Thermochimica Acta 510 (2010) 61–67

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Functionalization of HDPE with aminoester and hydroxyester by thermolysis method—An FTIR-RI approach

V. Parthasarathi[a], B. Sundaresan[a], V. Dhanalakshmi[b], R. Anbarasan[c,*]

[a] *Department of Physics, Ayya Nadar Janaki Ammal College, Sivakasi 626124, Tamil Nadu, India*
[b] *Department of Polymer Technology, KCET, Virudhunagar 626 01, Tamil Nadu, India*
[c] *Department of Mechanical Engineering, MEMS Thermal Control Lab, National Taiwan University, Taipei 10617, Taiwan, ROC*

ARTICLE INFO

Article history:
Received 22 December 2009
Received in revised form 21 June 2010
Accepted 23 June 2010
Available online 30 June 2010

Keywords:
HDPE
Esters
FTIR-RI
Kinetics
TGA
DSC

ABSTRACT

High density poly(ethylene) (HDPE) is functionalized with two different esters namely, amino ester and hydroxyl ester in an inert atmosphere at 160 °C under different experimental conditions by thermolysis method. The order of functionalization and olefin formation reactions are determined through FTIR spectroscopy. The energy of activation of different chemical reactions also determined from FTIR-RI method. Thermo gravimetric analysis and differential scanning calorimetric methods are used to access the thermal properties of the functionalized HDPE. Plausible reaction mechanism is proposed here to explain the experimental results obtained.

1. Introduction

In the recent years, polyolefin play a vital role in human life. Many industries have been involved in the manufacture of polyolefin due to its wide applications. Every year consumption of polyolefin has been increased all over the world. Simultaneously, problems associated with polyolefins increased due to its non-biodegradable nature. This is due to the absence of polar or hydrolysable group on the backbone of polyolefin. This problem can be outwitted by the surface functionalization reaction. It means that introduction of a functional group onto the backbone of polyolefin. Surface functionalization reaction is carried out by two methods namely, solid state and solution state method. Among these two methods, solid state method is an environmental green method due to the non-use of toxic and hazardous solvents. The present investigation aims to synthesize an environmental green polymer. Hence, we preferred the solid state surface modification reaction (i.e.) via thermolysis reaction. Among the polyolefins, one of the most important polymers is polyethylene (PE) which has a unique status due to its excellent household and industrial applications. Such a value added PE has been functionalized with different functionalities. For example, Semsarzadeh and Poursorkhabi [1] reported about the non-isothermal degradation kinetics of amide grafted HDPE. Surface modification of PE by heparin was reported for the improvement of antithrombogenicity [2]. Soy-protein grafted PE was synthesized and its bio-degradation behaviour by soil-burial method was studied [3]. Free radical grafting of glycidyl methacrylate onto HDPE was reported by Saeb and Garmabi [4]. Silane functionalized HDPE report is also available in the literature [5]. HDPE was grafted with hydroxyl [6], diethylmaleate [7], diamine [8], maleic anhydride [9] and multi functional [10] compounds. By thorough literature survey, we could not find any report based on the aminoester and hydroxyester functionalized HDPE in the presence of dicumyl peroxide as a free radical initiator.

After the surface melt grafting reaction, the amount of ester grafting can be quantitatively determined by chemical and analytical methods. The chemical method consumes larger quantity of toxic and hazardous solvents at higher temperature and not economically cheaper one. The analytical method particularly FTIR spectroscopy method is an in-expensive and eco-friendly method with more accurate results. FTIR spectrometer is a useful tool for various science and engineering fields, because of its low noise to signal ratio, easy and inexpensive one. FTIR spectroscopy is used for both the qualitative [11–15] and quantitative [16–30] applications. By thorough literature survey, we could not find any report based on the FTIR-RI study for the AB and HB functionalized HDPE. Hence, in the present investigation we took this job as a challenge and carried out the same successfully for the first time. The novelty of the present investigation is the surface grafting and

---

* Corresponding author. Tel.: +886 2 3366 4945; fax: +886 2 2363 1755.
E-mail address: anbu_may3@yahoo.co.in (R. Anbarasan).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.06.023

% ester grafting onto HDPE was determined by environmentally green method. Moreover, determination of olefin formation by FTIR-RI is a new and useful method. By the way of surface melt functionalization reaction the HDPE becomes an environmentally green polymer because of presence of functional group on its backbone.

2. Experiments

2.1. Materials

High density poly(ethylene) (HDPE) was purchased from Ottokemi, India. In order to remove the antioxidant present in the HDPE sample, it was purified prior to thermolysis reaction. Dicumyl peroxide (DCP, Ottokemi), 1,2-dichloro benzene (Loba Chemi, India), p-amino ethyl benzoate (AB, CDH, India) and p-hydroxy ethyl benzoate (HB, Ottochemi), dichloromethane (Merck, India), acetone (Paxmy, India) and toluene (Loba Chemi) were used as received.

2.2. Purification of HDPE

Five g of HDPE pellet sample was dissolved in 100 mL of toluene solvent at 130 °C for 3 h in order to remove antioxidants added during its long storage process. During the dissolution process the toluene solvent was boiled and evaporated. In order to avoid the loss of solvent molecules, the condenser unit was circulated with the ice-cold water. Once all the HDPE powder samples were dissolved in toluene, then cooled it and 800 mL of acetone was added to precipitate the HDPE. The content was filtered and dried at 60 °C for 24 h under vacuum. The dissolution and precipitation process were repeated for 3 times to further purify the HDPE. Finally, the dried samples were weighed and stored in a zipper bag.

