced carbon composites owing to their recycling properties and low-cost, easy synthesis process [23–25]. Despite the high mechanical strength, recyclability, and self-healing properties of the PHA polymers, the presence of thermally labile PHA and PHT core results in poor high-temperature performance [16,17,22]. Previous studies on PHT-based diamino end-capped oligomers (e.g., oligo(ethylene oxide), oligo(tetrahydrofuran)) intended to laser engraving applications revealed the occurrence of two decomposition processes, namely the initial decomposition of HT knots and that of oligomer chains [13]. In general, thermal properties can be tuned by the physical blending of various thermoplastic resins or by incorporating reactive species in the reaction mixture to improve homogeneity through chemical modification [22]. To improve the thermal stability, I studied CD-based composite PHA polymers. In this context, we prepared a sonicated precursor solution of cyclodextrins (CDs) and 4,4'-oxydianiline (ODA) in N-methyl-2-pyrrolidinone (NMP), which was treated with formaldehyde to obtain CDs/PHA composites. CDs are cyclic oligomers of glucose that exhibit a unique thermal stability range (252-400 °C) and char-forming ability upon degradation and are frequently used as environmentally benign diverse-functionality hosts for hydrophobic guests of suitable size in surfactant and functional polymer applications [26–29]. Even though the inclusion complex is formed with the hydrophobic guest in water, their application to the thermosetting polymer is limited by the following factors such as polar solvent, reactivity, and solid-state channel formation. In the polar solvents, dethreading of CDs occurs, whereas in solid-state channel inclusion complex formed through strong hydrogen bonds limited the reactivity of the complex [30,31]. In such a case, composite formation could be studied to change the physicochemical properties of the polymer due to aggregation behavior and shielding effects CDs. Bio-based natural fiberreinforced composite is an attractive area of research alternative to glass fiber and carbon fiber in automotive applications owing to their low-cost availability, biodegradable, and cellulose-rich core [32,33]. Despite the promise of PHT cross-link-based polymers, their applications in thermosets and composite reinforcement are scarce due to the lack of appropriate functionalization and solubilization procedures [12–13,16,21]. In particular, the synthesis of CDsbased PHA or PHT polymers has not been explored yet. To bridge this gap, we herein fabricated CDs/PHA composites and evaluated their thermal properties, glass transition temperatures (T_s) , decomposition temperatures (T_d), solubility, and recyclability. Among the three CDs (α -, β -, and

 γ -), α -CD was preferentially evaluated due to low-cost availability (food grade). The solubilities of the obtained polymers were evaluated using ionic liquids such as NMP/LiBr and dimethylacetamide DMAc/LiBr as solvents [34]. Recently, we addressed an interesting issue of CDs reaction with PFA to form polyoxymethylene (POM). POM polymers are a class of thermoplastic used as fuel additives and engineering thermoplastic based on their molecular weight distribution and type of co-polymers [35]. Typically, POM polymers are formed by the polymerization reaction of formaldehyde or oligomers of formaldehyde (paraformaldehyde (PFA), trioxane) as well as copolymerizing with dimethoxy methane or methanol over acid catalysts (Scheme 3). POM reaction is a useful reaction to dissolute cellulose in a mixture of paraformaldehyde and dimethyl sulfoxide (DMSO) to produce methylol cellulose [36]. In this respect, we extended our research to POM synthesis by reacting CDs with PFA in presence of catalytic amounts of para toluene sulphonic acid (p-TsOH) in DMF and DMSO to evaluate the composite behavior of CDs. Further, various alcohols (primary, secondary, and both primary and secondary hydroxyl groups containing alcohols) were used as model compounds to study the alcohol reaction with PFA. We assume CDs composites with PHA could be used to understand cellulose-based composite PHA formation.



Scheme 1. Previously prepared PHA- and PHT-based polymers with variable diamine spacers for thermoset, [12] organogel, [7] and flexographic plate [13] applications.

1.2 Experimental Section

1.2.1 Materials

ODA, 4,4'-methylenediamine (MDA), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP), and *N*,*N*-dimethyl-1,4-phenylenediamine (DMPD) were purchased from TCI and had purities of > 98%. α -CD (food-additive grade), NMP, and 100% formalin were purchased from Kanto Chemical Co., Inc. Paraformaldehyde (PFA) powder (95%) was purchased from Nakarai Chemicals, Ltd.

1.2.2 Methods

Solid-state FTIR was recorded on an FT/IR-6300 spectrometer (JASCO Corporation, Japan; power = 180 W, working range = $700-4000 \text{ cm}^{-1}$, 64 scans accumulated) at 25 °C using ATR method. Raman spectra were recorded on an NRS-7100 (JASCO Corporation, Japan; 32 scans accumulated) laser spectrometer featuring He-Cd and YAG laser sources with wavelengths of 325, 532, 785, and 1064 nm (600 mW) in the wavelength range of $100-3200 \text{ cm}^{-1}$. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker Advance Ultra Shield 400 (400.13 MHz) instrument (Bellerica, USA) using DMSO-d₆ as a solvent and tetramethylsilane as an internal standard. Wide-angle XRD patterns of powder and solid resin polymer samples were recorded under ambient conditions on an XRD RINT-2200 instrument (Rigaku, Japan) equipped with a Cu K ($\lambda = 1.54$ Å) source. DSC measurements were performed on a DSC-60 pulse instrument (Shimadzu, Japan) at a heating rate of 10 °C/min and an Ar flow rate of 25 mL/min using two different ranges (-40 to 40 °C and 40 to 400 °C). TGA-DTA (DTG-60A, Shimadzu, Japan) measurements were performed in a flow of Ar (25 mL/min) at a heating rate of 10 °C/min within a temperature range of 30 to 500 °C. FE-SEM imaging was performed on a JSM 6335F instrument (JEOL, Japan) using samples that were coated with Au to decrease charging. Atomic force microscopy (AFM) measurements were performed on an AFM VN-8010 instrument (Keyence, Japan). Elemental analysis was carried out on an EA1112 elemental analyzer (Thermo Electron, USA).

1.2.3 Synthesis procedure

Both ODA-PHA (Scheme 2, Path A, according to the literature [1]) and CDs/ODA-PHA composite (Scheme 2, Path B, newly designed process) were synthesized to facilitate manipulation and comparative studies, with their specifications listed in table 1 and thermal characteristics and elemental analysis data tabulated in Table 2.

1.2.4 Synthesis of ODA-PHA (Path A)

ODA-PHA was prepared as described elsewhere [12]. Additionally, the respective condensation reaction was performed using 100% formalin as a source of formaldehyde, with the results evaluated in the discussion section.

1.2.5 Synthesis of CDs/ODA-PHA (Path B)

A 100-mL oval-shaped round-bottom flask was charged with ODA (0.2045g, 1.0213 mmol, 1 eq.), α -CD (0.4968 g, 0.5106 mmol, 0.5 eq.) molar ratio relative to ODA, and NMP (4 mL), and the mixture was sonicated in an ultrasonic bath for 1 h to afford a clear solution (precursor solution), which was then treated with PFA or 100% formalin (0.1379 g, 4.5957 mmol, 4.5 eq. of CH₂O) molar ratio relative to ODA. The flask was immersed in an oil bath and equipped with a reflux condenser under Ar. The temperature was slowly raised to 55–60 °C while stirring magnetically and continued at that temperature for 3–4 h. The mixture was turned into a viscous liquid within 1 h, and finally, an opaque gel was obtained after 3–4 h. The obtained product was cooled to 25 °C and treated with 4 mL acetone. The precipitate was filtered, rinsed with 6–8 mL acetone, and washed with 8–10 mL water to remove excess α -CD, and the resulting white waxy resin was dried in an oil bath for 8–10 h at 50 °C and a vacuum of 13 Torr. The product obtained ~95 wt% (insoluble fraction), including solvent trapped in the polymer network. During the total-sonication synthesis, the initial synthesis of precursor solution was performed for 1 h at 25 °C, and 1.5 h sonication was performed at 50 °C after formalin addition. The obtained solid gel was re-precipitated in acetone, washed with water, and dried as above (Scheme S1).

Table 1. Reaction conditions of ODA-PHA and CDs/ODA-PHA composite formation. ^{*a*} The reaction was carried out using 1-h sonication for precursor solution preparation at 25 °C followed by 1-h sonication at 50 °C with formaldehyde (for polymerization).

ODA:CD molar ratio	PFA/formalin eq. vs. ODA	Sonication time/h	Reaction time/h	Isolated yield (wt%)
1:0 (ODA)	4.5 (PFA)	_	24	85–90
1:0.5 (α-CD)	4.5 (PFA)	1	8–10	85–90
1:0.5 (α-CD)	4.5 (formalin)	1	(2–3)	85–90
1:0.5 (α-CD)	4.5 (formalin)	2 at 50 $^{\circ}C^{a}$	-	95–100
1:0.5 (β-CD)	4.5 (formalin)	1	(3–4)	80-85
1:0.5 (γ-CD)	4.5 (formalin)	1	20–24	<75

1.

1.2.6 NMR assay of ODA-PHA and CDs/ODA-PHA composite formation in DMSO-d₆ before gelation

¹H NMR (400.13 MHz, DMSO-*d*₆) of ODA-PHA (Figure S1a): δ (ppm) 6.73–6.53 (Ar–H), 5.90 (Ar–NH–), 4.72 (–CH₂–), and 4.42 (–OH).

¹³C NMR (100 MHz, DMSO-*d*₆) (Figure S1b): δ (ppm) 149.1 (C_M), 143.8 (C_N), 119.4 (C_Q), and 115.4 (C_P), 89.9 (–CH₂–), 84.5 (PFA).

¹H NMR (400.13 MHz, DMSO-*d*₆) of α-CD/ODA-PHA (Figure S1c): δ (ppm) 6.97–6.45 (Ar–H), 6.25 (Ar–NH–), 5.56 (O₂H), 5.52 (O₃H), 4.82 (H₁), 4.69 (–CH₂–), 4.64 (O₆H), 4.40 (–OH), 3.73– 3.18 (H₅ to H₂).

¹³C NMR (100 MHz, DMSO-*d*₆) (Figure S1d): δ (ppm) 149.1 (C_M), 144.2 (C_N), 119.4 (C_P), 115.6 (C_Q), 102.4 (C₁), 89.9 (–CH₂–), 84.6 (PFA), 82.5 (C₂), 73.7 (C₃), 72.5 (C₄ and C₅), 60.5 (C₆).

¹H NMR (400.13 MHz, DMSO-*d*₆) of β-CD/ODA-PHA (Figure S1f): δ (ppm) 7.01–6.57 (Ar–H), 6.15 (Ar–NH–), 5.75 (O₂H), 5.69 (O₃H), 4.84 (H₁), 4.68 (–CH₂–), 4.49 (O₆H), 4.40 (–OH), 3.64– 3.25 (H₂ to H₅).

¹³C NMR (100 MHz, DMSO-*d*₆) (Figure S1g): δ (ppm) 149.2 (C_M), 143.9 (C_N), 119.4 (C_Q), 115.7 (C_P), 102.4 (C₁), 89.9 (–CH₂–), 84.5 (PFA), 82.0 (C₂), 73.5 (C₃), 72.9 (C₄), 72.5 (C₅), 60.4 (C₆). ¹H NMR (400.13 MHz, DMSO-*d*₆) of γ-CD/ODA-PHA (Figure S1h): δ (ppm) 6.69–6.55 (Ar–H), 6.21 (Ar–NH–), 5.79 (O₂H), 5.76 (O₃H), 4.89 (H₁), 4.64 (–CH₂–), 4.52 (O₆H), 4.40 (–OH), 3.63– 3.33 (H₂ to H₅).

¹³C NMR (100 MHz, DMSO-*d*₆) (Figure S1i): γ-CD: δ (ppm) 149.1 (C_M), 144.2 (C_N), 119.4 (C_Q), 115.5 (C_P), 102.1 (C₁), 89.9 (–CH₂–), 84.5 (PFA), 81.4 (C₂), 73.4 (C₃), 73.0 (C₄), 72.6 (C₅), 60.4 (C₆).

