

# Cyclodextrin Inclusion Complex Formation with Butylated Hydroxytoluene and Its Application in Polyethylene Film

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**ABSTRACT:** The phenolic antioxidant, butylated hydroxytoluene (BHT), is added during polymer processing to protect polymers from oxidative degradation. Because of its high-volatility, it is susceptible to loss through volatilization in high-temperature processing. Cyclodextrin (CD) inclusion complexation (IC) with volatile compounds can prevent losses of volatile compounds, because of volatilization. In this study, BHT was successfully included in  $\beta$ -CD and its complex was confirmed using Wide-Angle X-ray Diffraction (WAXD), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Nuclear Magnetic Resonance spectroscopy (NMR). Low-density polyethylene (LDPE) films with BHT itself and BHT- $\beta$ -CD-IC were produced on a pilot plant scale. After extrusion, it was found that 44 and 78% BHT was lost from the BHT- $\beta$ -CD-IC LDPE and BHT LDPE films, respectively. Hence, the complex proved to be more efficient in preventing loss of BHT, because of encapsulation of volatile BHT. In addition, microscopy studies indi-

cate that BHT- $\beta$ -CD-IC LDPE film shows small aggregates, uniformly distributed in the LDPE matrix over a large range. The BHT efficiency of the complex in the film was measured using DSC for determining the oxidation induction time. The oxidation induction time (OIT<sub>time</sub>) was 35 min for the BHT- $\beta$ -CD-IC LDPE film as compared with 16 min and 26 min values of LDPE and BHT LDPE films, respectively. Hence, the encapsulation of BHT in  $\beta$ -CD maximizes the efficiency and stability to thermal degradation for BHT- $\beta$ -CD-IC LDPE film. The viscoelastic behavior of the films was also studied using dynamic mechanical analysis. The results indicate increases in storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of the complex and a shift in the maxima of  $\tan \delta$  ( $E''/E'$ ) to lower temperature in the LDPE films processed with BHT,  $\beta$ -CD, and BHT- $\beta$ -CD-IC. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1184–1190, 2010

**Key words:** antioxidant; butylated hydroxytoluene; cyclodextrin inclusion complex; polyethylene film

## INTRODUCTION

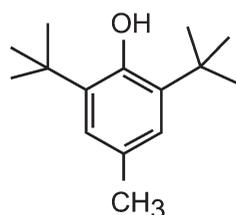
Nearly all polymeric resins require the addition of antioxidants to stabilize them during their processing, and to protect them throughout the service life of the finished product. Butylated hydroxytoluene (BHT) is one of the most widely used antioxidants in the world. BHT (Fig. 1) is a low-molecular weight, hindered-phenol antioxidant. Its physical properties are listed in Table I. The largest BHT usage worldwide is in plastics, such as polypropylene, low-density polyethylene (LDPE), high-density polyethylene (HDPE), etc. It comprises over 65% of the worldwide application of BHT. However, because of its high-volatility, it is susceptible to loss through volatilization in high-temperature applications.<sup>1–3</sup>

Cyclodextrins (CDs) are oligosaccharides produced by glucosyltransferase enzymatic degradation of amylase starch. CDs composed by  $\alpha$ -(1,4)-linked

D(+)-glucopyranose units and make up a family of three well-known cyclic members;  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CDs containing six, seven, and eight monosaccharide moieties, respectively. CDs are well-known for forming inclusion complexes (ICs) with various compounds (guests), because of the nature of their internal cavities. The CD inclusion complexation (IC) with guests can provide various advantages, such as preventing losses, because of volatilization, oxidation, thermal degradation, and storage. For example, the CD inclusion compound containing menthol guests has a much more prolonged shelf life, compared with pure menthol at room temperature. The inclusion compound of CD with guest vitamin A palmitate increases its half-life against photodegradation, whereas the pure vitamin degrades rapidly when exposed to light.<sup>4–12</sup>

As mentioned above, BHT is a rather small molecule, which is highly volatile. Therefore, it is susceptible to loss through volatilization during processing. Hence, by forming CD inclusion complex with BHT (BHT-CD-IC), volatilization of BHT can be greatly reduced during polymer processing and provide stability to polymers. However, there is little research

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**Figure 1** Chemical structure of BHT.

work focused on the formation of BHT-CD-ICs. In addition, so far, barely any research has been conducted in measuring the oxidative performance of CD inclusion complex with BHT except one patent.<sup>13</sup> Hence, there is a need to investigate the CD inclusion complex with BHT for the effectiveness as a stabilizer for polymers.