2.3. Methodology

Surface melt graft functionalization of HDPE with AB and HB were done through thermolysis reaction, an environmental green method. The procedure in brief: previously purified HDPE (2.0 g) was taken in a 25 mL round-bottom flask and a calculated quantity of ester and equal quantity of DCP were taken in a solution of 6 mL of dichloromethane (9 mL)/cyclohexane (1 mL) mixture. The contents were mixed for 2.5 h at room temperature. After being mixed, the solvents were removed with the help of rotary evaporator under reduced pressure until a constant mass was obtained. The polymer/peroxide/ester mixture thus obtained was placed in a Test tube reactor. The reactor was closed and degassed by the injection of sulphur free nitrogen gas for 30 min and then sealed. The reactor was heated in an oil bath at 160 °C for 2.5 h without any stirring. Once the reactants melted the reaction started and led to various processes, particularly surface graft functionalization, alkenes formation and cross-linking reactions. After the surface grafting reaction, the reactor was removed from the oil bath, cooled and the sample was cut into small pieces. These small pieces of samples were taken in a round-bottom flask fitted with a condenser and charged with 100 mL of dichlorobenzene at 130 °C for 3 h under the circulation of ice-cold water. During this dissolution process, the non-cross linked products were dissolved in the medium whereas the cross-linked products were insoluble in the medium. 500 mL of acetone was added to precipitate the soluble and functionalized HDPE. The ester functionalized samples were dried under vacuum at 60 °C over night and the dried samples were weighed and stored in a zipper bag.

2.4. Characterizations

FTIR spectra were recorded using 8400 S Shimadzu FTIR spectrometer, Japan, by KBr pelletization method from 400 to 4000 cm^{-1}. 3 mg of ester functionalized HDPE powder sample was accurately weighed and grinded with 200 mg of spectral grade KBr. After thorough mixing with the help of pestle, the contents were made into a pellet form by applying 7 tons of pressure. Thus obtained pellet was subjected to FTIR quantitative analysis. In order to avoid error while recording FTIR spectrum, the corrected peak area was considered. To cross check the corrected peak area values, the FTIR spectrum was recorded for the same sample disc in different parts. After proper base line correction with the aid of FTIR software, again one can get the same corrected peak area values. FTIR spectrum was recorded for three times for the same sample disc, one can get the same and repeated corrected peak area values within 1.1% error limit on each measurement. In analytical chemistry up to 2% error limit is allowed and hence it will not affect the present investigation. The FTIR spectrum was recorded without predicting the lower and upper limits of peak, because the software itself predicted exactly the lower and upper limits to nullify the errors. In such a way the errors were nullified. Further one can cross check the efficiency of FTIR software by manually predicting the lower and upper limits and the corrected peak area was determined. In this case one can get the same corrected peak area value as reported previously (without predicting the lower and upper peak limits). For the quantitative determination of % ester grafting, the following corrected areas of the peaks, which were assigned at 1730 (C=O form), 1604 (C=C form) and 730 (C–H out of plane bending vibration) cm^{-1} were determined and the relative intensity (RI) was calculated as follows:

$$\text{RI of ester carbonyl} = \frac{A_{1730}}{A_{730}}$$

$$\text{RI of C=C double bond} = \frac{A_{1604}}{A_{730}}$$

$$\%\text{Ester grafting} = \frac{\mathrm{RI}_{[\mathrm{C=O/CH}]} \times W}{C \times 1.52} \times 100$$

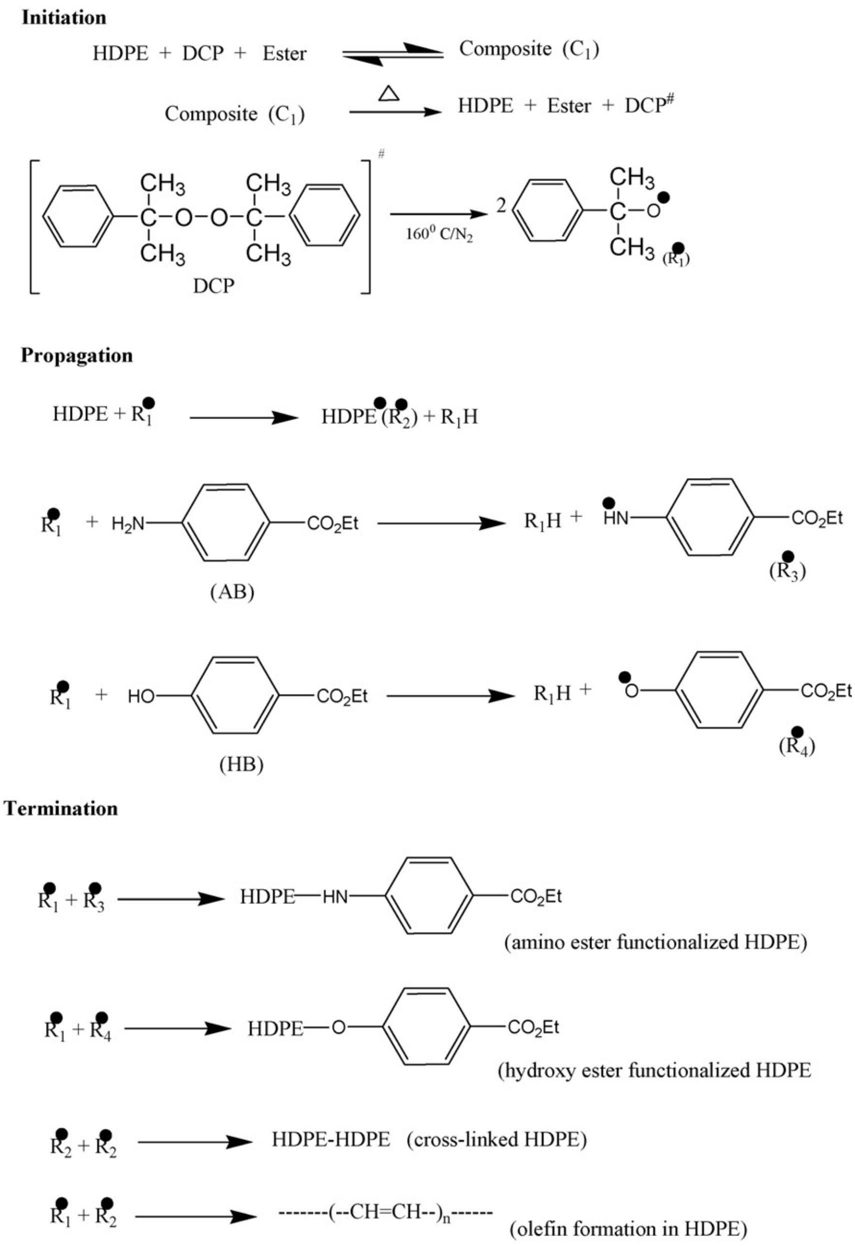
$$\%\text{C=C formation} = \frac{\mathrm{RI}_{[\mathrm{C=C/C-H}]} \times W}{C \times 0.35} \times 100$$