1.2.7 FTIR spectroscopic method

Figure 2 shows that the characteristic bands of ODA, $v (cm^{-1}) = 3388 (N-H)$, 1620 (N–H bending), 1499 (C=C of benzene), 1196 (C–N).

 α -CD, ν (cm⁻¹) = 3320 (O–H), 2925 (C–H), 1023 (C–O–C).

ODA-PHA polymer, v (cm⁻¹) = 3373 (O–H), 2918 (C–H), 1678 (C=O of NMP) [37–39], 1497 (C=C of benzene) [40], 1214 (C–N)

α-CD/ODA-PHA polymer. v (cm⁻¹) = 3347 (O–H), 2926 (C–H), 1672 (C=O of NMP), 1501 (C=C of benzene) [40], 1232 (C–N), 1230 (C–OH) [41], 1031 (C–O–C), 842 (Ar–C–H) [42–44].

1.2.8 Raman spectroscopic method

Figure 3 shows the recorded Raman bands of ODA, $v (cm^{-1}) = 3057 (N-H)$, 1620 (N–H bending), 1614 (C=C of benzene), 1198 (C–C).

 α -CD, ν (cm⁻¹) = 2918 (C–H), 1341 (O–H), 1121 (C–O).

ODA-PHA polymer, v (cm⁻¹) = 3068 (N–H), 2928 (C–H), 1614 (C=C [45]. Peaks at 1434, 1166, and 925 cm⁻¹ were assigned to different vibrational modes of C–H, C–C and C–N bonds [46,47]. α -CD/ODA-PHA polymer, v (cm⁻¹) = 2930 (C–H), 1613 (C=C) [45]. Peaks at 1437, 1168, and 930 cm⁻¹ were assigned to different vibrational modes of C–H, C–C, and C–N bonds [46,47].

1.3 Results and Discussion

Based on previous studies of PHT polymers (Scheme 1), we herein fabricated CDs/PHA composites with three cyclodextrins (α -, β -, and γ -) CDs. In this respect, a sonicated precursor solution of CDs and some aromatic diamines such as ODA, MDA, and BAPP were treated with paraformaldehyde in NMP at 60 °C to obtain CDs-deposited PHA composites. Both bulk polymerization and film formation were carried out to understand the matrix-assisted composite formation. The obtained polymers were characterized to confirm the PHA network formation and were subjected to thermal stability, solubility, and recyclability studies. The results showed that in the presence of CDs, aromatic diamines underwent condensation polymerization with formaldehyde to afford CDs/PHA composites. CDs incorporation resulted in a marked property change, i.e., the final products were obtained as solid resins as opposed to powders (Scheme 2 and S1). Different ODA: CDs molar ratios (1:1 and 1:0.5,) were used to optimize the properties of the resulting polymer, and the best result was obtained at a ratio of 1:0.5. Condensation reactions were carried out according to scheme 2, with path A used to prepare a reference material [12] and path B used to prepare CDs/PHA composites. Both paraformaldehyde (PFA) and 100% formalin were tested, and a total sonication workup was used in both cases, i.e., both precursor solution preparation between CDs and diamines and subsequent condensation with formaldehyde was performed through simultaneous sonication and heating. The reaction was faster in the case of 100% formalin (Table 1), which reflected the promotional effect of water in the reagent [21]. Moreover, formaldehyde had to be released from PFA by cracking, no such kinetic barrier was present in the case of 100% formalin. The time required to accomplish condensation during heating at 60 °C in an oil bath was determined (based on gelation) 3-4 h for α -CD/ODA-PHA. In contrast, when the condensation reaction of the similar precursor solution and PFA was carried out in a bath preheated to 50 °C upon sonication, the reaction time significantly decreased to 45 min, and the product was obtained in ~95% yield (weight percent yield). Both ODA-PHA and CDs/ODA-PHA composite films were prepared with 100% formalin by heating on a glass plate inside a fume hood (Scheme S1). The transparent α-CD/ODA-PHA film was obtained at 60 °C for 24 h in an open system exhibited better flexibility than the reference ODA-PHA film. Moreover, the ODA-PHA film shrank during thermal curing at 60 °C, whereas α-CD/ODA-PHA films strongly adhered to the glass surface because of their excellent adhesive properties. The thermal properties of the polymers, such as glass transition temperature (T_s) and decomposition temperature (T_d) , were probed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Apart from these spectroscopic assessments, elemental analysis confirmed the previously proposed formation of a solvent-stabilized PHA core [12] and allowed us to suggest segmental model analysis for both ODA-PHA and CDs/ODA-PHA composites (Figure

S3, Table S1). Finally, the recycling of both ODA-PHA and CDs/ODA-PHA composites was carried out in $1 \text{ N H}_2\text{SO}_4$ (aq.) and then in $1 \text{ M Na}_2\text{CO}_3$ (aq.) (Figure S4).



Scheme 2. Syntheses of ODA-PHA (Path A) and CDs/ODA-PHA (Path B) through polycondensation of ODA and PFA. Other diamines (MDA and BAPP) were also employed for this purpose.

1.3.1 FTIR analysis

FTIR spectroscopy was used to scrutinize the composite formation. Bands at ~1031 and ~3347 cm⁻¹ associated with C–O–C and O–H stretching vibrations, were observed for both α -CD and CDs/ODA-PHA (Figures 1) [48]. The intensity loss of the amine band at ~3384 cm⁻¹ and the concomitant intensity increase of C–H and C–N stretch at ~2926 and ~1232 cm⁻¹, confirm the hemiaminal core formation (Figures 1) [12]. The extra band at ~1678 cm⁻¹ observed even after vacuum-drying at 60 °C for 8–12 h, is ascribed to the C=O stretch of NMP, as has been previously reported for Path A synthesis [12]. Moreover, NMP is known to form hydrogen bonds with secondary amino groups in polyaniline polymers [49]. After acid-triggered depolymerization, the diamine monomer was recovered, and FTIR and NMR measurements were carried out. The observed pattern was like previously reported for ODA recovery (Figure S4).



Figure 1. Cumulative FTIR spectra of (A) α -CD (B) ODA (C) ODA-PHA and composite polymers (D) α -CD/ODA-PHA (E) β -CD/ODA-PHA (F) γ -CD/ODA-PHA.

1.3.2 Raman analysis

In the Raman spectra, the characteristic amine band of ODA at ~3057 cm⁻¹ was disappeared in both ODA-PHA and CDs/ODA-PHA (Figure 2). In contrast, a C–H band appeared at ~2928 cm⁻¹ associated with hemiaminal core formation. Compared with ODA-PHA, an intense C–H signal at ~2930 cm⁻¹ was observed for CDs/ODA-PHA due to overlap of C–H stretches of CD and hemiaminal bonds [45]. Moreover, the small sharp peak at ~3068 cm⁻¹ that was observed for both polymers and did not stem from α -CD is ascribed to the N–H (secondary amine) stretch of hemiaminal linkages. Further, two characteristic peaks at ~1614 cm⁻¹ and ~925 cm⁻¹ corresponding to the C=C stretch of the phenyl group and C–N stretch were observed for both ODA-PHA and CDs/ODA-PHA [50]. Notably, composite polymers showed identical but less intense Raman shifts with ODA-PHA within the range 500–1750 cm⁻¹. Thus, the above results clearly confirmed the deposition of CDs into the polymer matrix.



Figure 2. Raman spectra of (A) α -CD (B) ODA (C) ODA-PHA and composite polymers (D) α -CD/ODA-PHA (E) β -CD/ODA-PHA (F) γ -CD/ODA-PHA.

1.3.3 Powder X-ray diffraction analysis

The major diffraction peak of ODA-PHA appeared as a broad hump at $2\theta = 17.9^{\circ}$ associated with diffusion or scattering of incident radiation (Figure 3) [12]. A bunch of sharp peaks was observed for α -CD due crystalline nature of the native α -CD. Among the various peaks of α -CD, two significant peaks at $2\theta = 12.7^{\circ}$ and 19.0° are attributed to solid-state channel formation. Similarly, numerous crystalline peaks were observed for ODA. In contrast, both ODA-PHA and CDs/ODA-PHA polymer peaks were appeared as broad hump due to the aggregation behavior of CDs in a composite manner [28]. The emergence of a new α -CD peak at $2\theta = 20.0^{\circ}$ [50] and the significant shift of the major broad peak at $2\theta = 13.2^{\circ}$ confirmed that the originally crystalline α -CD became amorphous upon composite formation [46]. Similarly, β -CD/ODA-PHA and γ -CD/ODA-PHA polymer peaks were shifted to $2\theta = 15.4^{\circ}$ and 16.2° , with respect to β - and γ -CDs peaks at $2\theta = 20.0^{\circ}$ & 20.1° . Thus, the above results confirm the CDs-based composite PHA network formation.



Figure 3. XRD spectra of (A) α -CD (B) ODA (C) ODA-PHA and composite polymers (D) α -CD/ODA-PHA (E) β -CD/ODA-PHA (F) γ -CD/ODA-PHA.

1.3.4 Thermo-gravimetric analysis (TGA)

TGA analysis was used to evaluate the thermal stability and decomposition phenomenon of both ODA-PHA and CDs/ODA-PHA composites. Typically, complete decomposition of aromatic diamines occurs within temperature range 30-400 °C with ~99 % weight loss. In TGA thermograms, three weight-loss areas, namely 23.3, 12.6, and 29.5% for α -CD/ODA-PHA; 16.7, 15.3, and 42.1% for β -CD/ODA-PHA, and 12.5, 18.5, and 38.0% for γ -CD/ODA-PHA were observed within the range 30-450 °C (Figure 4). The first weight loss is ascribed to solvent and water volatilization, while the second and third ones are related to CD decomposition and the degradation of aromatic residues to furnish charcoal (Table S2) [14], respectively, in agreement with expected values. CD decomposition was assumed to proceed via dehydroxylation and involve the breakage of CD ring glycosidic linkages, affording char [26,47]. As expected, no related weight loss was observed for the CD-free ODA-PHA. Notably, the final decomposition temperature significantly increased upon the incorporation of CDs into CDs/ODA-PHA, which is ascribed to the formation of an insulating char barrier by CD decomposition and the slow diffusion of oxygen and nitrogen through this primary char [26,28]. Unlike CDs/ODA-PHA, ODA-PHA showed two-weight losses of 30.4 (major) and 28.8% (minor). The acquired data were used to calculate charcoal yields at points corresponding to the decomposition of CDs and the final decomposition of ODA-PHA and CDs/ODA-PHA (Table S2). All polymers showed almost identical charcoal yields at the final polymer decomposition temperature, with some variation observed only at the first decomposition temperature. The obtained results indicate that the CDs act as sources of primary char until stable char is produced at the final decomposition temperature. Further, selected aromatic diamines (MDA and BAPP) were subjected to TGA to gain further insights into polymer decomposition behavior (Figure S6), and the decomposition temperature was found to depend on the type of the central bond between two aromatic units (Ar–O–Ar in ODA, Ar–CH₂–Ar in MDA, and Ar–CMe₂–Ar followed by two ether linkages in BAPP) and on the distance between two cross-links [51]. Although BAPP was expected to exhibit the highest bond strength among the three diamines, the presence of two ether linkages next to aromatic carbons resulted in a bond strength slightly less than that of MDA; i.e., bond strength decreased in the order: MDA > BAPP > ODA, which corresponds to the stability order determined by TGA for the three polymers (Figure S6).



Figure 4: TGA graphs of (A) α -CD (B) ODA (C) ODA-PHA and composite polymers (D) α -CD/ODA-PHA (E) β -CD/ODA-PHA (F) γ -CD/ODA-PHA.