In this study, BHT was successfully included in  $\beta$ -CD, and its complex was confirmed using Wide-Angle X-ray Diffraction (WAXD), Differential Scanning Calorimetry (DSC), Thermogravimetric Analyzer (TGA), and Nuclear Magnetic Resonance (NMR) spectroscopy. Three sets of LDPE films with the addition of BHT- $\beta$ -CD-IC, BHT, and  $\beta$ -CD were produced on a pilot plant scale. Morphologies of the films were examined by microscopy. The oxidative performance of the films was measured using DSC for determining the oxidation induction time and temperature (OIT). In addition, the viscoelastic behavior of the films was studied using dynamic mechanical analysis (DMA).

## EXPERIMENTAL

### Materials

Synthetic phenolic antioxidant, BHT, and  $\beta$ -CD were obtained from Ciba Specialty Chemicals (Charlotte, NC) and Wacker Chemicals (Adrian, MI), respectively. Chloroform, dimethylformamide (DMF), and dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) were purchased from Sigma Chemical, and used as supplied. LDPE chips were obtained from Plastics Color Corporation, NC.

### Preparation of IC of BHT with $\beta$ -cyclodextrin (BHT- $\beta$ -CD-IC)

BHT- $\beta$ -CD-IC was prepared by a slow and dropwise addition of 0.1 g of BHT dissolved in chloroform (2 mL) to 11.0 mL of an aqueous solution with 1.00 g of  $\beta$ -CD held at 60°C. After stirring it continuously for 3 h at 60°C, the covered flask was removed from the hot plate, and the solution containing a white precipitate was left unperturbed overnight. The white precipitate was collected by filtration, and the

crystals were washed with distilled water and air-dried.

### Characterization of BHT- $\beta$ -CD-IC

#### Wide-angle X-ray diffraction (WAXD)

WAXD measurements were performed with a Siemens type F X-ray diffractometer using a Ni-filtered  $\text{CuK}\alpha$  radiation source ( $\lambda = 1.54 \text{ \AA}$ ). The diffraction intensities were measured every  $0.1^\circ$  from  $2\Theta = 10$  to  $30^\circ$  at scanning speed of  $2\Theta = 5^\circ/\text{min}$ . The supplied voltage and current were 30 kV and 20 mA, respectively.

#### Differential scanning calorimetry (DSC)

DSC experiments were carried out on 3–10 mg samples with a Perkin-Elmer DSC 7 under nitrogen purge gas. BHT and BHT- $\beta$ -CD-IC samples were heated at a heating rate of  $20^\circ\text{C}/\text{min}$  from 25– $100^\circ\text{C}$  and 25– $250^\circ\text{C}$ , respectively.

#### Thermogravimetric analyzer (TGA)

TGA scans of  $\beta$ -CD, BHT, and BHT- $\beta$ -CD-IC were obtained with Perkin-Elmer Pyris1 thermogravimetric analyzer. Samples weighing 8–10 mg were placed in an open platinum pan that was hung in the furnace. The weight percentage of remaining material in the pan was recorded during heating from 25 to  $600^\circ\text{C}$  at a heating rate of  $30^\circ\text{C}/\text{min}$ . Nitrogen was used as the purge gas.

#### Nuclear magnetic resonance spectroscopy (NMR)

$^1\text{H}$ -NMR solution spectra of BHT and BHT- $\beta$ -CD-IC dissolved in DMSO- $d_6$  were recorded on a Bruker Avance 300 MHz spectrometer. One dimensional  $^1\text{H}$  data sets, containing 16k data points and scans sufficient to obtain good S/N, were collected.

### Manufacture of LDPE film

Three sets of LDPE polymer chip (4536 g) with the BHT (9 g), BHT- $\beta$ -CD-IC (171 g of  $\beta$ -CD and 9 g of BHT), and  $\beta$ -CD (171 g) were compounded at

**TABLE I**  
Physical and Chemical Properties of BHT

Properties	BHT
Chemical name	3,5-di-tert-butyl-4-hydroxytoluene
Molecular formula	$\text{C}_{15}\text{H}_{24}\text{O}$
Molar mass	220.35 g/mol
Appearance	White powder
Solubility in water	Insoluble
Melting point	$70\text{--}73^\circ\text{C}$
Boiling point	$265^\circ\text{C}$

Plastics Color Corporation. The LDPE, BHT LDPE, BHT- $\beta$ -CD-IC LDPE, and  $\beta$ -CD LDPE films were prepared from the compounded chips by a single screw film casting extruder (Killion Film Extruders, Houston, Texas) at the Clemson Packaging Center. After film extrusion, the BHT contents of the two films, BHT LDPE film and BHT- $\beta$ -CD-IC LDPE film, were measured using Gas chromatography-Mass Spectrometry (GC-MS, Hewlett Packard).