where W is the weight of non-cross linked polymer, C is the % weight of peroxide and 1.52 and 0.35 are calibration co-efficient taken from our earlier publication [28]. The reactions are mentioned in Scheme 1. DSC was recorded for the samples by using SDT 2960 simultaneous TGA and DSC, TA instruments under nitrogen atmosphere at the heating rate of 10 °C/min. The TGA analysis was performed under air purge and at the heating rate of 10 °C/min by using the SDT 2960 simultaneous TGA and DSC, TA instrument. The % cross-linking was determined by using the following formula:

$$\%\text{cross-linking} = \frac{(\text{weight of polymer taken for functionalization}) - (\text{weight of non-cross linked polymer obtained after functionalization})}{\text{weight of polymer taken for functionalization}} \times 100$$

3. Results and discussions

For the functionalization of HDPE, two types of esters such as AB and HB were used. Equal (% weight of DCP) and esters were used.



Scheme 1. Melt functionalization of HDPE with AB and HB.

Functionalization reaction was carried out under different experimental conditions like variation in (% weight of DCP), different temperature and with different intervals of reaction time.

3.1. FTIR characterization

The FTIR spectrum of HDPE before and after functionalization with different (% weight of DCP) or (% weight of AB) are shown in Fig. 1. Fig. 1a represents the FTIR spectrum of pristine HDPE. The important peaks are characterized below. Peaks between 2600 and 3000 cm^{-1} are due to the C–H stretching vibrations. The C–H bending vibration is observed at 1490 cm^{-1}. A sharp peak at 730 cm^{-1} is associated with the C–H out of plane bending vibration. Fig. 1b–f indicates the FTIR spectra of 3–7% weight of AB loaded HDPE. The stretching of C═O can be seen at 1723 cm^{-1}. A new peak appears at 1050 cm^{-1} is used to confirm the C–O–C ester linkage. The C–N and N–H stretching are observed at 1366 and 3374 cm^{-1} respectively. Appearance of these new peaks confirmed the chemical surface grafting of AB onto HDPE backbone. Fig. 2a–e illustrates the FTIR spectra of 3–7% weight HB loaded HDPE. In this system also the above-mentioned peaks are observed. The FTIR spectra of AB and HB functionalized HDPE under different temperature and time interval is not shown here for the sake of convenience.

3.2. Effect of time on RI of functionalization, olefin formation and % C.L

Grafting of AB onto HDPE in the presence of DCP was carried out at different intervals of time by keeping the other experimental conditions as constant. The reaction time was varied between 3600 and 12,600 s. In the present investigation, we used the equal concentration of DCP and AB ester. While increasing the reaction time interval, the RI value of [C═O/CH] is increased linearly. It indirectly indicated that the % grafting increased linearly. Fig. 3a represents the effect of time on $\mathrm{RI}_{[\mathrm{C{=}O/C{-}H}]}$ for HDPE–DCP–AB system (i.e.) the plot of time vs. $\mathrm{RI}_{[\mathrm{C{=}O/CH}]}$. Normalized values are presented here.

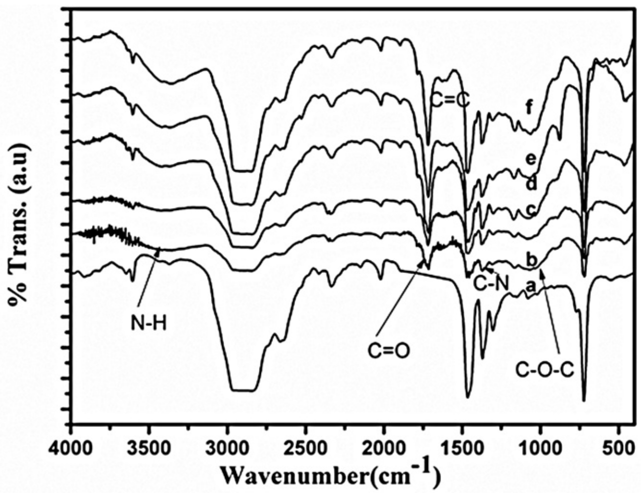


Fig. 1. FTIR spectra of HDPE loaded with AB at (a) 0% weight, (b) 3% weight, (c) 4% weight, (d) 5% weight, (e) 6% weight, and (f) 7% weight.