1.3.5 Differential scanning calorimetric analysis (DSC)

The melting behavior and glass transition temperature ($T_g s$) of ODA-PHA and CDs/ODA-PHA composites with α -, β -, and γ -CDs were investigated by DSC at temperatures from 40 to 400 °C. Typically, ODA and MDA show a sharp melting point, which on polymerization evolves as a broad amorphous peak (Figure 5). The $T_g s$ of the CDs/ODA-PHA decreased in the order: α - > β - > γ-CD, and that of ODA-PHA (107 °C) was close to previously reported values. Two major broad exothermic peaks appeared for ODA-PHA and the three CDs/ODA-PHA, which clearly indicate the amorphous nature of these polymers [52]. The first exothermic peaks and the corresponding enthalpies were determined to be 258 °C and 8.84 J/g for ODA-PHA, 247 °C and 119.8 J/g for α-CD/ODA-PHA, 241 °C and 74.8 J/g for β-CD/ODA-PHA, and 237 °C and 59.2 J/g for γ-CD/ODA-PHA. Thus, the incorporation of CDs resulted in an increase of the first exothermic peak at the final decomposition point were determined as 80.8 J/g for ODA-PHA, 67.4 J/g for α-CD/ODA-PHA, 106.3 J/g for β-CD/ODA-PHA, and 94.5 J/g for γ-CD/ODA-PHA. Further, DSC analysis was carried out at temperatures from -40 to 40 °C, and one small transition was observed for ODA-PHA (at -4.4 °C) and α-CD/ODA-PHA (at -7.1 °C). These peaks, ascribed to the *T*_gs of polymers in the low-temperature region, have not been previously reported (Figure S7).



Figure 5. DSC thermograms of (A) α -CD (B) ODA (C) ODA-PHA and composite polymers (D) α -CD/ODA-PHA (E) β -CD/ODA-PHA (F) γ -CD/ODA-PHA.

1.3.6 Elemental analysis

The results of elemental analysis obtained for ODA-PHA and α -CD/ODA-PHA prepared at ODA:CD molar ratios of 1:1 and 1:0.5 agree with theoretical values determined by considering four fragmental components of hemiaminal dynamic covalent bonds (Figure S3 and Table 2). For other polymers, i.e., β -CD/ODA-PHA, γ -CD/ODA-PHA, α -CD/MDA-PHA, and α -CD/BAPP-PHA, the experimental results were observed to deviate from theoretical values, which is

ascribable to CD distribution in the polymer or environmental contributions. Four fragments were considered namely the hemiaminal core (C1), NMP (C2), CDs (C3), and water (C4) (Figure S3).

Table 2. Final decomposition temperature (T_d), charcoal yield, and elemental analysis data (threecomponent consideration) of ODA-PHA and CDs/ODA-PHA composite (four-components consideration) prepared at an ODA:CD molar ratio of 1:0.5. ^{*a*} Determined from TGA curves for all polymers (Figure S8a). ^{*b*} Calculated from TGA data at T_d . ^{*c*} Determined from the results of elemental analysis. ^{*d*} Elemental compositions are calculated based on the above-mentioned formulas by considering possible polymer components and bound solvent contribution (Figure S3).

Compound	$T_d (^{\circ}\mathrm{C})^a$	Char yield (wt%) ^b	Experimental	Calcd. C/H/N/O contents (wt%) ^d
			C/H/N/O contents (wt%) ^c	
ODA-PHA	293	65.5	65.9/6.1/11.4/16.6	66.5/7.3/12.2/14.0
				$(C_{19}H_{25}N_3O_3)$
ODA-α-CD-PHA	365	39.8	50.6/6.4/4.6/38.5	50.3/6.5/3.2/40.2
				$(C_{50}H_{85}N_{3}O_{33})$
ODA-β-CD-PHA	366	42.9	55.3/6.8/6.7/31.2	49.6/6.4/2.8/41.2
				$(C_{61}H_{95}N_3O_{38})$
ODA-γ-CD-PHA	365	41.1	54.7/6.9/6.2/32.2	49.1/6.4/2.6/42.0
				$(C_{67}H_{105}N_3O_{43})$
DDM-α-CD-PHA	362	38.0	55.9/7.0/6.3/30.8	54.3/6.6/2.8/36.2
				$(C_{68}H_{99}N_3O_{34})$
BAPP-α-CD-PHA	358	49.8	57.1/7.2/7.6/28.1	51.2/6.6/3.2/39.0
				$(C_{56}H_{87}N_3O_{32})$

1.3.7 Field emission scanning electron microscopy analysis (FE-SEM)

Figure 6 shows FE-SEM images of ODA-PHA, demonstrating the 3D porous structures of the ODA-PHA sample [53]. However, layered structure with small grove was observed in α -CD/ODA-PHA composite.



Figure 6: Microscale FE-SEM image of α -CD/ODA-PHA (A, B) and ODA-PHA (C, D) polymer after gold coating.

1.3.8 Atomic force microscopy analysis (AFM)

AFM measurement also revealed that the α -CD/ODA-PHA film featured a surface smooth on a micrometer scale, whereas a rougher surface was observed for the ODA-PHA film (Figure 7). A smooth surface could be due to a layer of cyclodextrin deposited on the ODA-PHA rough surface.



Figure 7: AFM nano scale images of ODA-PHA (A and B) and α -CD/ODA-PHA (C and D) films prepared at 60 °C.

1.3.9 Hemiaminal bond formation assay by ¹H-NMR measurement

Hemiaminal bond formation was monitored by a real-time ¹H NMR assay prior to gel formation at NMR probe temperature of 55 °C with respect to time (direct procedure). To do so required amount of ODA was dissolved in DMSO- d_6 and NMR spectrum was recorded. Prepared another tube filled with ODA (1.0 equivalent) and PFA (2.5 equivalents relative to ODA) in DMSO- d_6 and immediately recorded the NMR spectrum at the starting point. Further, NMR measurement was continued with respect to time (Figure 8). Hemiaminal bond formation was observed after 10 minutes, confirmed by the evolution of new peaks due to hemiaminal bond formation and consumption of PFA peaks. Moreover, the relative integral values of the hemiaminal peaks were increased with the decrease of the typical PFA peak (-CH₂-) with respect to time. The molar ratio was calculated based on relative integral values of hemiaminal peaks (-NH- and -OH) and methylene proton peaks and plotted with respect to time. The molar ratio dramatically increased with the increase of time. Similarly, ¹H NMR measurement was performed using a model compound (DMPD). The emergence of hemiaminal peaks was observed at 5.30 ppm (–NH–), 4.54 ppm (-CH₂-), and 4.39 ppm (-OH) (Figure S9). However, a synergistic methylene peak arising from the hemiaminal bond evolved near the methylene protons of the PFA. The integral values of the hemiaminal peaks increased with a decrease in PFA peaks. Composite formation was monitored via NMR measurements at 55 °C by reacting a precursor solution of α -CD, ODA, and formalin in DMSO-d₆. As the reaction proceeded, some new peaks emerged at 5.98 ppm, 4.70 ppm, and 4.62 ppm due to hemiaminal protons, such as -NH-, -CH₂-, and -OH, respectively (Figure S10). Notably, the aromatic and hydroxyl proton peaks of α -CD broadened significantly with time owing to gel formation. However, the α -CD cavity and anomeric protons remained unchanged for up to 120 min. Hemiaminal core formation was monitored indirectly. In this case, the required amounts of diamine and 100% formalin (4.5 eq.) were placed in a small flask, and DMSO-d₆ was added instead of NMP. The mixture was then heated to 60 °C for 20 min, and NMR spectra were recorded. In the ¹H NMR spectra, hemiaminal protons associated with (Ar-NH–), –CH₂–, and –OH appeared at 5.90 ppm, 4.72 ppm, and 4.42 ppm, respectively (Figure S1a). In the ¹³C NMR spectrum, a hemiaminal carbon peak appeared at 89.9 ppm (Figure S1b). To monitor the composite formation, the required amounts of diamine and the CDs were dissolved in DMSO- d_6 , followed by sonication (1 h), the addition of formalin (4.5 eq.), and stirring. An aliquot was then transferred to an NMR tube and heated at 60 °C for 20 min. In the ¹H NMR spectrum of α-CD/ODA-PHA, hemiaminal protons, such as (Ar-NH-), -CH₂-, and -OH, were assigned at 6.25 ppm, 4.69 ppm, and 4.40 ppm, respectively. Notably, a hemiaminal carbon resonance peak was observed at the same position as ODA-PHA at 89.9 ppm for all composites (Figure S1c and S1d).



Figure 8: ¹H-NMR spectra of ODA-hemiaminal bond formation at 55 °C NMR probe temperature up to 100 minutes after 10 minutes intervals. Hemiaminal -NH-, -CH₂-, and -OH peaks are denoted by a, b, and c respectively.



Time versus molar ratio plot

Figure 9: Molar ratio plot of hemiaminal proton and PFA protons based on relative integral values of -NHproton of hemiaminal bond and -CH₂- protons of PFA.

1.3.10 Solubility assay of both ODA-PHA and CDs/ODA-PHA polymers

Previous studies on polyrotaxane solubility and post-derivatization employed DMAc/LiCl and DMAc/LiBr with salt contents of 8–9 wt% as alternative solvents to solubilize polyrotaxanes and

facilitate their acetylation and densylation [34]. The low solubility of polyrotaxanes is probably due to intra- and intermolecular hydrogen bonding among the hydroxyl groups of CDs [28,34]. Herein, we employed NMP/LiBr and DMAc/LiBr to evaluate the solubility of ODA-PHA and CDs/ODA-PHA polymers. The maximum portion of CDs/ODA-PHA films (<68 wt% of initial weight) was digested in NMP/LiBr mixture (8–9 wt% LiBr) at 80–90 °C for 3–5 h remaining film residue was collected for FTIR analysis, and the resulting solution was clear and yellow, whereas the ODA-PHA film remained unchanged at this temperature even when treatment was continued for more than three days. The concentration of the resulting solution afforded a sticky viscous liquid that was poured into water to afford a brown precipitate. This precipitate was collected and vacuum-dried, and later characterized by FTIR spectroscopy. Notably, the corresponding FTIR spectra featured all characteristic bands observed except C–N stretching for the dissolved portion (Figure S8). Further, the portion of α -CD/ODA-PHA film that was not dissolved in NMP/LiBr was sequentially washed with water and methanol several times, kept in methanol for one day, and vacuum-dried at 60 °C for 3–4 h. In the FTIR spectrum of the undissolved portion, no C–O– C band with a sharp C–N stretching well fitted with ODA-PHA, confirming that the matrix core is ODA-PHA (Figure 10). A similar procedure was used using DMAc/LiBr, in which a heterogeneous mixture was observed.



Figure 10: FTIR spectrum of both ODA-PHA film and the undissolved portion of α -CD/ODA-PHA films in NMP/LiBr (8–9 w/w%) solvent.

1.3.11 POM formation reactions of CDs and some alcohols with PFA

Typical POM synthesis involves a direct reaction of alcohol and oligomers of formaldehyde in the presence of an acid catalyst in a high boiling polar aprotic solvent. During thermal cracking of the oligomers for example paraformaldehyde formaldehyde is released to bring the POM reaction

Reaction 1



Scheme 3. POM formation reaction of alcohols and CDs with formaldehyde sources using an acid catalyst in polar aprotic solvent.

To study the POM formation, herein we studied β -CD reaction with PFA through time-resolved NMR measurement. The reaction condition was optimized by reacting equimolar amount of PFA relative to hydroxyl groups of β -CD at 80 °C in the presence of catalytic amounts of p-TsOH in DMSO-*d*₆. ¹H-NMR measurement was carried out to identify the POM chain formation and growth at the NMR probe temperature of 80 °C for 2 h after 10 minutes interval. Typically PFA peaks were assigned at 9.57 ppm for CH₂O followed by 5.85 ppm for extended (-OCH₂-) and 4.71 ppm for the terminal (-OCH₂-OH). As the reaction triggered between PFA and hydroxyl groups new sets of peaks emerged at different positions with the elimination of PFA peaks (Figure 11). Plots of integral ratios of new peaks and normalized values of DMSO-*d*₆ with respect to time reveal the concurrent increase of new peaks and decreasing of PFA peaks (Figure 12). In general, primary hydroxyl groups are reactive toward formaldehyde released during the decomposition of PFA. However, time-resolved NMR measurement was carried out for a bunch of alcohols including primary alcohol (ethanol), secondary alcohol (isopropanol), and both primary and

secondary hydroxyl groups containing alcohols such as 1,3-butanediol and glycerol. It was observed that both primary alcohol and secondary alcohol reacted with PFA to form POM (Figure S11). Therefore, it could be related to CDs reaction with PFA to realize both types of hydroxyl groups are affected by the PFA during the heating process.