### Characterization of the LDPE film

#### Morphology

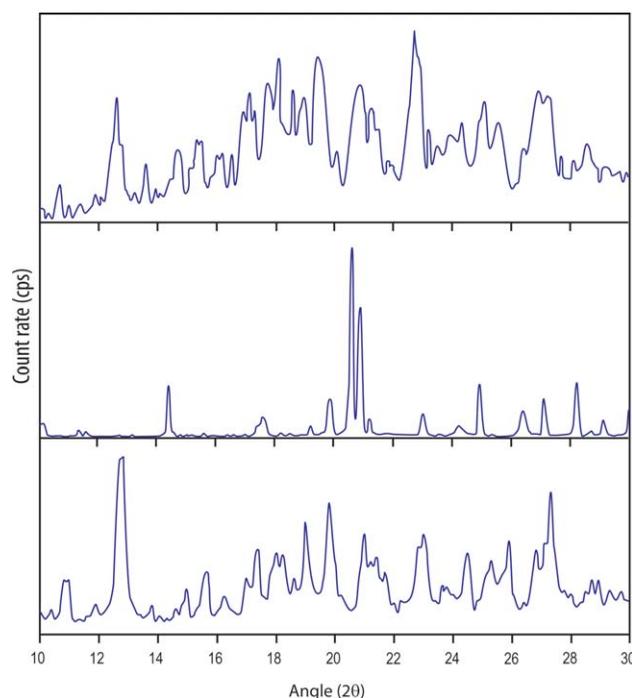
Microscopy studies were done on LDPE film,  $\beta$ -CD LDPE film, and  $\beta$ -CD-BHT-IC LDPE film using SMZ-1000 stereo microscope in transmission mode. The samples were placed on the glass slide of the microscope. The optical micrographs were captured using Nikon DS-F1 digital camera mounted on the instrument. The software version used was NIS Elements F 2.20.

#### Oxygen induction time (OIT<sub>time</sub>) and temperature (OIT<sub>temp</sub>) measurement

The OIT<sub>time</sub> testing was performed using a method based on ASTM D 3895-07 "Oxidative Induction time of Polyolefins by Differential Scanning Calorimetry". Initially the sample (5–6 mg) was held for 5 min at room temperature (25°C) under a flow of nitrogen gas (55 cc/min). After reaching 190°C, the sample was held there for 5 min, after which the gas was switched from nitrogen to oxygen (60 cc/min). This changeover point to oxygen flow is considered the zero time of the experiment. Then, isothermal operation was continued until the maximum exotherm was reached to analyze complete sample. In the case of oxygen induction temperature measurement, 5–6 mg sample was heated up continuously from room temperature (25°C) until the oxidation of the material was evidenced as an exothermic peak under pure oxygen atmosphere (60 cc/min) at the heating rate of 10°C/min.

#### Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of the films were studied using a dynamic mechanical analyzer, model Q 800 (Texas Instrument). The storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) were obtained in a tension film multifrequency controlled stress configuration suited for semicrystalline thermoplastic polymer samples. These properties were measured at a frequency of 1 Hz and in the temperature range of -40°C–110°C. The heating rate was 5°C/min. The specimens tested were 30.28 × 6.25 × 0.11 mm (length, width, thickness).