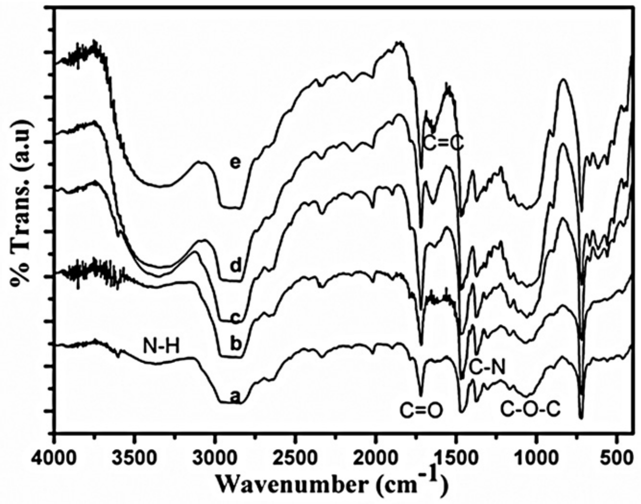


Fig. 2. FTIR spectra of HDPE loaded with HB at (a) 3% weight, (b) 4% weight, (c) 5% weight, (d) 6% weight, and (e) 7% weight.

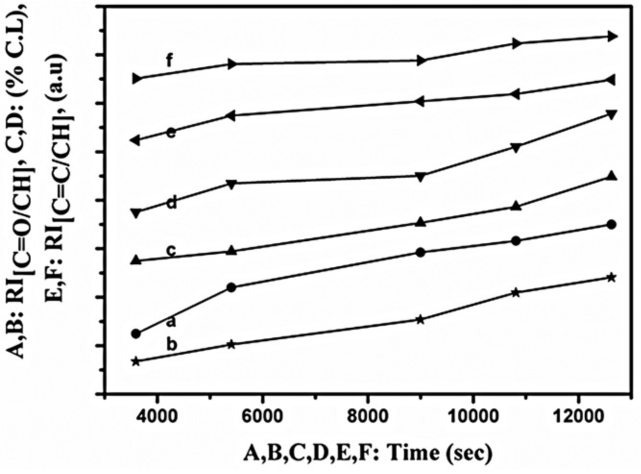


Fig. 3. Effect of time on (a and b) (RI$_{[C=O/CH]}$), (c and d) (% C.L), (e and f) (RI$_{[C=C/CH]}$) of (a, c and e) HDPE–DCP–AB and (b, d and f) HDPE–DCP–HB systems. % weight of DCP – 5%, weight of HDPE – 2.0 g, temperature – 160 °C.

The plot shows a straight line and infers that increase in time leads to increase in % ester grafting. Longer interval of reaction time leads to the possible interaction between HDPE macro radicals with AB radicals resulting with higher % grafting. Under identical experimental conditions, HDPE was melt functionalized with another one ester namely HB. While increasing the reaction time interval the RI of [C=O/CH] is increased linearly. This is due to the coupling reaction between the HB radicals and HDPE macro radicals. Fig. 3b represents the plot of time vs. RI$_{[C=O/CH]}$. The plot shows a straight line, which indicates that during the longer reaction time interval the % ester grafting is increased. On critical comparison, the HDPE–DCP–AB system yielded higher % grafting values. This is due to the following reason. On interaction with cumyl oxy radical, the AB formed an amino radical which actively participated in the functionalization process with HDPE. In the case of HB, it formed a phenoxy radical which was resonance stabilized with the phenyl ring of HB and formed a semi quinone like structure and resulted with lower % functionalization values.

During the melt functionalization reaction, cross-linking and olefin formations are the simultaneous competitive reactions. While increasing the reaction time interval, the % C.L also increased in a linear manner for both systems. C.L is due to the coupling between the HDPE macro radicals. Fig. 3c and d indicates the plots of time vs. (% C.L) for HDPE–AB and HDPE–HB systems respectively. The plots showed a straight line. On comparison, the HB system exhibited higher % C.L values due to the resonance stabilization of HB radical with phenyl ring of HB. This resonance stabilization delays in coupling between HDPE macro radical with HB radical and which indirectly activated the coupling of HDPE macro radicals. As a result of HDPE macro radicals coupling reaction, the cross-linking was resulted.

The second competitive reaction to the functionalization reaction is the olefin formation. This is due to the oxidative degradation reaction. While increasing the reaction time interval the olefin formation is also increased in a linear manner. Fig. 3e and f indicates the plots of time vs. RI$_{[C=C/CH]}$ for both AB and HB systems respectively. On comparison, the later system experienced more olefin formation reaction. This is again due to the resonance stabilization of phenoxy radical with benzene ring of HB. In overall comparison, the AB system yielded higher % functionalization whereas the HB system yielded higher % C.L and % C=C double bond formation values.

3.3. Effect of (% weight of DCP) on the RI of functionalization, olefin formation and % C.L

The (% weight of DCP) and AB were used in an equal concentrations. In the present study, the (% weight of AB) was varied between 3 and 7% weight while keeping the other experimental conditions as constant under inert atmosphere at 160 °C. The RI of [C=O/CH] was increased with the increase in (% weight of DCP). This is due to the availability of more and more free radicals derived from DCP for grafting of AB onto HDPE surface. The order of functionalization reaction can be determined from log–log plot. (i.e.) The plot of log(% weight of DCP) vs. log(RI$_{[C=O/C-H]}$) (Fig. 4a). Fig. 4a represents a straight line with the slope value of 1.56, which confirms the 1.50 order of functionalization reaction with respect to (% weight of DCP). The rate of functionalization (R_f) can be written as follows: $R_f \propto (\%\text{ weight of DCP})^{1.56}$. It means that 1.50 mol of DCP is required to functionalize one mol of HDPE. The % grafting values are listed in Table 1. In 2005, Anbarasan et al. [26] reported the % functionalization values for HDPE–DCP–thioester system. The present investigation shows somewhat lower % grafting values due to the difficulty in the hydrogen abstraction from AB by a cumyl oxy radical. Because the amino group of AB contains one lone pair of electron and moreover it is attached with an electron rich benzene