Figure 11: Time-resolved ¹H-NMR spectra obtained by reacting equimolar amount of β -CD and PFA in the presence of 0.01 equivalent p-TsOH relative to β -CD in DMSO- d_6 at 80 °C NMR probe temperature up to time 2 h.



Figure 12: Plots of integral ratios of new peaks and DMSO- d_6 with respect to time. Each measurement was carried out after 10 minutes interval up to 2 h at 80 °C NMR probe temperature.

1.4 Conclusions

Herein, we studied the formation of CDs-based PHA composites, revealing that CDs incorporation results in high thermal stability and the emergence of two decomposition phenomena. Moreover, CDs were found to form POM with PFA, which contributes to the composite behavior of CDs through Van der Walls forces. Hemiaminal bond formation was monitored by real-time ¹H NMR measurement at NMR probe temperature of 55 °C with respect to time. Further, POM formation was assessed by reacting PFA with CDs and some other alcohols at NMR probe temperature of 80 °C with respect to time. The adopted catalyst-free simple synthesis approach employs readily available chemicals such as food-additive grade α -CD, 100% formalin, and a simple aromatic diamine, and is, therefore, suitable for industrial applications. The introduction of α -CD through high-throughput synthesis may potentially reduce material costs, and the non-toxicity and environmental friendliness of α -CD coupled with the acidtriggered recyclability of the prepared polymers make the developed process environmentally viable [53]. The early-stage decomposition of CDs and the photo lability of the triazine knot make the prepared compound a potential component of flexographic materials for laser engraving. Previous laser ablation studies employed various aliphatic polyether diamines-based PHTs polymers with 10–20 wt% carbon black to obtain flexible polymers [13]. Hence, the CD-based composite prepared herein can offer inherent flexibility and act as a source of carbon for laser ablation and nanocomposite studies. Moreover, the thermal stability of CDs is very near to cellulose combined with char forming ability could be applied as a model compound to study thermal insulating and intumescence behavior. Also, CDs could be used to improve the thermal stability of other thermosetting polymers.

1.5 References

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Chapter 2

Title: Comparative study of inclusion complex formation between β cyclodextrin (host) and aromatic diamines (guests) by mixing in hot water, co-precipitation, and solid-state grinding methods.

Abstract: Aromatic diamines are essential components of polyimide and many other thermosetting polymers. Recent attention has been growing on the threading of cyclodextrins (CDs) onto diamine monomers intended to improve solubility in water or other aprotic solvents and thermal stability of the resultant polymers. The co-precipitation method is typically used to prepare inclusion complexes (ICs) of aromatic diamines and other sparingly water-soluble aromatic guest molecules with the β -CD host. To find the viability of other methods, I studied ICs formation between β-CD and some aromatic diamines by mixing in hot water, co-precipitation, and solid-state grinding. ICs formation in hot water was carried out by solid guest dispersion into the β -CD solution at 80 °C with high-speed stirring magnetically. In contrast, solid-state grinding was employed by the addition of a small amount of water to favor the ICs formation. Thus, ICs prepared in hot water and solid-state grinding was crystallized by changing the saturation rate of the complex solution and cooling at 4 °C. Structures of the ICs in solution are confirmed by chemical shifts changes of the cavity protons of β -CD in ¹H NMR and the interaction of resonance of aromatic protons and the cavity protons of β-CD in ¹H-¹H ROESY NMR. FTIR and XRD are used to evaluate solid ICs. Further, Job's plot and NMR titration experiments are used to determine the stoichiometric ratio of host and guest in solution. The binding constant was determined by the UV-spectrophotometric method. Decomposition kinetics was studied by the Flynn-Wall-Ozawa method at the variable rate of temperature.

Keywords: Cyclodextrins; Inclusion complexes; Aromatic amines; Crystallization process

2.1 Introduction

Cyclodextrins (CDs) are a unique class of cyclic oligomers of glucopyranose units that show unique properties of water-soluble, functionalizable, nontoxic low-cost substances with inherent thermal stability range (252–400 °C) and are widely used as environmentally friendly diversefunctionality hosts for hydrophobic guests of complementary size in drug formulation, functional material designing, surfactants, catalysis, and sensor applications [1–5]. CDs are hollow truncated cone-shaped structures composed of 6, 7, and 8 glucopyranose units and the cavity size of 0.47, 0.60, and 0.75 nm respectively (Figure 1, Table 1) [6–8]. All the glucopyranose units of CDs are linked together by the α -glycosidic linkage between anomeric carbons of one glucose unit to the C₄ carbon of the next glucose unit through an ether bridge. Therefore, the primary hydroxyl groups linked to C_6 carbons of glucopyranose units reside at the narrow rim, and secondary hydroxyl groups linked to C_3 and C_2 positions are at the wide rim. All the hydroxyl groups are positioned outside of the CD structure to make the outer surface hydrophilic, and the cavity remains hydrophobic [1,2]. Moreover, all C_3 -OH and C_2 -OH are aligned in a circular fashion to make secondary hydrogen bonds (H-bonds) to build a CD structure. Therefore, β -Cyclodextrin $(\beta$ -CD) achieves the highest rigid structure among the CDs due to the complete H-bond distribution among the glucopyranose units in anhydrous conditions. In contrast, α -Cyclodextrin (α -CD) forms imperfect H-bonds causing distorted cyclic formation due to one of the glucopyranose units twisting toward the cavity along the central axis. However, γ -Cyclodextrin (γ -CD) forms a flexible structure to minimize the strain generated by the increasing number of glucopyranose units. Hence, the solubility sequence of three CDs is γ -CD> α -CD> β -CD [1]. CDs inclusion complexes (ICs) formation occurred in multiple steps. Typically, CDs form ICs with water to form hydrated form which is further displaced by the solvent molecules to form solvated structure in a solvent system. At this point CDs form ICs complexes with numerous guest molecules by the displacement of either water or entrapped solvent. In general, α -CD forms ICs with aliphatic guests, β -CD with aromatic guests, and γ -CD with large molecules like steroids, through hydrophobic interactions [9-10]. The formation ICs affects the physicochemical properties of the molecules due to the shielding effect provided by the ring sliding along the axle or the restricted movement of the CDs rings [5,6]. ICs formation depends on the geometrical fit between CDs and the guest molecules as well as the nature of the solvent. In polar solvents, ICs formation is ambiguous, and dethreading is prominent. In water, ICs are formed because the hydrophobic environment of the CD cavity is favorable for hydrophobic guests. The stability of ICs depends on three main factors such as 1) entropically favorable water ejection from the cavity by guest molecule 2) hydrophobic interaction between the hydrophobic cavity and hydrophobic guest 3) CH- π interactions (Figure 2). Moreover, dissociation of ICs into components required

some activation free energy (Figure 2) [1]. As β -CD has selectivity to the aromatic guest, that could bring the possibility of their application to the thermosetting polymer to solve the issues of solubility and thermal stability [7,11]. Aromatic diamines such as 4,4'-oxydianiline (ODA), 4,4'methylenedianiline (MDA), 1,4-phenylenediamine (PD), and 2,2-bis[4-(4aminophenoxy)phenyl]propane (BAPP) are widely used as monomers for synthesizing polyimide, polyamide, polyurethane, and polyhemiaminal thermosetting polymers [12-14]. In contrast, spacer containing aromatic diamines such as (1,2-bis(4-aminophenoxy)ethane (BAPE) and 1,4bis(4-aminophenoxy)butane (BAPB)) are used to improve the flexibility of the polymers [15]. Unless functionally modified, thermosetting polymers often suffer from poor solubility owing to their high cross-link densities. The incorporation of CDs into thermosetting polymers such as polyimide, polyamide, fullerene, and polyaniline has been reported to enhance thermoset solubility and thermal stability [6,7,11,16]. CDs bearing polymers were typically prepared by the inclusion of CDs into aromatic diamines followed by a polycondensation reaction [17]. Various methods have been established for the preparation of ICs solid such as co-precipitation, freezedrying, kneading, and solid-state grinding [18,19]. The co-precipitation method is typically used to prepare CD-ICs of various aromatic diamines and other aromatic guests [20,21]. In the coprecipitation method, IC formation with aromatic guests is achieved by the co-precipitation of complexes in a mixture of water and alcohol. In this process, alcohol is used to diffuse the guest molecules into an aqueous CD solution to obtain a homogeneous solution, and the reaction is accomplished through IC precipitation. As CDs have a large hydroxyl surface, guest dissolution in alcohol is unnecessary, and the simple dissolution of CDs and aromatic guests in hot water could afford ICs. To solve this issue, we investigated the factors regulating IC formation and crystallization in water as well as solid-state grinding (Scheme 1).

IC formation in hot water is a reliable method because the co-solvent is eliminated. In this case, IC formation is favored by entropy-driven water ejection from the CD cavity and hydrophobic interaction at high temperatures [22,23]. Notably, aliphatic polyether amines and polyethylene glycols-based ICs with many threaded CDs form a precipitate in water due to CDs aggregation in a single chain and hydrogen bonding among neighboring CDs [3]. However, small molecules such as ODA and MDA, which have few threaded CDs, could offer soluble ICs in water due to free CD hydroxyl groups.

On the other hand, solid-state grinding is also an efficient method for the ICs formation of small drug molecules and CD [18,24]. In this process, strong mechanical force is applied in the form of friction to the host-guest mixture to obtain IC with respect to grinding time.

Further, a comparative study has been made based on results obtained from three different methods (mixing in hot water, co-precipitation, and solid-state grinding) to rationalize the most

suitable method for the ICs formation of aromatic diamines and β -CD. IC formation and structure of the complexes were confirmed by NMR spectroscopy, FTIR, and XRD. Job's plot (a continuous variation method) and ¹H NMR titration method were applied to determine the stoichiometric ratio of expected ICs in solution [21]. Elemental analysis was used to calculate the composition of ICs. The thermal characteristics were evaluated by differential scanning calorimetry (DSC) and thermogravimetric (TGA) analysis.



Truncated cone shape

Figure 1. Structure of cyclodextrins (α -, β - and γ -)CD [1].

Table	1.	Physical	properties	of	CDs
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CDs	Molecular weight (g/mol ⁻¹)	Solubility in water (298 K) / (w/v)	Cavity diameter (nm)	Height of torous (nm)	Diameter of outer periphery (nm)
β-CD	972.84	14.5	0.47~0.53	0.79	1.46
α-CD	1134.98	1.85	0.60~0.65	0.79	1.56
γ-CD	1297.12	23.2	0.75~0.83	0.79	1.75



Figure 2. Factors regulating the stability of ICs formation (1) entropically favorable water ejection from the cavity by the guest molecules (2) hydrophobic interaction between the hydrophobic cavity and hydrophobic guests (3) CH- π interaction between CH protons of the CDs cavity and resonance π -electrons of the aromatic system (4) Energy diagram of threaded and dethreaded state of IC [1,3,8].

2.2 Experimental Section

2.2.1 Materials

ODA, BAPP, and PD were purchased from TCI and had purities of > 98%. BAPE, and BAPB were prepared according to the procedure mentioned in the reference [21]. MDA and β -CD were purchased from Kanto Chemical Co., Inc.