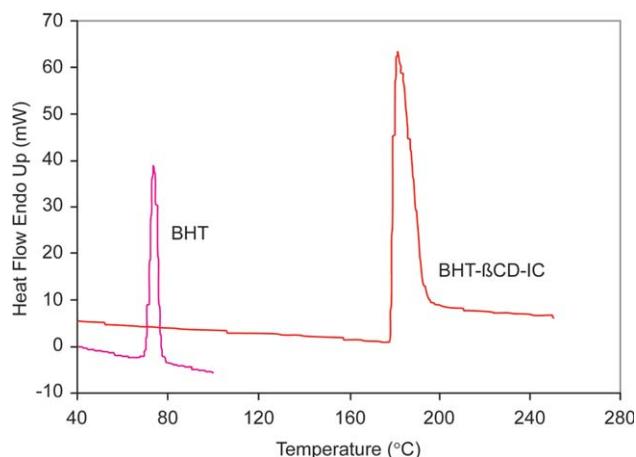
**Figure 2** X-ray diffraction patterns of  $\beta$ -CD (bottom), BHT (middle), and BHT- $\beta$ -CD-IC (top). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

## RESULTS AND DISCUSSION

### Characterization of BHT- $\beta$ -CD-IC

The X-ray diffractogram of the inclusion complex was primarily used to verify the successful inclusion of the BHT guest. The most intense and characteristic for the cage structure of  $\beta$ -CD was in the position of  $2\theta = 12.8^\circ$  and this peak also appears in BHT- $\beta$ -CD-IC shown in Figure 2. Hence, no change was made in the cage structure of  $\beta$ -CD after formation of the inclusion complex. However, the most intense peaks in the diffraction patterns of the inclusion complex and BHT are observed at  $2\theta = 22.7$  and  $20.6^\circ$ , respectively. This indicates the formation of the inclusion complex between BHT and  $\beta$ -CD, since no prominent peak from BHT is observed in the complex.

The DSC technique was used to determine whether the inclusion compounds obtained contained uncomplexed free BHT guest molecules. When BHT is complexed, it is surrounded by the CD molecules preventing interactions with other BHT molecules. Therefore, BHT in the complex is unable to crystallize. As shown in Figure 3, the absence of BHT melting peak at 70°C in the heating scan of the inclusion complex indicates that the formation of the CD complex without free uncomplexed BHT. In addition, an endothermic peak in the heating scan of BHT- $\beta$ -CD-IC appears at about 182°C, which

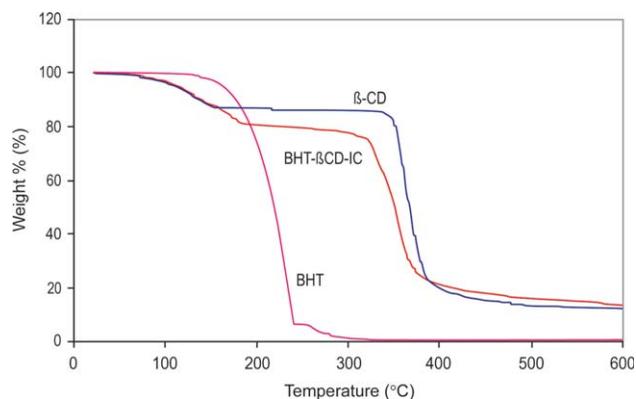


**Figure 3** DSC scans of BHT and BHT- $\beta$ -CD-IC. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

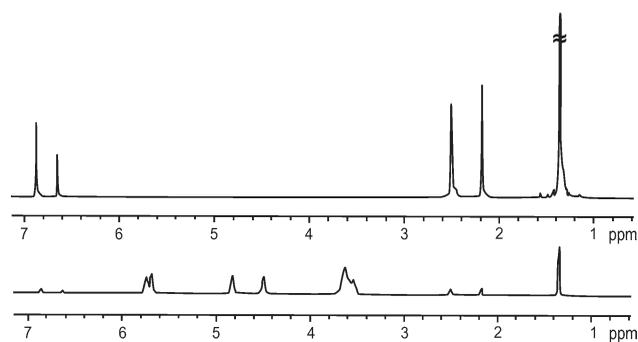
indicates the dehydration of water molecule in the  $\beta$ -CD molecule.

Figure 4 shows the thermal stability and decomposition behavior of  $\beta$ -CD, BHT, and BHT- $\beta$ -CD-IC. The CD complex has higher decomposition temperature as compared with pure BHT. The decomposition temperature of BHT- $\beta$ -CD-IC is also consistent with  $\beta$ -CD sample. Hence, formation of inclusion complex prevents loss of BHT and improves the thermal stability of BHT. Furthermore, BHT- $\beta$ -CD-IC shows a heating profile similar to  $\beta$ -CD, where the whole process takes place in three stages, namely in first stage removal of water, second major weight loss because of the chemical degradation, and finally degradation of the residue.

