

Thermolysis of LDPE with Mercaptoesters – A Comparative Thermal Study

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Abstract- Low Density Polyethylene (LDPE) was chemically grafted with two different mercaptoesters such as butyl3-mercaptopropionate (B3MP) and ethyl2-mercaptopropionate (E2MP) using dicumylperoxide (DCP) as a free radical initiator in an inert atmosphere at 160 °C by thermolysis method. Functionalization reaction was done under various % weight loading of esters. During the functionalization process, crosslinking and C=C formation reactions were competitive. The order of reactions was analyzed by FTIR based kinetics. The ester functionalized LDPE was further characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) methods. The results were critically compared.

Keywords- LDPE; Functionalization; DSC; TGA; Kinetics; Crosslinking

I. INTRODUCTION

Polyolefins are one of the fastest emerging classes of thermoplastics, due to their consistent physical and chemical properties, low cost, light-weight and favorable processing. Some polyolefins find applications in packaging, electric insulating bottles and automobile sectors. Hence, in the modern civilization polymers are very essential to mankind. The majority of plastic products such as polyethylenes are made from petroleum based synthetic polymers that do not degrade in a land fill or in a compost-like environment. Hence, the disposal of these products creates serious environmental pollution problem worldwide. This is due to the absence of hydrolysable or polar group in the polyolefins backbone. Interest in bio-based polymers has increased recently and researchers from various R&D sectors have been closely examining the bio-degradable plastics. The bio-degradable plastics can be made by functionalization process. Functionalization can be done by two methods namely solution and solid state thermolysis method. The solid state thermolysis method is an environmental green method because of non-utilization of toxic and hazardous solvents. Functionalization of low density polyethylene (LDPE) by melt grafting with glycidylmethacrylate was reported by Wei et al [1]. Itaconic acid functionalized LDPE was utilized for the adhesion purpose [2]. Free radical modification of LDPE with vinyl triethoxysilane was reported by Fabris et al [3]. Surface grafting of PE by methyl acrylate vapor was reported in the literature [4]. Recently, Shi et al [5] reported about the dimethyl ammonium propane sulfonate grafted LDPE film. LDPE was grafted with resole [6], dimethyl ammonium propane sulfonate [7], acrylic acid [8], maleic anhydride [9-10], methacrylic acid [11] and trifluoroacetic acid allyl ester [12]. γ -ray induced functionalization of LDPE with poly(vinylpyrrolidone) [13] was reported in the literature. UV induced graft copolymerization of poly (ethylene glycol) with LDPE was reported by Wang P. et al [14]. γ -ray assisted grafting of mono stearic acid and mono maleic acid glycerol diesters onto LDPE were recently reported [15]. Soy protein grafted LDPE was synthesized and its bio-degradation behavior by soil burial method was done by Kaur et al [16]. After the melt functionalization process the amount of ester grafted onto LDPE backbone can be determined by two methods namely, chemical and analytical methods. Chemical method consumes a lot of toxic and hazardous solvents and causes environmental pollution. Hence, we preferred analytical methods particularly, FTIR spectroscopy method because FTIR spectrometer is a useful tool for various science and engineering fields, because of its eco-friendly, high sensitivity or detectivity towards traces amount of substance, low noise to signal ratio, moreover, this method is an easy and inexpensive one. FTIR spectroscopy is used for both qualitative [17-19] and quantitative [20-29] applications. By thorough literature survey, we could not find any report based on the mercaptoester functionalized LDPE, particularly with thermal studies. In the present investigation, our research team tried to functionalize LDPE by introducing a mercaptoester onto LDPE backbone as a side chain by thermolysis method and the thermal properties were followed by DSC and TGA methods.