2.2.2 Methods

¹H (400.13 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker Advance Ultra Shield 400 (400.13 MHz) instrument (Bellerica, USA) using D₂O with 2,2-dimethy-2silapentane-5-sulfonate- d_6 sodium salt (DSS- d_6) as internal standard and DMSO- d_6 solvents with tetramethylsilane as an internal standard. Data for ¹H NMR are reported as chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. Integral ratio (IgR) is calculated by rationing the integral values of anomeric protons of β -CD to aromatic protons. A short form of an integral ratio (IgR) is used after the name of a type of complex to designate the specification of the ICs in all the captions. Further, 2D ROESY NMR was recorded in both D₂O and DMSO- d_6 solvents to observe the correlation peaks. Elemental analysis was carried out on an EA1112 elemental analyzer (Thermo Electron, USA). Wide-angle XRD patterns of powder samples were recorded under ambient conditions on an XRD RINT-2200 instrument (Rigaku, Japan) equipped with a Cu *K* ($\lambda = 1.54$ Å) source. DSC measurements were performed on a DSC-60 pulse instrument (Shimadzu, Japan) at a heating rate of 10 °C/min and an Ar flow rate of 25 mL/min using two different ranges (40 to 300 °C). TGA-DTA (DTG-60A, Shimadzu, Japan) measurements were performed in a flow of Ar (25 mL/min) at a heating rate of 10 °C/min within a temperature range of 30 to 400 °C. Solid-state FTIR spectra were recorded on an FT/IR-6300 spectrometer (JASCO Corporation, Japan; power = 180 W, working range = 700–4000 cm⁻¹, 92 scans accumulated) at 25 °C using ATR method. UV spectra were recorded on a UV spectrophotometer (V-630 spectrophotometer, JASCO Corporation, Japan).

2.2.3 A representative synthesis procedure of ICs in hot water

A 100-mL big neck oval-shaped round-bottom flask, β -CD (2.85 g, 2.51 mmol) was dissolved in 30 mL deionized water at 80 °C in an oil bath for 15 min to stabilize. ODA (0.50 g, 2.49 mmol) was added portion-wise (five portions, approximately 0.10 g portion each time) as solid to the flask at 30 min intervals and stirred magnetically at high speed. After adding the final portion reaction continued for two different times 6 h and 24 h respectively at 80 °C. Flask was cooled to room temperature (24°C). The ODA- β -CD complex solution was filtered and washed with extra 6-8 mL of deionized water then transferred into a petri dish by a pipette and concentrated by heating at 50 °C (4–5 ml solution or maintaining the saturation level). After that, the concentrated solution was transferred into a round bottom flask and kept for crystallization in the refrigerator. To avoid the loss of complex solution in petri dish evaporation, another process was introduced to evaporate excess water by air blowing on the liquid surface by using a small diaphragm pump. In this process, a complex solution cooled to 24°C was filtered, and washed with 6-8 mL of deionized water into a 100 ml round bottom flask and to the liquid surface air blown by a small diaphragm pump while stirring magnetically at 50 °C. Crystallization was observed after 1 h and continued for 48 h then filtered and washed by 6-8 mL deionized water then dried initially in the rotary evaporator at 50 °C then under a vacuum of 1.1 torrs, at 40 °C for 24 h. After filtering the crystal filtrate again concentrated to 6-8 mL and kept in the refrigerator to obtain further crystallization. Less than 5% of crystals were isolated for ODA- β -CD in the second crystallization. Notably, to obtain good crystals small portion of the filtered complex solution is stored in the test tube for 15-30 days. A similar, procedure was adopted for PD-β-CD, MDA-β-CD, BAPP-β-CD, BAPE- β -CD, and BAPB- β -CD. Notably, a clear solution was observed during the complexation reaction of ODA-β-CD, MDA-β-CD, BAPE-β-CD, BAPB-β-CD, PD-β-CD at 80 °C except BAPP- β -CD in which precipitation occurred during the complexation process. Apart from that some ratio complexes of ODA- β -CD (host:guest, 1:1, 1.5:1, 2:1, 2.5:1 & 3:1) and BAPE- β -CD

(host:guest, 1:1, 2:1, 2.5:1 & 3:1) were prepared by similar procedure and weight percent yield is calculated based on integral ratio (IgR) factor of anomeric protons to aromatic protons and tabulated in the Table S1.

2.2.4 A representative synthesis procedure of ICs by co-precipitation method

A 50-mL big neck oval-shaped round-bottom flask, β -CD (0.29g, 0.25 mmol) was dissolved in 7 mL deionized water and heated at 50 °C in an oil bath for 15 min to stabilize then cool to room temperature. ODA (0.05 g, 0.25 mmol) was dissolved in 3 mL methanol. ODA mixture was added into β -CD solution by a pipette dropwise while stirring magnetically. The reaction mixture was kept stirring at 24 °C for 24 h. After 24 h the mixture turned into a hazy mixture. The resultant mixture was kept for precipitation in the refrigerator for 48 h. The precipitate was filtered and rinsed with 4 mL water then dried initially in the rotary evaporator at 50 °C then under vacuum for 24 h. The resultant solid IC was collected and used for spectroscopic assessment.

2.2.5 A representative synthesis procedure of ICs by solid-state grinding method

 β -CD (0.36 g, 0.31 mmol) and ODA (0.06g, 0.31mmol) were taken in a mortar added 0.25 mL water to that mixture. The resultant slurry mixture was ground by a pastel for 15 minutes. Notably, every three minutes solid mixture was accumulated by spatula. After 15 minutes solid mixture was collected in a 50 mL flask. The remaining solid in the mortar and pastel was rinsed with 1 mL water three times then the total mixture was suspended in 7 mL water to make 10 mL volume. The resultant solution was heated at 50 °C in an oil bath for 30 min to solubilize the ICs. The suspension was filtered after cooling at room temperature then concentrated to 4 ml solution and kept in the refrigerator for crystallization. Crystals were appeared within 5 h and continued for a further 48 h. Crystals were filtered and rinsed by 4 mL and dried initially in the rotary evaporator at 50 °C then under a vacuum of 1.1 torr, at 40 °C for 24 h.



Scheme 1. Schematic representation of ICs formation between aromatic diamines (guests) and β -CD (host) by mixing in hot water, co-precipitation, and solid-state grinding methods. Details procedure is included in the supporting information.

Table 2. Percent yield calculation of ICs prepared by three methods based on β -CD. ^aShort forms HW, CP, and SG are used to indicate three methods such as mixing in hot water, co-precipitation, and solid-state grinding. ^bIgR is representing the integral ratio of anomeric ¹H of β -CD to aromatic ¹H and the IgR values were used to calculate percent yield. ^cProducts were defined to inclusion complex (IC) or mixture of IC and excess β -CD (mix). For both chemical shift changes and ROESY correlation, \bigcirc mark was used to represent observed chemical shift change and ROESY correlation and \times mark for not observed.

Entry	β-CD	Aromatic		Synthesis	Yield	IgR ^b	Product ^c	Yield	ICs form	nation
	amount	diamine ar	nount	Method ^a	wt/mg			(% Y)		
	mmol	Compound							Chemical	ROESY
		(mmol)							shift	NMR
									change	
1	2.53	ODA	2.50	HW	2610	0.90	IC	75.6	\odot	\odot
2	0.19	ODA	0.11	HW	90	0.96	IC	32.8	\odot	\odot
3	0.25	ODA	0.25	СР	280	0.91	IC	81.2	\odot	\odot
4	0.31	ODA	0.31	SG	140	0.92	IC	32.4	\odot	\odot
5	1.02	MDA	1.04	HW	1110	0.88	IC	81.6	\odot	\odot
6	0.52	MDA	0.26	HW	170	1.01	IC	21.6	\odot	\odot
7	0.26	MDA	0.27	CP	280	0.91	IC	78.2	\odot	\odot
8	0.35	MDA	0.34	SG	270	0.88	IC	57.9	\odot	\odot
9	0.48	BAPE	0.10	HW	330	2.05	mix	23.7	\odot	\odot
10	0.36	BAPE	0.18	СР	190	4.59	mix	8.5	\odot	\odot
11	0.28	BAPB	0.09	HW	200	3.31	mix	15.7	\odot	\odot
12	0.26	BAPB	0.02	HW	100	3.74	mix	7.5	\odot	\odot
13	0.24	BAPP	0.12	HW	200	0.50	mix	44.9	\odot	×
14	0.13	BAPP	0.07	СР	100	0.96	IC	46.2	0	×
15	0.23	PD	0.26	HW	220	6.24	mix	12.0	\odot	63. ×
16	0.24	PD	0.93	HW	230	2.02	IC	34.7	\odot	\odot
17	0.24	PD	0.99	СР	150	1.91	IC	24.1	O	\odot
18	0.19	PD	0.76	SG	140	2.02	IC	27.0	\odot	\odot

2.3 Results and Discussion

To find the suitable method of ICs formation of aromatic diamines and β -CD, three different methods (in hot water, co-precipitation, and solid-state grinding) were studied. In this research, six different aromatic diamines such as PD, MDA, ODA, BAPE, BAPB and BAPP were used as guests of β -CD host (Scheme 1). Among those diamines, PD and MDA are reported to soluble in water (PD = 40 mg/1 mL and MDA = 1 mg/mL at 25 °C) according to PubChem database system. No water solubility report was available for other studied diamines elsewhere. It is important to know the solubility of guest molecules prior to studying their ICs formation with β -CD. Also, all the studied diamines were classified according to their geometric arrangements, for example, ODA and MDA are in one group, BAPE and BAPB are in another group considered as flexible diamines, BAPP as a rigid structure, and PD as a small diamine.

According to the co-precipitation method, ICs formation was carried out by diffusing aromatic diamines using ethanol or methanol into the aqueous solution of β -CD at room temperature for 24 h followed by precipitating on cooling at 4 °C [19,20]. Thus, the precipitate obtained was collected and characterized accordingly.

To assess the advantages of large hydroxyl surface of CDs, IC formation was carried out in hot water by the addition of solid guest directly into β -CD aqueous solution at 80 °C. Herein, we describe a simple four-step procedure including high dilution work up of host-guest mixture at 80 °C for 24 h, filtration, evaporation of excess water at 50 °C, and crystallization upon cooling at 4 °C to afford IC crystals (Scheme 1 and 2). The high dilution conditions with portion-wise addition of solid guests into host solution at high temperature and high-speed stirring magnetically render the solubility of hydrophobic aromatic diamines. Conceptually, during the inclusion process, a microenvironment exists in water with a balance between hydrophobic and hydrophilic partners. As soon as hydrophobic guests enter the hydrophobic for CD, a dominant hydrophilic environment leads to the dissolution of hydrophobic guests in water. After reaction workup to remove excess water, the high IC concentration in the solution could trigger crystallization, as decreasing solvent volume generally results in a concentration gradient that promotes crystallization [25–27].

In this process, various molar ratios of β -CD host and diamine guests were employed as follows (host: guest = 1:1, 2:1, 3:1) for both ODA and MDA; (1:1, 1/4:1) for PD; (2:1, 3:1) for both BAPE and BAPB, and 2:1 for BAPP. ICs crystals obtained from all the studied diamines were represented in supporting information (Figure S1A). Notably, above the host and guest molar ratio of 2:1 of ODA- β -CD and MDA- β -CD, in situ crystallization of β -CD to form a large aggregate occurred (Figure 1B). Those large aggregates are identical to β -CD crystals obtained by the recrystallization in water by dissolving in hot water and then cooling at 24 °C for a week (Figure S1C).

Apart from co-precipitation and in hot water synthesis of ICs, the solid-state grinding method was also applied. To do so, a host-guest mixture (0.4 g scale) was ground with 0.25 mL of water (to make a slurry) for 15 minutes then the mixture was suspended in 10 mL water and heated for 30 minutes at 50 °C and filtered. Thus, complex solutions extracted were crystallized by cooling at 4 °C. ICs crystals obtained from the filtrate portions were considered for percent yield calculation. ICs formed above three methods were denoted as follows PD- β -CD, ODA- β -CD, MDA- β -CD, BAPE- β -CD, BAPB- β -CD, and BAPP- β -CD. Among the ICs, BAPP- β -CD IC was precipitated during the reaction workup. This is possible because of the hydrophobic domination of the central two methyl groups of BAPP. However, crystals isolated from the filtrate portion of the BAPP- β -CD complex mixture were β -CD confirmed by ¹H NMR in D₂O. Percent yield was calculated by

introducing the integral ratio factor of anomeric protons to aromatic protons (Table 2). The molar feed ratio of host and guest was correlated with the integral ratio of anomeric protons to aromatic protons to calculate the stoichiometry of the ICs. Both ODA-β-CD and MDA-β-CD ICs obtained by three methods showed an integral ratio of 0.9, at a molar feed ratio of 1:1. In contrast, PD- β -CD showed an integral ratio of 0.9 corresponds to a molar feed ratio of 1/4:1. A small variation of integral ratio was observed between BAPE- β -CD ICs prepared in hot water and coprecipitation methods. This is due to the statistical distribution of β -CD into relatively large guest molecules to render the solubility of resultant ICs. Similar behavior was observed for BAPB- β -CD and BAPP- β -CD. The low percentage yield was observed at a host-guest molar ratio of 1:1 of BAPE- β -CD IC owing to full coverage of BAPE by the maximum amount of β -CD to solubilize in hot water. Notably, a mixture of ICs and excess β -CD was obtained by solid-state grinding between β-CD and BAPE or BAPB diamines at different grinding times (15, 30, 45, and 60 minutes), confirmed by the ROESY NMR analysis. In this case, the addition of a small amount of water and different grinding times were evaluated to overcome the issues of the slow diffusion problem of large guest molecules (BAPE, BAPB, and BAPP). In contrast, small PD molecules readily form IC in the solid-state grinding method.