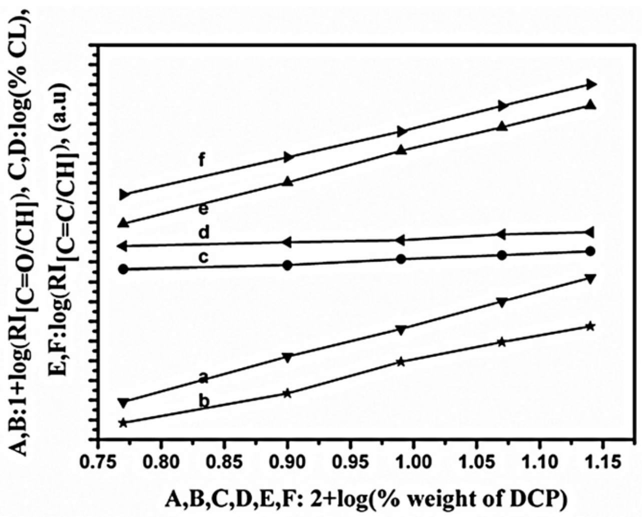


Fig. 4. Effect of (% weight of DCP) on (a and b) ($RI_{[C=O/CH]}$), (c and d) (% C.L), (e and f) ($RI_{[C=C/CH]}$) of (a, c and e) HDPE–DCP–AB and (b, d and f) HDPE–DCP–HB systems. Time – 2.5 h, temperature – 160 °C, weight of HDPE – 2.0 g.

ring. These two electron rich centres were involved in the resonance stabilization process. Under the same experimental conditions HB was melt functionalized with HDPE. Here also one can observe that while increasing the % weight of DCP, the RI of [C=O/CH] is increased in a linear manner. This is due to the above said reasons. In order to find out the order of functionalization reaction, the plot of log(% weight of DCP) vs. log($RI_{[C=O/C-H]}$) (Fig. 4b) was drawn and slope value was determined as 1.30 which confirmed the 1.25 order of reaction with respect to (% weight of DCP). The R_f can be written as follows: $R_f \propto (\%\text{ weight of DCP})^{1.25}$. It means that 1.25 mol of DCP is required to functionalize one mol of HDPE. The % grafting values are indicated in Table 1. On comparison, the AB system produced higher % functionalization values than the HB system due to the ready interaction between the amino radical of AB with HDPE macro radical. When compared with the mercapto ester [28], the present system showed lower % functionalization values at the same time the present system exhibited somewhat better results when compared with succinimide grafting [25] and metal ester grafting [29]. By critical comparison, one can come to a conclusion that melt grafting reaction depends on the nature of the material to be grafted onto polymer backbone, particularly depends on the hydrogen donating nature of material to be grafted.

The first competitive reaction to the melt functionalization reaction is the C.L reaction. While increasing the % weight of DCP, the % C.L value is also increased. This is due to the availability of more and more free radicals derived from DCP. The order of C.L for the HDPE–AB system can be determined by drawing a plot of log(% weight of DCP) vs. log(% C.L) (Fig. 4c). The slope was determined from the above plot as 0.26. This inferred the order of C.L as 0.25 with respect to % weight of DCP. The rate of C.L ($R_{C.L}$) reaction can be written as follows: $R_{C.L} \propto (\%\text{ weight of DCP})^{0.25}$. It explains that 0.25 mol of DCP is required to cross-link one mol of HDPE. A similar type of plot was made for the HB–HDPE system too. (i.e.) the plot of log(% weight of DCP) vs. log(%C.L) (Fig. 4d). The plot indicated a straight line and the slope value was determined from the same as 0.25. This confirmed the 0.25 order of C.L reaction with respect to (% weight of DCP). The % C.L values are mentioned in Table 1. Even though both the systems yielded the same order of C.L reaction, the % C.L values of HB system is higher than that of AB system.

Table 1
Effect of (% weight of DCP) on % functionalization, % C.L and % C=C formation.

% weight of DCP	% functionalization		% C.L		% C=C formation	
	AB	HB	AB	HB	AB	HB
3	28.06	06.86	04.5	28.3	1.00	1.23
4	41.05	11.62	07.3	42.0	1.28	2.35
5	54.90	17.98	11.0	51.6	1.71	3.74
6	70.30	22.13	16.2	63.3	2.07	5.80
7	85.56	30.92	22.3	79.4	2.24	9.10

Table 2
Effect of temperature on % functionalization, % C.L and % C=C formation.

Temperature	% functionalization		% C.L		% C=C formation	
(K)	AB	HB	AB	HB	AB	HB
413	31.13	11.48	01.5	27.8	0.88	03.74
423	48.17	19.87	08.3	48.0	1.15	06.52
433	64.90	27.98	14.3	64.6	2.71	09.94
443	81.03	34.15	22.2	73.5	3.48	11.57
453	95.68	39.11	29.5	86.4	4.91	17.34

The second competitive reaction due to oxidative degradation reaction is the olefin formation. While increasing the % weight of DCP, the RI of C=C is also increased for both AB and HB systems. The order of double bond formation reaction for the HDPE–AB system can be determined by the log–log plot. The plot of log(% weight of DCP) vs. log($RI_{[C=C/CH]}$) (Fig. 4e) was drawn and the slope value was determined as 1.29 which confirmed the 1.25 order of double bond formation reaction with respect to % weight of DCP. The rate of double bond formation ($R_{D.B}$) can be written as follows: $R_{D.B} \propto (\%\text{ weight of DCP})^{1.29}$. 1.25 mol of DCP is required to form one mole of olefin bond in HDPE backbone. In the case of HDPE–HB system, the same type of plot was made, log(% weight of DCP) vs. log($RI_{[C=C/CH]}$) (Fig. 4f), and the slope value was calculated as 1.54. This declared the 1.50 order of double bond formation reaction with respect to % weight of DCP. Table 1 indicates the double bond formation values while varying the % weight of DCP. On comparison, the later system gave higher %C=C values due to the slow coupling reaction of HB radical with HDPE macro radical. In overall comparison, the AB system produced the higher % functionalization values whereas the HB system produced higher %C.L and %C=C values.