NMR provides an additional means to verify complex formation. Figure 5 shows  $^1\text{H-NMR}$  spectra of BHT and BHT- $\beta$ -CD-IC. The proton peaks of BHT and BHT- $\beta$ -CD-IC at about 2.5 ppm were identified as DMSO- $d_6$ . The peak corresponding to side chain 18 methyl protons of BHT was identified at about



**Figure 4** TGA scans of  $\beta$ -CD, BHT, and BHT- $\beta$ -CD-IC. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



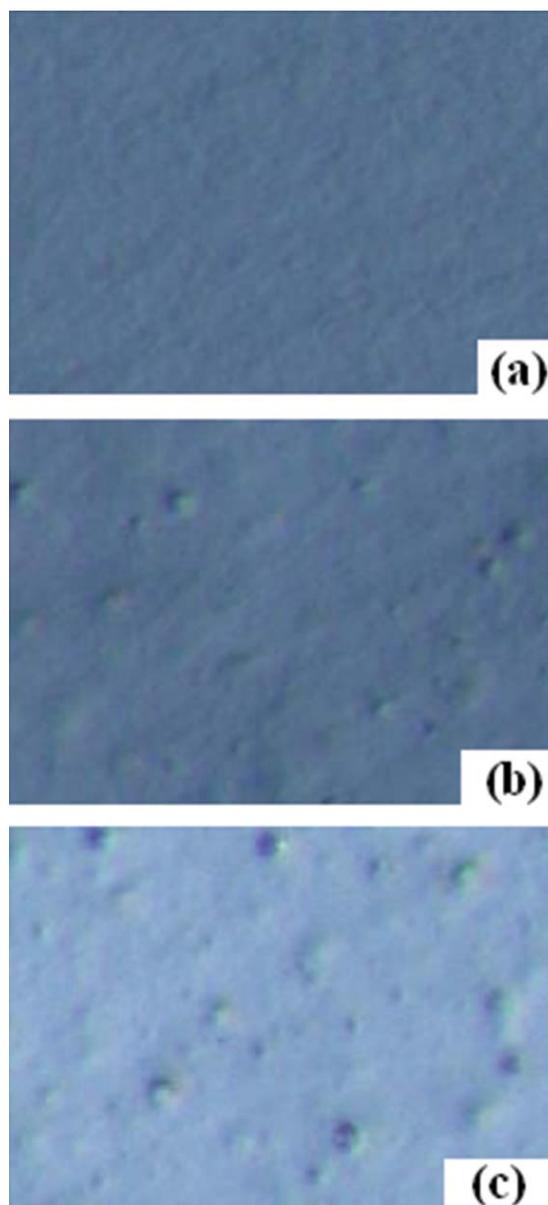
**Figure 5**  $^1\text{H-NMR}$  spectra of BHT (top) and  $\beta$ -CD-BHT-IC (bottom).

1.35 ppm. The peaks of BHT at about 2.2 ppm, 6.65 ppm, and 6.85 ppm were because of three protons of methyl group, protons of the phenyl group, and a proton present in the  $-\text{OH}$  group, respectively. The peaks at about 4.82, 5.71, 5.67, 4.45, 3.63, and 3.54 ppm because of H1, H2, H3, H4, H5, and H6 of the  $\beta$ -CD in the complex were confirmed, respectively.<sup>14</sup> New proton resonances in the inclusion complex spectra at about 6.65 and 6.85 ppm are contributed by the phenyl ring and  $-\text{OH}$  group of the BHT, respectively. In addition, several peaks in the 1.35 and 2.2 ppm are contributed by methyl and side chain methyl groups. Therefore,  $^1\text{H-NMR}$  confirms the presence of BHT in the BHT- $\beta$ -CD-IC sample.

#### Characterization of the LDPE films

The BHT LDPE and BHT- $\beta$ -CD-IC LDPE films were manufactured with  $\sim 3968 \mu\text{g}$  of BHT/2 g of the film initially. After the film extrusion, Gas chromatography-Mass Spectrometry analysis indicates that the BHT contents of the BHT- $\beta$ -CD-IC LDPE film and BHT LDPE film were  $858 \mu\text{g}/2 \text{ g}$  and  $2235 \mu\text{g}/2 \text{ g}$  of the films, respectively. Therefore, there were about 78% and 44% losses of BHT from the extruded BHT LDPE and BHT- $\beta$ -CD-IC LDPE films, respectively. Hence, the CD inclusion complex (BHT- $\beta$ -CD-IC) LDPE film proved to be more efficient in preventing loss of BHT from the extrusion.