Scheme 2. Synthesis scheme of ICs formation between aromatic diamines (guests) and β -CD (host) by mixing in hot water, co-precipitation, and solid-state grinding methods.

2.3.1 ICs formation by ${}^{1}H$, ${}^{13}C$ NMR assay in both D₂O and DMSO-d₆

¹H NMR is an essential tool to study the structure of CD ICs [28]. IC formation was evidenced by chemical shift changes of both aromatic protons and the cavity protons due to the ring current effect of the aromatic system [22]. The observed chemical shifts changes and broadening of CD peaks can give insight information of conformational changes of supramolecular assemblies. Typically, six different proton peaks were assigned for β -CD in D₂O such as H₁ doublet at 4.92 ppm, H_3 doublet of doublet at 3.81 ppm, H_6 multiplet at 3.72 ppm, H_5 multiplet at 3.70 ppm, H_2 doublet of doublet at 3.50 ppm, and H_4 doublet of doublet at 3.43 ppm respectively (Figure S2). Despite the low water solubility of the studied diamines, NMR measurement was carried out in D₂O to assign their proton peaks and to compare them with ICs. To do so, each diamine was suspended in D₂O and heated in the vial at 80 °C for 24 h while stirring magnetically. ODA, BAPE, and BAPB were syringe filtered to discard undissolved diamines and nmr measurement was carried out. Among the diamines, MDA, ODA, and PD spectrums were recorded successfully (Figure S2a–2c). In contrast, BAPE, BAPB, and BAPP diamines exhibited very low-intensity peaks covered by noise, which is due to the low solubility of those diamines in D_2O . Further, ¹H NMR of ODA- β -CD, MDA- β -CD, BAPE- β -CD, BAPB- β -CD, and PD- β -CD ICs were recorded in D_2O (Figure S2d–2y). Chemical shift and complex induced shift changes were tabulated in (Table 3), coverage ratio was calculated by rationing the integral values of anomeric protons of β-CD to aromatic protons of diamines (Table 2). ¹H NMR spectra (in D₂O) of MDA-β-CD prepared by three methods showed a significant up-field chemical shift of resonance of cavity protons i.e., H_3 and H_5 (Figure 3 and S2d–2g). Notably, the biggest up-field shift between H_3 and H_5 protons was observed for H_5 cavity protons located along the narrow rim, indicating shallow penetration of the guest molecules inside the cavity. Similarly, a significant up-field shift of methylene protons of MDA was observed in MDA- β -CD ICs with loss of intensity. The low intensity of methylene protons is probably due to suppression exerted by the cavity protons of β -CD. However, a mixture of IC and excess components obtained from molar feed ratio 3:1 (Host: guest), was lack of complete chemical shift changes due to the excess amount of β -CD. Also, ¹H NMR spectrum of MDA- β -CD IC was recorded in DMSO- d_{β} to assign all proton peaks including hydroxyl protons of β-CD (Figure S2h). Moreover, chemical shift changes were also observed by mixing MDA and β -CD in D₂O (Figure 3 (F)). The coverage ratio of MDA- β -CD ICs prepared by molar feed ratio MDA: β -CD (1:1 and 1:2.0) were 0.9 and 1.0, which indicated nearly 1:1 complex was formed (Table S1). In contrast, chemical shift changes of H₃ protons of ODA-β-CD ICs were found to be two times bigger than those found in MDA- β -CD ICs, indicating that the relatively large strain produced by ODA inside the β -CD cavity (Figure S2i–2m). The coverage ratio of ODA- β -CD ICs prepared by the molar feed ratio of ODA: β -CD (1:1 and 1:1.5) were 0.9

and 1.0, which indicated 1:1 complex. Notably, the coverage ratio of β -CD was drastically increased at a high β -CD molar feed ratio due to in situ crystallization of β -CD (Figure S1 (B) and S21). This behavior appeared at host-guest molar ratio 2:1 and other high ratio complexes of ODA- β -CD and MDA- β -CD due to a mixture of ICs and excess components. On the other hand, small chemical shift changes of the cavity protons of BAPE-β-CD and BAPB-β-CD ICs were observed due to the threading of both aliphatic spacer parts and aromatic parts on to β -CD cavity (Figure S2n–2s) [29, 30]. Additionally, coverage ratio calculation of BAPE-β-CD and BAPB-β-CD ICs reveals that 2, 3, and 4 β-CD are threaded onto BAPE and BAPB (Figure S20–2s). Further, a ¹H NMR assay of BAPE, a mixture of BAPE and β -CD, and BAPE- β -CD ICs was carried out (Figure S2t). Typically, BAPE showed low-intensity aromatic peaks due to low solubility. In contrast, an equivalent mixture of BAPE and β -CD showed a coverage ratio of 4.1, which is due to the high proportion of β -CD. However, BAPE- β -CD ICs also showed a coverage ratio of 3.6, which could be related to β -CD mixture of ICs and excess components. Such behavior was associated with in situ crystallization of β -CD (Figure S(1B)). Notably, aromatic proton peaks of PD-β-CD ICs prepared at a molar ratio 1:1 were very weak due to suppression exerted by the cavity protons (Figure S2u) [16]. Hence, coverage ratio calculation remains unpredictable. In contrast, aromatic proton peaks of PD- β -CD ICs prepared at a molar feed ratio 1:4 (β -CD :PD) were clearly observed and the coverage ratio was found 2.0, which indicated two PD threaded in one β -CD (Figure S2v–2x). On the other hand, NMR spectrums of BAPP- β -CD IC were recorded in DMSO- d_6 due to low solubility in D₂O. Three different proton peaks were assigned for aromatic protons at (7.12-6.58) ppm (Figure S2x–2z'). The Host-guest integral ratio of BAPP- β -CD IC prepared by mixing in hot water was found 1:1 complex, which is presumably due to 3D bend structure of BAPP. Such structural strain could limit multiple β -CD threading as well as low water solubility in water. In contrast, an integral ratio of ICs prepared by co-precipitation and solid-state grinding is 2:1. This unusual behavior was further assessed by Job's method in solution. Notably, there is a possibility of β -CD threading onto two central methyl groups.



Figure 3. ¹H NMR spectra (400.13 MHz, in D₂O, 298 K, internal standard DSS- d_6) of (A) β -CD (B) MDA and MDA- β -CD prepared by three methods such as (C) mixing in hot water (D) co-precipitation (E) solidstate grinding for 15 minutes (F) mixing equimolar amount of MDA and β -CD in D₂O (G) MDA- β -CD (Host:guest = 3:1 ratio complex) prepared by mixing in hot water.

Table 3. Complex induced chemical shift changes (CICS = d_{host} - $d_{complex}$) of the ICs prepared by three methods. H₃ and H₅ are cavity protons whereas H₁ and H₆ are outer protons. The negative sign indicates the downfield shift (deshielding).^a short form of three methods are used as follows, hot water (HW), co-precipitation (CP), and solid-state grinding (SG)

Community & mode of		Changes of o	chemical shift (β-Cl	D)
Compounds & method	H ₁	H_3	H_5	${ m H_6}$
ODA-β-CD (HW)	0.0079	0.1175	0.2594	0.0750
ODA-β-CD (CP)	-0.0076	0.1044	0.2432	0.0617
ODA-β-CD (SG)	0.0131	0.1213	0.2757	0.0799
MDA-β-CD (HW)	-0.0261	0.0566	0.2357	0.0678
MDA-β-CD (CP)	-0.0290	0.0495	0.2315	0.0645
MDA-β-CD (SG)	-0.0388	0.0367	0.2296	0.0495
BAPE-β-CD (HW)	0.0046	0.0473	0.0739	0.0294
BAPE-β-CD (CP)	0.0040	0.0296	0.0589	0.0723
BAPE-β-CD (SG)	-0.0010	0.0060	0.0035	0.0090
BAPB-β-CD (HW)	-0.0026	0.0517	0.0608	0.0218
BAPB-β-CD (CP)	0.0026	0.0356	0.0578	0.0207
BAPB-\beta-CD (SG)	-0.0040	0.0027	0.0054	-0.0042
PD-β-CD (HW)	-0.0041	0.0077	-0.0024	0.0268

PD-β-CD (CP)	0.0036	0.0284	0.0429	0.0124
PD-β-CD (SG)	-0.0046	0.0068	-0.0029	0.0254

On the other hands, significant downfield chemical shift of cavity carbons (C₃ and C₅) was observed for β -CD upon inclusion of aromatic diamines in ¹³C NMR (Figure S3–3m).

2.3.2 ICs formation by ¹H NMR titration study in D_2O

Further, ¹H NMR titration method was used to study the ICs formation between β -CD and some diamines (MDA, ODA, PD, and BAPE) (Figure 4 and S3–S3c). ¹H NMR titration of MDA by β -CD indicated an initial increase of chemical shift of H₅ protons at molar ratios of MDA/ β -CD at 0.94 followed by a decrease at 0.47, 0.31, 0.24, and 0.19 (Figure 4). A similar trend of chemical shift changes was observed in the ¹H NMR titration spectra of ODA/ β -CD and PD/ β -CD, (Figure 4 and S3). However, BAPE and β -CD titration spectra recorded at 25°C and 80 °C showed a well resolved up-field shift of methylene proton peaks (Figure S3b and S3c). Further, ¹H NMR titration graphs plotted based on chemical shift changes of β -CD protons indicated the formation of 1:1 complex between β -CD and some diamines such as MDA, ODA, PD, and BAPE (Figure 5, S3d, and S3e).



Figure 4. ¹H NMR titration spectra (400.13 MHz, D₂O, 298 K, internal standard DSS-d₆) of (A) β -CD recrystallized from water and the different molar ratio of guest and host (B) MDA: β -CD = 0.94, (C) 0.47, (D) 0.31, (E) 0.24, (F) 0.19.



Figure 5. ¹H NMR titration (400.13 MHz, D₂O, 298K for MDA- β -CD and 358K for ODA- β -CD) graphs of chemical shift changes of β -CD protons and aromatic protons at molar ratios of MDA: β -CD (A, B) = 0.19, 0.24, 0.31, 0.47, 0.94, and 1.98 and ODA: β -CD (C, D) = 0.17, 0.19, 0.24, 0.31, 0.47, 0.94, and 1.98

2.3.3 ICs formation by ¹³C NMR in DMSO-d₆

On the other hand, complex induced ¹³C NMR chemical shift changes were observed in the ICs (Figure 6). In the ¹³C NMR of ODA- β -CD and MDA- β -CD ICs, significant downfield chemical shifts of the cavity carbons (C3 and C5) were observed due to the threading of β -CD onto ODA and MDA (Figure S4–S4m). However, a significant up-field shift was observed for PD- β -CD ICs, which is indicating that the relative position of PD at the narrow rim (Figure 6). Also, it was reported that guest molecules such as benzoic acid having in-depth penetration in the CD cavity undergo shielding of ¹³C NMR peaks.[28] However, chemical shift changes of the cavity carbons were barely observed for the mixture of products obtained from BAPE, and BAPB with high β -CD content. (Figure S4).