3.4. Effect of temperature on % functionalization, % olefin formation and % C.L

Melt surface grating of AB and HB onto HDPE backbone was carried out under different reaction temperature. The reaction temperature was varied between 413 and 453 K while the other experimental conditions were kept constant. While increasing the reaction temperature, the RI of ester grafting was increased linearly. This is due to the following reasons. (1) At higher temperature the ester molecules and HDPE moieties were activated. (2) At higher temperature production of more and more free radicals from DCP. (3) At higher temperature there is a chance for the formation of more aggressive methyl free radical from DCP. The % grafting values corresponding to the RI of ester groups were determined and produced in Table 2. The energy of activation (E_a) for the functionalization reaction can be determined from the famous Arrhenius plot. The plot was drawn between $1/T$ and log($RI_{[C=O/C-H]}$) (Fig. 5a) for HDPE–AB system. The slope value was determined and the E_a value was calculated as 325.4 kJ/mol. The % grafting values are shown in Table 2. The E_a for the functionalization of HB onto HDPE was determined as 402.1 kJ/mol from the plot of $1/T$ vs. log($RI_{[C=O/CH]}$) (Fig. 5b). This reveals that HB consumes more amount of heat energy for functionalization rather than AB. The lower E_a value supported the higher % grafting of AB onto HDPE backbone.

The role of temperature on % C.L of HDPE in the presence of DCP and AB ester was tested. Fig. 5c represents the plot of $1/T$ vs. log(% C.L) for HDPE–DCP–AB system with the E_a value of 348.6 kJ/mol.

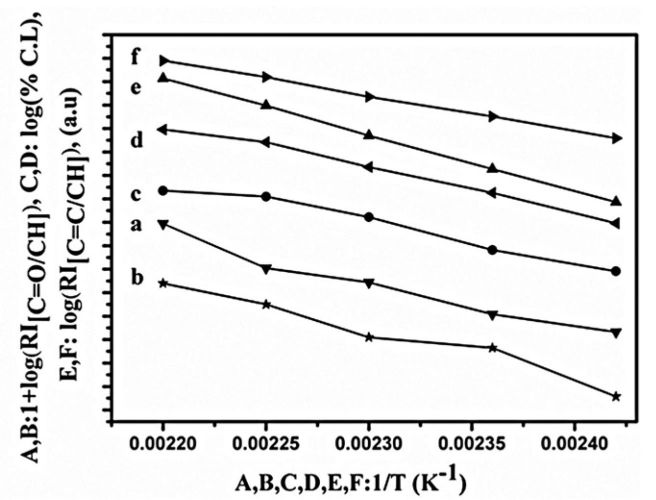


Fig. 5. Effect of temperature on (a and b) ($RI_{[C=O/CH]}$), (c and d) (% C.L), (e and f) ($RI_{[C=C/CH]}$) of (a, c and e) HDPE–DCP–AB and (b, d and f) HDPE–DCP–HB systems. Time – 2.5 h, % weight of DCP – 5%, weight of HDPE – 2.0 g.

Similar type of plot {1/*T* vs. log(% C.L)} was made for HDPE–DCP–HB system as Fig. 5d. The E_a value was calculated as 370.5 kJ/mol. This concluded that C.L reaction consumed less amount of energy than the functionalization reaction for HB–HDPE system. The % C.L values are entered in Table 2. On comparison, the HDPE-HB system consumed less amount of heat energy for C.L reaction and resulted with higher % C.L values.

Effect of temperature on % C=C formation was also tested. While increasing the temperature, the RI of C=C was also increased in a linear manner. The E_a for the C=C formation of HDPE–AB system was determined from the plot of 1/*T* vs. log($RI_{[C=C/CH]}$) (Fig. 5e) as 363.3 kJ/mol. The same type of plot (i.e.) 1/*T* vs. log($RI_{[C=C/CH]}$) (Fig. 5f) was made for HDPE–HB system and the E_a value was calculated as 384.8 kJ/mol. In comparison, the HDPE–HB system consumed less amount of heat energy for C=C formation and resulted with more amount of % C=C double bond formation than the HDPE–AB system. The % C=C values are indicated in Table 2. For the first time, we are reporting here about the determination of E_a values based on the FTIR-RI method for functionalization, olefin formation and C.L reactions. This infers that by using FTIR-RI method one can able to find out the E_a value for particular reaction.

Table 2 critically compares the % grafting values for both esters. The HB system showed higher values in both % C.L and olefin formation reactions whereas the AB system showed higher value in % functionalization reaction.

3.5. DSC profiles

Melt functionalization of HDPE with different esters such as AB and HB led to the change in physical and chemical properties of HDPE. In the case of AB functionalized HDPE, while increasing the (% weight of DCP) from 3 to 7 wt%, the T_m value is decreased and is shown in Fig. 6a–e. The reasons are as follows: (1) the microstructure of HDPE was slightly modified during the melt functionalization process; (2) this is due to the HDPE chain scission with terminal double bonds; (3) chain scission process accompanied with decrease in molecular weight accounted for the reduction in T_m; (4) the formation of double bond in the middle of HDPE chain is one of the possible reactions.

Fig. 7a–e shows the DSC of different % weight of HB functionalized HDPE system. Here also, the T_m value was decreased while increasing the (% weight of HB). Further research work on GPC measurement is going on in our laboratory. Recently, maleic anhydride functionalized PP was reported by Tian et al. [31] in which the author described that decrease in T_m value for the functionalized one. The decrease in T_m value was thoroughly explained by Campos and Petri [32] for the tetrahydrophthalic and maleic anhydride grafted polyolefins in solution. Our results are in coinside with the above-mentioned references [31,32].