Figure 6 shows the microscopic photos of LDPE,  $\beta$ -CD LDPE and BHT- $\beta$ -CD-IC LDPE films. LDPE film is very clear and does not show any granule aggregation. This leads to conclusion that during extrusion the LDPE, pellets were homogeneously mixed with each other. However, in  $\beta$ -CD LDPE film, very small amount of granular formation is seen more or less in the form of aggregates, which are uniformly distributed in LDPE matrix. This may be due to the fact that LDPE is hydrophobic whereas  $\beta$ -CD is hydrophilic, so this causes phase separation



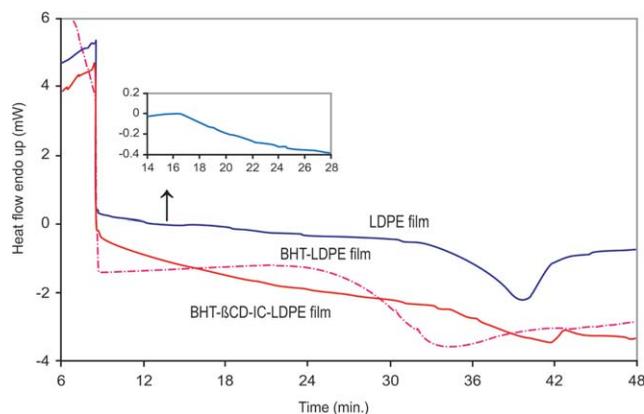
**Figure 6** Microscopic photographs of the films extruded from (a) virgin LDPE, (b) LDPE film with 2%  $\beta$ -CD, and (c) BHT- $\beta$ -CD-IC LDPE film (magnification 80 $\times$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

in the blends leading to small aggregates formation. It is reported that a lubricant, paraffin oil, was used to avoid the aggregation of the  $\beta$ -CD in the mix of  $\beta$ -CD powder and the LDPE granules. However, it was found in an aggregated state, although  $\beta$ -CD is more or less evenly distributed within the film.<sup>15</sup> Thus, as the amount of  $\beta$ -CD increases in the PE matrix, the  $\beta$ -CD aggregates become bigger in size leading to nonhomogeneity. However, the micrograph of BHT- $\beta$ -CD-IC LDPE film shows that it has small aggregates uniformly distributed in the LDPE matrix over a large range similar to  $\beta$ -CD-LDPE film. It is reported that the CD complexation results in more

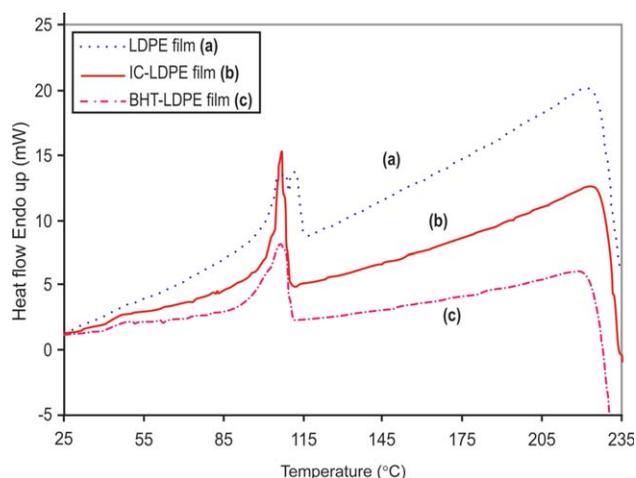
homogeneous distribution of the active component in the polymer matrix.<sup>16</sup>

The oxidative performance of CD inclusion complex with BHT in the film was measured using DSC. As shown in Figure 7, the oxidation induction time ( $OIT_{time}$ ) values of LDPE film, BHT LDPE film, and BHT- $\beta$ -CD-IC LDPE film were about 16, 26, and 35 min, respectively. The highest induction time was observed for BHT- $\beta$ -CD-IC LDPE film as compared with LDPE and BHT LDPE films. The thermal degradation of the LDPE film starts earlier than the other two films. This means that BHT- $\beta$ -CD-IC LDPE film was most resistant to oxidative degradation as compared with commercially available antioxidant BHT. Therefore, encapsulation of BHT in CD prevents its volatilization. Hence, it indicates that on addition of CD inclusion complex with BHT during melt processing of LDPE films can substantially increase the stability of polymer under thermal degradation. In the case of oxidation induction temperature ( $OIT_{temp}$ ), a sharp endotherm was observed for all three films (LDPE, BHT LDPE, and BHT- $\beta$ -CD-IC LDPE) in the range of 106–109 $^{\circ}$ C in Figure 8, which is attributed to the melting peak of LDPE.<sup>17</sup> The  $T_{onset}$  values of the oxidation, where the exothermic transition causes a shift in the baseline for the LDPE, BHT-LDPE, and BHT- $\beta$ -CD-IC LDPE films, are 223, 222, and 228 $^{\circ}$ C, respectively. The BHT- $\beta$ -CD-IC LDPE film shows highest value of  $OIT_{temperature}$ , although there was only a slight difference as compared with BHT LDPE and LDPE films. Therefore, our results are in agreement that dynamic OIT method is less sensitive as compared to static OIT method.<sup>18</sup>