Figure 6. ¹³C NMR spectra (100 MHz, D₂O, 298 K, internal standard DSS- d_6) of (A) β -CD recrystallized from water (B) ODA- β -CD (IgR = 0.9, HW), (C) MDA- β -CD (IgR = 0.9, HW), (D) PD- β -CD (IgR = 2.0, HW).

2.3.4 ¹H-¹H ROESY NMR analysis of ICs

Further, ¹H-¹H ROESY NMR spectroscopy was used to estimate the relative position of guest molecules inside the β -CD cavity of ICs. This experiment reveals the interactions between the CD cavity and the guest molecules. The representative ROESY spectrum (in D_2O) of MDA- β -CD prepared by mixing in hot water showed a strong correlation between the aromatic protons at 6.83 (H₀) and 6.66 (H_P) ppm and the β -CD cavity protons at 3.75 (H₃) and 3.47 (H₅) ppm, confirms the threading of MDA inside the β -CD cavity (Figure 7a). Apart from cavity protons, a strong correlation was observed between aromatic protons and H₆ protons linked to the narrow rim of the β -CD, which indicates the in-depth penetration of guest molecules inside the β -CD cavity. Similarly, MDA-β-CD and ODA-β-CD ICs prepared by co-precipitation and solid-state grinding methods also produced strong cross-peaks in the ¹H-¹H ROESY spectrums (Figure S5-S5f). In contrast, a small correlation was observed between aromatic protons at 6.81 (H_Q) and 6.46 (H_P) ppm and the β -CD cavity proton at 3.55 (H₅) ppm in ¹H-¹H ROESY spectrum (DMSO d_{6}) of MDA- β -CD ICs prepared in hot water, indicates the dethreading of guest molecule from the cavity in a polar solvent (Figure 7b). Additionally, a simple mixture of β -CD and some diamines (MDA, PD, BAPE, and BAPB) in D₂O exhibited correlation peaks in ¹H-¹H ROESY analysis. However, correlation peaks were not observed for a simple mixture of β-CD and ODA

or BAPP at 25 °C due to the low solubility and slow diffusion of those diamines in D₂O. On the other hand, strong interaction was observed between cavity protons and aromatic protons of various ratio complexes of BAPE-β-CD (2:1, 2.5:1, and 3:1) and BAPB-β-CD (2:1 and 3:1) (Figure S5g–S5j). Both diamines were found to be deeply penetrated the β-CD cavity. Notably, instead of two separate pairs of proton peaks, a coalesced peak associated with entire aromatic protons were observed for BAPE-β-CD ICs, which is presumably due to different IC conformations in D₂O (Figure S5h) [11,30]. In contrast, the intense cross peak was observed between aromatic protons of PD and H₅ cavity protons of β-CD, which reveals the relative position of PD at the narrow rim of the β-CD cavity (Figure 7c). NMR measurement of BAPP-β-CD was carried out in DMSO- d_6 due to the low solubility of this complex in D₂O. In the ROESY spectra, no correlation peak was observed owing to the dethreading of β-CD in a polar solvent (Figure S5n). Notably, PD-β-CD (1:1 molar feed ratio complex) showed less intense aromatic peaks in the ¹H NMR spectrum owing to the full coverage of PD by the β-CD cavity (Figure S2p) [16]. In contrast, PD-β-CD ICs (1:0.25 molar feed ratio complex) prepared by three methods showed correlation peaks between aromatic protons and the cavity protons.



Figure 7. ¹H-¹H ROESY NMR spectra of MDA- β -CD prepared by mixing in hot water (A, D₂O), (B, DMSO- d_6), PD- β -CD (C, D₂O) and BAPE- β -CD (D, D₂O).

2.3.5 Dynamic behavior studies of ICs by ${}^{1}H{}^{-1}H$ ROESY NMR in D₂O and DMSO-d₆

Dynamic behavior of ODA- β -CD IC was studied by the ¹H-¹H ROESY correlation studies by changing the solvent environment. Generally, host-guest equilibrium is more shifted toward the threaded state in D₂O. However, the sequential addition of organic polar aprotic solvent (DMSO- d_6) shifts the equilibrium to the dethreaded state confirmed by the disappearance of correlation peaks of aromatic protons and cavity protons of β -CD.



Figure 8. ¹H-¹H ROESY NMR spectra of ODA- β -CD prepared by mixing in hot water (A, in 0.4 mL D₂O), (B, in 0.2 mL DMSO- d_6), (C, in 0.4 mL DMSO- d_6) and (D, in 0.6 mL DMSO- d_6).

2.3.6 FTIR analysis of ICs

FTIR was used to study the ICs obtained by three different methods. In general, guest stabilization in the CD cavity causes different vibrational modes in the IR region [19]. Representative FTIR spectra of MDA-β-CD ICs were used to study the ICs (Figure 9). In the FTIR spectra, the OH stretching band was predominated over the NH stretching band at ~3413 cm⁻¹. Similarly, the intensities of the aromatic stretching band at ~1513 cm⁻¹ and CN stretching band at ~1272 cm⁻¹ were decreased in the ICs due to coverage of the aromatic diamines by the β-CD cavity. In addition, characteristic aromatic CH bending at ~801 cm⁻¹ and CN stretching band at ~1196 cm⁻¹ for ODA-β-CD ICs (1:1) prepared by three methods were well resolved (Figure S6). On the other hand, an extra band assigned for ether linkage (COC) at 1071 cm⁻¹and 1046 cm⁻¹ of BAPE and BAPB compounds was suppressed by β-CD in the ICs (Figure S6a–S6b). On the other hand, FTIR patterns of both PD-β-CD and BAPP-β-CD prepared by three methods were like ODA-β-CD ICs (Figure S6c–S6d). A distinguishable feature was observed between ODA-β-CD and MDA-β-CD ICs prepared in water and physical mixing of ODA and β-CD (Figure S6e). In this figure, amine stretching and OH stretching were overlapped with that aromatic CH bending at ~801 cm⁻¹ was not suppressed by the β-CD. To confirm the distribution of β-CDs and aromatic diamines in the isolated products, different portions of the two different ICs of ODA-β-CD (1:1) and MDA-β-CD (1:1) were subjected to FTIR assay (Figure S6f and S6g). No significant differences were observed in the fingerprint region.



Figure 9. FTIR spectra of (A) β -CD (B) MDA and MDA- β -CD prepared by three methods such as (C) mixing in hot water (D) co-precipitation (E) solid-state grinding for 15 minutes.

2.3.7 Powder X-ray diffraction analysis of ICs

The XRD diffraction pattern of β -CD comprises numerous crystalline peaks in 2 θ range 10°–30°, including two characteristic peaks at 10.8° and 12.7° due to cage-type structure (Figure 10) [7, 31]. All the aromatic diamines also showed characteristic crystalline peaks in the 2θ range 10° -30°. Notably, instead of numerous crystalline peaks, two types of broad peaks were observed for MDA- β -CD at $2\theta = 11.7^{\circ}$, 17.7° (in hot water), 11.3°, 17.6° (co-precipitation) and 11.4°, 17.6° (solid-state grinding), indicating that identical crystal structures (channel-type structures) of ICs were produced by three methods (Figure 10). Identical XRD diffraction patterns of MDA-β-CD ICs prepared by three methods were presumably due to similar crystallization procedures and drying conditions used to obtain solid ICs crystals. Similarly, ODA-β-CD ICs showed two types of diffraction peaks at $2\theta = 11.5^{\circ}$, 17.5° ; 11.7° , 18.2° , and 11.6° , 17.7° related to characteristic channel-type structure (Figure S7). In contrast, BAPE- β -CD and BAPB- β -CD ICs exhibited two characteristic peaks at 10.8° and 12.7° associated with a cage-type structure (Figure S7a and S7b). This is possibly due to different conformations of flexible diamines inside the β -CD cavity and the statistical distribution of β -CD onto a single strand of diamines. It was reported that the crystal structure of β -CD and 4-[2-(4-aminophenyl)ethyl]-benzenamine complex comprises dimeric stacking [29]. Also, an earlier report on α -CD-methyl orange (2:1) complex comprises four possible superposition structures [30]. On the other hand, PD- β -CD ICs prepared by mixing in hot water and in solid-state grinding were found to form channel-type structures, confirmed by characteristic peaks at 11.9°, 12.0°, 17.7°, and 18.8° (Figure S7c). In contrast, the cage-type structure was observed for PD-β-CD IC prepared by the co-precipitation method, which is possibly due to the cage-type arrangement of β -CD. Typical, channel-type peaks at around 11.1° and 17.7° were observed for BAPP-β-CD ICs prepared by hot water method and solid-state grinding method (Figure S7d). However, a different XRD pattern was observed for BAPP-β-CD ICs prepared by the co-precipitation method. Further, a cumulative XRD pattern was represented to distinguish between a physical mixture and solid ICs of β -CD with ODA and MDA (Figure S7e). In this figure physical mixture exhibited an overlapped diffraction pattern different from solid ICs. It is worth mentioning that solid crystals of all the ICs except BAPP- β -CD were obtained from the filtrate portion, which could reduce the emergence of unwanted peaks generated from insoluble portions i.e diamines. However, there is a possibility of the emergence of unthreaded β -CD peaks with ICs prepared by a high molar feed ratio.



Figure 10. XRD patterns of (A) β -CD (B) MDA and MDA- β -CD prepared by three methods such as (C) mixing in hot water (D) co-precipitation (E) solid-state grinding for 15 minutes.

2.3.8 Stoichiometric determination of host-guest ratio in solution

The continuous Variation Method (Job's plot method) is a practically useful method to study the complexation ratio of host and guest in solution [32]. In this research, Job's plot was used to determine the host-guest ratio of ICs in the solution. A sequential procedure is represented in figure S8. To do so, the total concentration of aromatic diamines and β -CD were kept constant and the molar concentration of both aromatic diamines and β -CD was changed. UV analysis was carried out for a series of complex mixtures containing mole fraction range 0.1 to 0.9 of each component. Stoichiometry of the ICs was determined by plotting the mole fraction of aromatic diamines versus absorbance difference graph. The largest changes in absorbance were observed for ODA/ β -CD, MDA/ β -CD, BAPE/ β -CD, and PD/ β -CD at mole fraction 0.5 indicating that 1:1 host-guest complexes were formed (Figure 11). However, a 1:1 complex was observed between BAPP and β -CD, which is presumably due to the 3D bend structure of BAPP that constrain the threading of multiple β -CD (Figure S7). In contrast, BAPB/ β -CD stoichiometry was found to be 1:1, indicating that one-mole β -CD was threaded onto one-mole BAPB (Figure

S8). Experimental conditions and UV spectrums were represented in the supporting information (Table S2 and Figure S8a–S8f).



Figure 11. Job's plot of MDA-β-CD, ODA-β-CD, BAPE-β-CD, and PD-β-CD.

2.3.9 Binding constant determination

The binding constant was calculated by the Benesi-Hildebrand equation (1 & 2) from the UV measurement data obtained from different molar ratio mixtures of host and guest remaining the total concentration of the mixture the same.

To measure the UV spectrums a β -CD stock solution was prepared with a concentration of 4.25 $\times 10^{-5}$ mol/l and MDA and ODA solutions with concentrations of 4.25 $\times 10^{-5}$ and 4.32 $\times 10^{-5}$ mol/l. Different molar ratio mixture of diamine and β -CD was prepared by mixing (0.5-4.5) ml of each of the components by keeping the total concentration the same. UV spectrums were recorded accordingly.

$$1/[A-A_o] = 1/[\Delta\varepsilon] + 1/K[\Delta\varepsilon][Diamine]_o[\beta-CD]_o....(1)$$
$$K = 1/slope[A-A_o]....(2)$$

Where $[A-A_o]$ is the absorbance difference before and after the addition of β -CD. $[\Delta \epsilon]$ is absorption co-efficient difference before and after the addition of β -CD. K is binding constant. [Diamine] $_o$ and $[\beta$ -CD] $_o$ are the initial concentration of diamine and β -CD. Binding constants were found based on 1:1 stoichiometry complex ODA and MDA with β -CD are 44.5 and 39.3 M⁻¹.