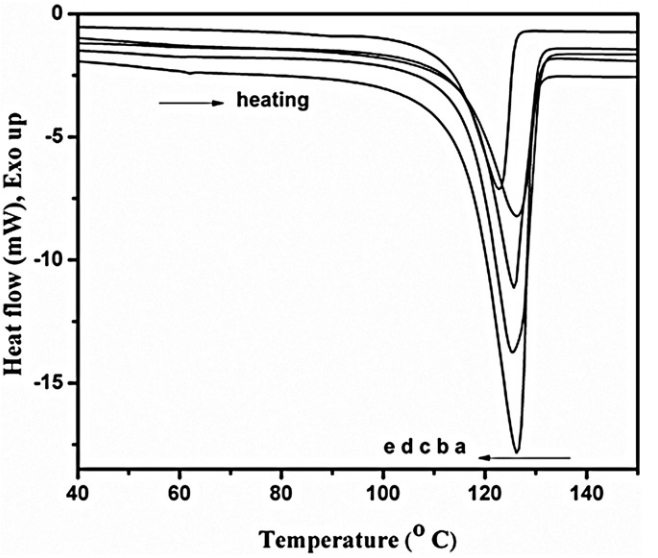


Fig. 6. DSC of HDPE functionalized with AB at (a) 3% weight, (b) 4% weight, (c) 5% weight, (d) 6% weight, and (e) 7% weight.

3.6. TGA history

The thermal stability of functionalized HDPE was tested with the help of TGA instrument. The TGA was recorded at the heating rate of 10 °C/min under air atmosphere. The TGA of 3–7% weight AB loaded HDPE is mentioned in Fig. 8a–e. The thermogram showed a single step degradation process. Up to 450 °C, there is no change in the thermal stability of HDPE. The major weight loss started around 460 °C and extended up to 500 °C. This accounts for the HDPE main chain degradation. The important point noted here is while increasing the (% weight of AB), the thermal stability of HDPE is slightly affected. Due to the random grafting of AB onto HDPE, the extra thermal stability due to grafted side chain was not observed. Moreover, while increasing the (% weight of AB), the initial degradation temperature (T_{id}) is shifted towards lower temperature with

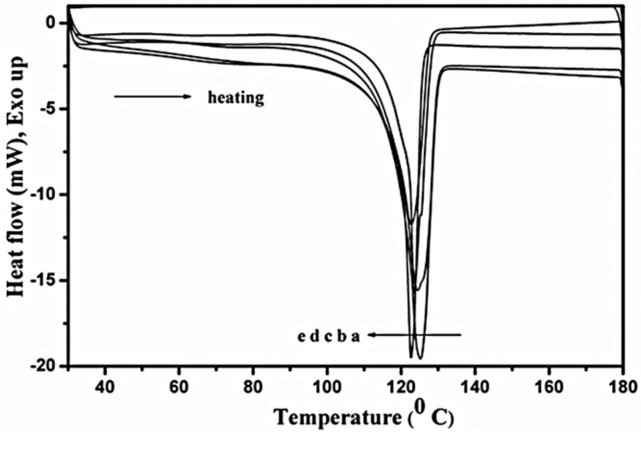


Fig. 7. DSC of HDPE functionalized with HB at (a) 3% weight, (b) 4% weight, (c) 5% weight, (d) 6% weight, and (e) 7% weight.

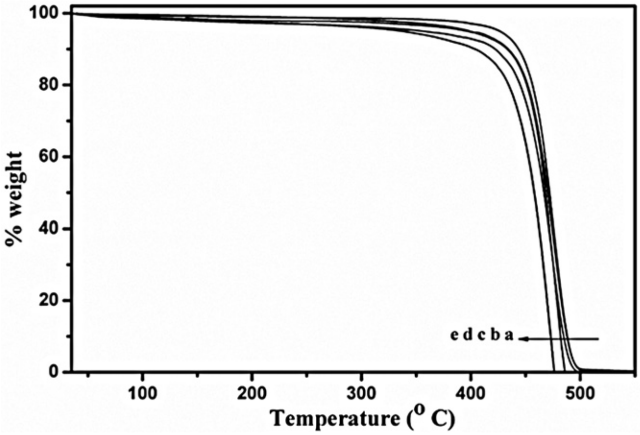


Fig. 8. TGA of HDPE functionalized with AB at (a) 3% weight, (b) 4% weight, (c) 5% weight, (d) 6% weight, and (e) 7% weight.

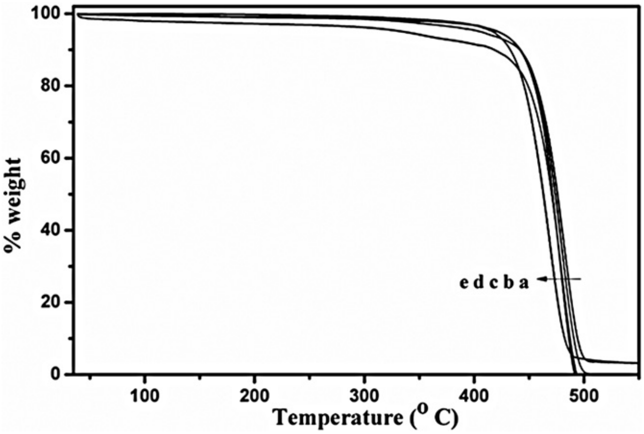


Fig. 9. TGA of HDPE functionalized with HB at (a) 3% weight, (b) 4% weight, (c) 5% weight, (d) 6% weight, and (e) 7% weight.

slight decrease in degradation temperature of HDPE. Mostafa [33] reported in his article about the TGA of vinyl imidazole functionalized PP fibers. The authors explained that after functionalization process the thermal stability of PP was drastically reduced. When compared with his report our results yielded somewhat better one.