The viscoelastic behavior of the films was also studied using DMA. Figure 9 shows that, LDPE film has the lowest storage modulus value. However, addition of BHT,  $\beta$ -CD, and BHT- $\beta$ -CD-IC to virgin



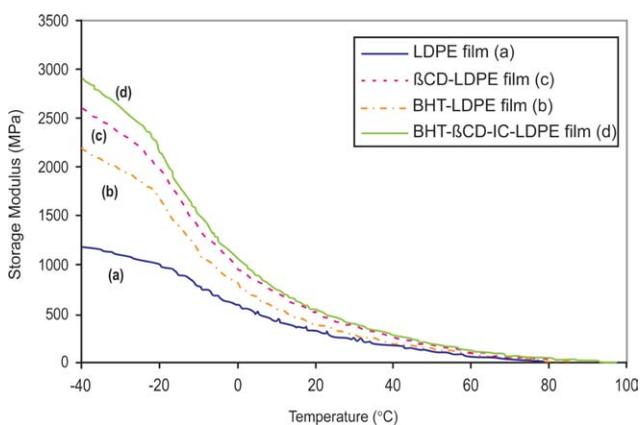
**Figure 7** DSC scans of (a) LDPE film, (b) BHT LDPE film, and (c) BHT- $\beta$ -CD-IC LDPE film held at 190 $^{\circ}$ C in isothermal condition. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



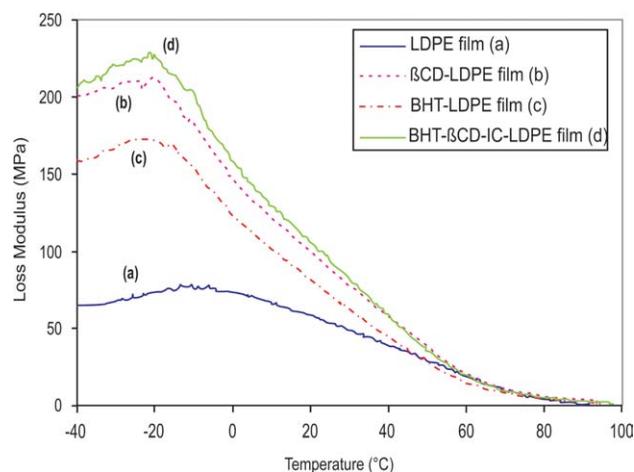
**Figure 8** DSC scans of (a) LDPE film, (b) BHT- $\beta$ -CD-IC LDPE film, and (c) BHT LDPE film under pure oxygen atmosphere at heating rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

LDPE film increased the storage modulus in increasing order of magnitude. Storage modulus is related to the elastic component of polymer. Hence, higher storage modulus values represent higher rigidity. When comparing between  $\beta$ -CD LDPE and BHT LDPE films, the former has higher storage modulus. This may be due to the fact that both BHT and LDPE are hydrophobic in nature, which causes this blend to mix well imparting chain mobility. However,  $\beta$ -CD exterior is hydrophilic and so this causes blends to become incompatible, hence reducing its chain mobility. Also, it can be assumed that  $\beta$ -CD simulates starch by acting as filler and the storage modulus value usually increases due to stiffening effect of granules.<sup>17</sup>

Loss modulus ( $E''$ ) refers to loss of heat, because of viscous component of the material. Lower  $E''$  values mean higher elastic recoveries. Hence, LDPE