Figure 12. Binding constant determination of ODA- β -CD and MDA- β -CD by UV-spectrophotometric method.

2.3.10 Elemental analysis of ICs

Elemental analysis was used to confirm the compositions of each molecule and coverage ratios of the IC crystals. The presence of nitrogen indicated IC formation between β -CD and aromatic diamines. Note that a certain amount of water was embedded in the IC crystals owing to the outer hydrophilic surface of the CDs. Considering the number of CDs threaded onto the guest molecule and water, the theoretical elemental compositions were calculated and correlated with the experimental data (Table 4). From the experimental elemental compositions, the coverage ratio or the number of guests included in the host cavity was calculated. The PD- β -CD, ODA- β -CD, and MDA- β -CD crystals showed a 1:1 coverage ratio, consistent with the initial feed ratio. The BAPP- β -CD crystals showed a coverage ratio of 1:2, i.e., two β -CD molecules threaded onto one BAPP molecule, which also corresponded to the feed ratio. In contrast, BAPE- β -CD and BAPB- β -CD showed coverage ratios of 1:3 and 1:4, respectively, which differed from the initial feed ratios (1:1, BAPE: β -CD and 1:2, BAPB: β -CD). In this case, the amount of β -CD threaded onto BAPE or BAPB was maximized for solubilization in water. The host: guest integral ratios in the ¹H NMR spectra indicated similar coverage ratios (Figure S2g–S2i).

Table 4. Elemental composition, melting point, and percent weight loss results of ICs crystals. ^{*a*} Calculated from formulas including hydrated water. ^{*b*} Determined by elemental analysis. ^{*c*} Calculated from the experimental elemental composition. ^{*d*} Determined by DSC and ^{*e*} by TGA thermogram.

compound	Calculated elemental Experimental		Coverage	Coverage Melting point	
	Composition	elemental	ratio	$(^{\circ}\mathbf{C})^{d}$	TGA at 170–
	(C/H/N/O) ^a	composition	of ICs	40–300 °C	380 °C ^e
		(C/H/N/O) ^b	(β-CD:guest) ^c		
ODA-β-CD	46.7/2.0/ 6.4/45.0	46.6/2.0/6.4/45.0	1:1	105.9	~63 %
	$C_{54}H_{82}N_2O_{36.}3H_2O$				
MDA-β-CD	47.0/2.0/6.6/44.4	46.4/2.0/6.5/45.1	1:1	117.4	~69 %
	C55H84N2O354H2O				

BAPE-β-CD	41.9/0.7/6.7/50.7	40.6/1.0/6.4/52.0	3:1 (mix)	112.7	~64 %
	$C_{140}H_{226}N_2O_{127.}20H_2O$				
BAPB-β-CD	42.8/0.6/6.6/50.7	40.1/0.7/6.5/52.8	4.1 (mix)	105.8	~61 %
	$C_{184}H_{296}N_2O_{142.}10H_2O$				
PD-β-CD	45.1/2.2/6.5/46.3	46.4/2.0/6.5/45.1	1:1	122.8	~65 %
	$C_{48}H_{78}N_2O_{35.}2H_2O$				
BAPP-β-CD	48.0/1.6/6.9/43.6	48.2/1.7/5.9/44.2	1:1	114.0	~62 %
	$C_{69}H_{96}N_2O_{37.10}H_2O$				

2.3.11 Differential scanning calorimetric analysis (DSC) of ICs

DSC analysis is broadly used to study the various interactions of CDs ICs. ICs formation can be evidenced by the change in peak positions or evolution of new peaks. The melting behavior of the ICs was studied by DSC analysis. Typically, distinct sharp melting peaks are observed for aromatic diamines. In general, CDs crystals are in the hydrated state containing both cavity water and outer surface water [33]. CDs dissolution in water is an endothermic process. Therefore, a broad endothermic peak was observed at ~118.7 °C due to the dissolution of hydrated β-CD crystals (Figure 12). In the β -CD thermogram, a small endothermic peak was observed at ~216.0 °C, which could be associated with a small transformation [19,29]. Typically, β-CD threading onto diamines causes suppression of diamine peaks. No sharp melting peak was observed for MDA- β -CD ICs prepared by three methods. Instead of the second endothermic peak of β -CD, an exothermic peak was observed for MDA- β -CD ICs, which reveals the topological transformation by the inclusion of aromatic diamines [4,19]. A similar phenomenon was observed for ODA-β-CD ICs (Figure S9). Instead of, sharp melting peaks a broad peak at 112.6 °C difference from the β-CD peak was observed for BAPE-β-CD ICs prepared in hot water (Figure S9a). In contrast, a small sharp peak stemmed in BAPE- β -CD ICs prepared by co-precipitation. Notably, major DSC peaks observed for BAPE-\beta-CD and BAPB-\beta-CD ICs prepared by solidstate grinding methods were identical with β -CD, which reveals that the total composition was β -CD.



Figure 13. DSC spectra of (A) β -CD (B) MDA and MDA- β -CD prepared by three methods such as (C) mixing in hot water (D) co-precipitation (E) solid-state grinding for 15 minutes.

2.3.12 Thermo-gravimetric analysis (TGA) of ICs

TGA measurement was carried out to study the weight loss and decomposition phenomenon of ICs. The typical thermograms of the studied diamines, β -CD, and ICs were represented in (Figure 13, and S10–S10e). About ninety-nine percent weight loss was observed for all studied diamines up to temperature 500 °C except PD, in which total degradation occurred within 250 °C. In contrast, β -CD showed two weight-loss areas, ~11.0 % initial weight loss at ~109 °C was observed due to loss of cavity water and surface water followed by ~69.7 % weight loss at ~500 °C to furnish residual char. CD degradation involves the desorption of cavity and outer surface water above 100 °C followed by ring-opening (loss of glycosidic linkages), dehydroxylation (tar formation), and carbonization (char formation) at 200–500 °C [4, 33]. Total degradation of ICs of ODA- β -CD, MDA- β -CD, BAPE- β -CD, and BAPB- β -CD were recorded within the range 200–400 °C, leading to total weight losses of 60–70%, which is less than observed for the individual host and guest molecules, indicated that distribution of aromatic diamines and β -CD in the total

composition of the ICs. Notably, about 52–58 % weight loss was recorded for PD- β -CD ICs prepared by three methods. In this case total final degradation temperature of PD- β -CD ICs was larger than the PD degradation temperature. In contrast, up to ~70 % weight loss was observed for BAPP- β -CD ICs at 400 °C, which is less than the total weight loss of BAPP. Notably, the final degradation temperature of BAPP is higher than ICs prepared by three methods.



Figure 14. TGA thermograms of (A) β -CD (B) MDA and MDA- β -CD prepared by three methods such as (C) mixing in hot water (D) co-precipitation (E) solid-state grinding for 15 minutes.

2.3.13 Water desorption and char yield calculation

As we mentioned earlier in the figure 14 about water desorption from both cavity and outer surface, herein TGA analysis was used at a rate of the temperature of 5 °C to understand the desorption process and char yield before and after inclusion of guest into CD (Figure 15). The number of moles of water desorbed from the unit structures of β -CD and MDA- β -CD ICs was calculated based on weight loss percent in TGA thermogram by using the empirical formula given below. Further, charcoal yield was calculated at 400 °C to evaluate the charring behavior of the host and guest molecules. It was observed that 7.4–7.8 moles of water were desorbed from β -CD (bulk) and recrystallized within the range of 25–115 °C (Table 4). In contrast, a small amount of water

(4.4, 4.2, and 3.7 moles) was desorbed from the unit structure of MDA- β -CD ICs prepared by three methods. On the other hand, char yield was observed to increase in the MDA- β -CD ICs, which is possibly due to the high bond energy of double bonds of aromatic groups of diamines.



Figure 15. TGA thermograms of β -CD, β -CD recrystallize, and MDA- β -CD prepared by three methods (mixing in hot water, co-precipitation, and solid-state grinding). All the measurements were carried out in the range of (25–450 °C) and with ramping temperature of 5 Kmin⁻¹.

Number of moles (n) water in unit structure:

$$\frac{18n}{18n + 1135} = w \ (wt. \ loss \ \%)$$

Table 4. The number of moles of water desorbed from the unit structure during heat flow (25–115 $^{\circ}$ C) and charcoal yield calculated at 400 $^{\circ}$ C

Compound/ process	no. of moles water (n)	Char. Yield (%)
β-CD	7.4	16.0
β-CD Recrystalize	7.8	13.7
MDA-β-CD (HW)	4.4	31.2
MDA-β-CD (CP)	4.2	33.1
MDA-β-CD (SS)	3.7	33.1

2.3.14 Decomposition kinetics of ODA-β-CD IC

The thermal decomposition of IC is affected by the heating rate in TGA analysis. With the increase in heating rate melting decomposition point also increases of ICs [34]. Therefore, the

rate constant (*k*) of decomposition is also high. Thermal decomposition kinetics of ODA- β -CD IC was determined by Flynn-Wall-Ozawa method [35]. The activation energy (E), frequency factor (A), and dynamic compensation effects were calculated by using simple decomposition equations (1) and Flynn-Wall-Ozawa equations (2) and (3). To do so 6 to 7 runs of TGA measurement at each rate of temperature were carried out for one sample (Figure 16). Temperatures were tabulated for the same weight loss at different points of the TGA plot. A linear relation was observed for each rate by plotting the reciprocal of temperature (versus the reciprocal of lnln(1-a), indicating the first-order decomposition kinetics of ODA- β -CD IC (Figure 17 (A)). Similarly, a linear relation was observed by plotting the reciprocal of temperature versus log Φ for each rate based on the Ozawa equation (Figure 17 (B)). Further, apparent activation energy and frequency factor were calculated from the linear relation. It was observed that average activation energy is low, which in turn reveals the presence of Van der Waals force between β -CD and ODA in the IC.

Flynn-Wall-Ozawa equation:

$$\log \Phi = \log(-AE/Rf(a)) - 2.315 - 0.4567(E/RT).....(2)$$

Where $f(a) = \int da/(1-a)n$
$$\log \Phi = \log(-AE/R \ln(1-a)) - 2.315 - 0.4567(E/RT)....(3)$$



Figure 16. TGA thermograms were recorded at a heating rate of 5, 10, and 15 Kmin⁻¹ of ODA- β -CD IC prepared by mixing in hot method.



Figure 17. Decomposition kinetic studies by plotting (A) $\ln(1/1-a)$ versus 1/T and (B) $\log \Phi$ versus 1/T based on Ozawa theory.

2.4 Conclusion

In this research, a comparative study of ICs formation between β-CD and some aromatic diamines has been carried out by mixing in hot water, co-precipitation, and solid-state grinding to rationalize the most suitable method. Among three methods, ICs formation by mixing in hot water was found to be reliable as in this case co-solvent was avoided and a simple synthesis process was adopted. Solid-state grinding is also an effective method of β-CD-ICs formation of studied diamines. However, low yield and the mixture of IC and excess components are two issues for large guest molecules. In such cases, a combination between solid-state grinding and mixing in water synthesis could be further investigated. Thus, ICs obtained in water and solid-state grinding were crystallized by changing the saturation rate of the complex solution and then cooling at 4 °C. Based on overall spectroscopic assessment ICs formation was confirmed. Stoichiometry of the ICs was found 1:1 from Job's plot and ¹H NMR titration methods in solution. The binding constant of ODA-β-CD and MDA-β-CD ICs was determined by the spectrophotometric method. Thermal characteristics and structural relationships were determined by TGA analysis based on desorption of water, and char yield analysis. Further, decomposition kinetics of ODA-β-CD IC was studied by changing the rate of temperature. In many cases co-precipitation method is chosen preferentially as a synthesis process of ICs of sparingly soluble guests with CDs host prior to study in water or solid-state grinding methods. In such cases, ICs formation could be studied in water. It is worth noting that, the ICs we studied could be potentially studied for the preparation of the nitrogen-based thermosetting polymer. Further, ICs formation of ODA could be studied to purify ODA from a crude mixture in the industrial process.

2.5 References

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List of publications

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