Fig. 9a–e shows the TGA of HB functionalized HDPE. Here also there was almost no change in thermal stability due to the random functionalization of HB onto HDPE in the presence of DCP. Due to the random grafting of HB onto HDPE, with very low % of HB used for functionalization process, an extra thermal stability due to grafted HB side chain was not observed. But there was change in the T_{id} of HB functionalized HDPE. At higher (% weight of HB), the HDPE showed a considerable decrease in thermal stability.

4. Conclusions

From the above FTIR-RI based kinetic study the important points are presented here as conclusions. (1) The RI of C=O peak increased with increase in % weight loading of AB and HB onto HDPE. (2) HB showed higher % C.L and % C=C values than AB. (3) AB consumed lower amount of heat energy for functionalization rather than HB. (4) AB showed 1.50 order of reaction for functionalization reaction whereas HB exhibited 1.25 order of functionalization reaction with respect to (% weight of DCP). (5) DSC concluded the slight decrease in T_m for functionalized HDPE by both esters. (6) TGA explored the decrease in T_{id} for both ester grafted HDPE.

Acknowledgement

DST, New Delhi is greatfully acknowledged for their financial support (Ref. No. SR/FTP/CS-39/2005).

References

[1] M.A. Samserzadeh, V. Poursorkhabi, Polym. Degrad. Stab. 94 (2009) 1860–1866.
[2] Z. Guowei, C. Yashao, D. Tao, W. Xiaoli, Plasma Sci. Technol. 9 (2007) 202–205.
[3] I. Kaur, T.C. Bhalla, N. Deepika, N. Gautam, J. Appl. Polym. Sci. 111 (2009) 2460–2467.
[4] M.R. Saeb, H. Garmabi, J. Appl. Polym. Sci. 111 (2009) 1600–1605.
[5] Y. Zhang, J. Chen, H. Li, Polym. Bull. 59 (2007) 427–438.
[6] Y. Sun, G. Wan, B. Wang, J. Zhao, Y. Feng, J. Polym. Res. 16 (2009) 165–172.
[7] J.G. Fatou, B.R. De Gascue, Polym. Bull. 44 (2000) 285–292.
[8] A. Colbeaux, F. Fenouillot, J.F. Taha, M. Wautier, Polym. Int. 54 (2005) 692–697.
[9] H.R.Z. Sheshkal, H. Nazokdast, J. Appl. Polym. Sci. 105 (2007) 1869–1881.
[10] A. Colbeaux, F. Fenouillot, L. David, J. Appl. Polym. Sci. 105 (2007) 2605–2610.
[11] S.F. Hameed, M.A. Allam, J. Appl. Sci. Res. 2 (2006) 27–33.
[12] S. Chakraborty, S. Bandyopadhyay, A.S. Deuri, Polym. Test 26 (2007) 38–41.
[13] F. Svegl, B. Orel, Mater. Technol. 37 (2003) 29–31.
[14] J. Copikova, A. Synytsya, M. Novotna, Czech J. Food Sci. 19 (2001) 51–56.
[15] J.S. Wang, J.S. Shi, J.G. Wu, World J. Gastroenterol. 9 (2003) 1897–1899.
[16] S. Rathika, I. Baskaran, R. Anbarasan, J. Mater. Sci. 44 (2009) 3542–3555.
[17] K. Duraimurugan, S. Rathika, R. Anbarasan, Chin. J. Polym. Sci. 26 (2008) 393–398.
[18] M. Saule, S. Navarre, O. Babot, B. Maillard, Macromolecules 36 (2003) 7469–7476.
[19] M. Saule, S. Navarre, O. Babot, B. Maillard, Macromolecules 38 (2005) 77–85.
[20] S. Navarre, B. Maillard, J. Polym. Sci. Part A: Polym. Chem. 38 (2000) 2957–2963.
[21] M.F. Parveen, V. Dhanalakshmi, R. Anbarasan, J. Mater. Sci. 44 (2009) 5852.
[22] M.F. Parveen, V. Dhanalakshmi, R. Anbarasan, NANO 4 (2009) 147–156.
[23] A. Yelilarasi, J. Juliat Latha Jayakumari, B. Sundaresan, V. Dhanalakshmi, R. Anbarasan, Spectrochim. Acta A 74 (2009) 1229–1234.
[24] A. Yelilarasi, J. Juliat Latha Jayakumari, B. Sundaresan, R. Anbarasan, Polym. Polym. Compos. 17 (2009) 397–407.
[25] R. Anbarasan, S. Kanchana, S. Gayathri, T. Jayalakshmi, V. Dhanalakshmi, J. Appl. Polym. Sci. 115 (2010) 315–323.
[26] R. Anbarasan, O. Babout, B. Maillard, J. Appl. Polym. Sci. 97 (2005) 761–765.
[27] R. Anbarasan, O. Babout, M. Dequil, B. Maillard, J. Appl. Polym. Sci. 97 (2005) 766–774.
[28] V. Parthasarathi, B. Sundaresan, V. Dhanalakshmi, R. Anbarasan, Polym. Eng. Sci. 50 (2010) 474–483.
[29] R. Anbarasan, K. Rajasulochana, M. Anusuya, V. Dhanalakshmi, J. Appl. Polym. Sci. 115 (2010) 2582–2590.
[30] R. Anbarasan, S.A. Anton Kumanan, R. Siva, V. Dhanalakshmi, Int. J. Pure Appl. Chem. 4 (2009) 47–54.
[31] X. Tian, G. Jia, J. Qian, Macromol. React. Eng. 1 (2007) 185–190.
[32] P.G.S. Campos, D.F.S. Petri, J. Br. Chem. Soc. 15 (2004) 532–540.
[33] T.B. Mostafa, J. Appl. Polym. Sci. 111 (2009) 11–18.