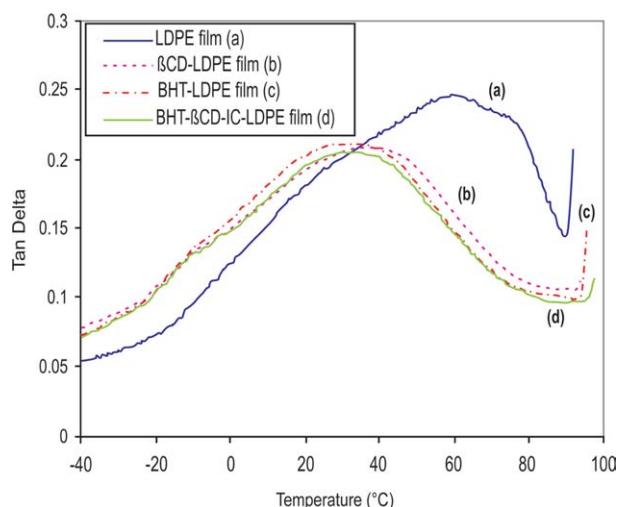


**Figure 9** Storage modulus plot as a function of temperature for the LDPE films. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 10** DMA curves of loss modulus vs temperature for the LDPE films. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

film has the lowest  $E''$  value followed by the addition of BHT,  $\beta$ -CD, and BHT- $\beta$ -CD-IC to LDPE films as shown in Figure 10. In general, the rapid rise in the loss modulus curve shows an increase in the irreversible structural mobility of polymer causing mobility along the larger parts of individual polymer chains.<sup>19</sup> It is also known that the  $E''$  increases as crystallinity decreases.<sup>20</sup> The crystallinity of these films determined by DSC was found to be 49, 46, 40, and 37% for LDPE, BHT LDPE,  $\beta$ -CD LDPE, and BHT- $\beta$ -CD-IC LDPE films, respectively. The LDPE film shows a broad transition between -20 to 0°C.<sup>21</sup> However, the LDPE melting transition in films decreases in temperature with the addition of BHT,  $\beta$ -CD, and BHT- $\beta$ -CD-IC into the LDPE matrix.



**Figure 11** DMA curves of tan  $\delta$  vs temperature for the LDPE films. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Tan  $\delta$  is the ratio of  $E''/E'$ , and it can be considered as an index of viscoelasticity. The primary transition referred to as the glass transition ( $T_g$ ), is generally attributed to increased mobility of main polymeric chains.<sup>22</sup> However, the glass transition of polyethylene is in the range of  $-100$  to  $-125^\circ\text{C}$ , which is an unusual case.<sup>23</sup> In Figure 11, another transition of LDPE film lies in the range of  $50$ – $70^\circ\text{C}$  as observed by Jagannath et al.<sup>24</sup> The addition of BHT,  $\beta\text{CD}$ , and BHT- $\beta\text{CD}$ -IC causes this transition to decrease and the curves shift to lower temperatures along with the broadening of peaks over a wider temperature range.

### CONCLUSIONS

The  $\beta$ -cyclodextrin inclusion complex with the phenolic antioxidant BHT was successfully formed and characterized using DSC, TGA, WAXD, and  $^1\text{H-NMR}$ . We extruded LDPE films with BHT itself and BHT- $\beta\text{CD}$ -IC on a pilot scale. After extrusion, the amount of BHT in the BHT LDPE film and BHT- $\beta\text{CD}$ -IC LDPE film was determined using GC-MS. The results show that 44% BHT was lost from BHT- $\beta\text{CD}$ -IC LDPE film, whereas 78% BHT was lost from the BHT LDPE film. Hence, the complex proved to be more efficient in preventing loss of BHT, because of encapsulation of volatile BHT guest. In addition, microscopy indicates that BHT- $\beta\text{CD}$ -IC LDPE film shows small aggregates uniformly distributed in the LDPE matrix over a large range.

The BHT antioxidant efficiency of the complex in the films was investigated using oxidation induction time (OIT<sub>time</sub>) method. The OIT<sub>time</sub> was 35 min for the BHT- $\beta\text{CD}$ -IC LDPE film as compared with a 26 min value for BHT LDPE films. It indicates that addition of the complex during extrusion can substantially increase the resistance toward oxidative degradation of the film. The viscoelastic behavior results of the films obtained from DMA study indicate increases in storage modulus and loss modulus and shift in the maxima of tan  $\delta$  to lower temperature in the LDPE films processed with BHT,  $\beta\text{CD}$ , and BHT- $\beta\text{CD}$ -IC.

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