II. EXPERIMENTAL

A. Materials

Low density polyethylene (LDPE) was purchased from Ottokemi, India. In order to remove the antioxidant present in the LDPE sample, it was purified prior to thermolysis reaction. The purification procedure was explained in our previous publication [28]. Dicumyl peroxide (DCP, Ottokemi, India), 1,2-dichloro benzene (AR, LobaChem, India), Butyl3-mercaptopropionate (B3MP, Lancaster, UK), Ethyl2-mercaptopropionate (E2MP, Ottokemi, India), Dichloromethane (AR, Merck, India), Acetone (AR, Paxmy, India) and Toluene (LobaChem, India) used for further experimentation were used without subjecting them to any process.

B. Thermolysis Reaction

Graft functionalization of LDPE with mercaptoesters was carried out through thermolysis reaction. This procedure is illustrated further: Previously purified LDPE (2.0 g) was taken in a 25 mL round-bottom flask and a definite quantity of mercaptoester and equal quantity of DCP (5% weight) 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. The mixture of solvents was used only for the uniform mixing of mercaptoesters throughout 2g of LDPE. During the mixing process, the mercaptoester was adsorbed on the powder surface of LDPE. If there is no uniform mixing of this ester onto LDPE, simply that leads to the agglomeration of mercaptoester and resulting with lower % functionalization. After being mixed, the solvents were removed with the help of rotavapour 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. The reactor was heated in an oil bath at 160 °C for 2.5 h without any stirring. Once the reactants were melted the reaction started and led to various processes, particularly surface graft functionalization, alkene formation and crosslinking (C.L) reactions. After thermolysis reaction, the products were cut into small pieces and dissolved in DCB at 120 °C for 2 h. During this dissolution process, the non-cross linked (mercaptoester functionalized) part is soluble in DCB solvent whereas the crosslinked polymer is insoluble in DCB. 800 mL of acetone was added to precipitate the non-crosslinked and mercaptoester functionalized polymer. By this way, both non-crosslinked and crosslinked polymers were isolated. By repeating the dissolution and precipitation process for 3 times, the mercaptoester functionalized LDPE has been purified. The possible reactions are mentioned in our earlier publication [24].

C. Characterizations

The functionalized LDPE samples can be characterized by various analytical techniques. The functionalities present in the LDPE after functionalization reaction can be confirmed through FTIR spectroscopy. FTIR spectra of LDPE samples in the form of neat pellet before and after functionalization process were recorded, using Shimadzu 8400 S FTIR spectrophotometer instrument. For FTIR sample preparation, the non-crosslinked part of the mercaptoester functionalized LDPE alone was considered. Then the spectrum was recorded. The baseline correction was made carefully and the corrected area of the peaks was determined using FTIR software. The corrected peak area was determined without predicting the lower and upper limits and ratio between the relative intensities was determined. In order to confirm the results, FTIR spectrum was recorded for 3 times for the same film at different places. On each measurement, the instrument produced the same corrected peak area results. For the quantitative determination of percentage grafting, the corrected area of the peaks at 1730 (C=O stretching), 1610 (C=C stretch) and 720(C-H out of plane bending vibration) cm^{-1} was determined and relative intensity was calculated as follows:

$$\text{Relative intensity carbonyl (RI)} = A_{1730}/A_{720}$$

$$\text{Relative intensity of C=C (RI)} = A_{1604}/A_{720}$$

$$\% \text{ Ester grafting} = \frac{\text{RI}_{\text{ester}} \times W}{C \times 1.52} \times 100 \quad (1)$$

$$\% \text{ C = C formation} = \frac{\text{RI}_{[\text{C=C-H}]} \times W}{C \times 0.35} \times 100 \quad (2)$$

Where, W is the weight of non-crosslinked ester grafted polymer taken for FTIR study, C is the % weight of peroxide used, 1.52 and 0.35 are the proportionality constants, as mentioned in our earlier publication [28]. The % crosslinking was determined by using the following formula:

$$\% \text{ crosslinking} = \frac{[\text{Weight of Polymer taken for Functionalization}] - [\text{Weight of Non - crosslinked polymer obtained after Functionalization}]}{\text{Weight of Polymer taken for Functionalization}} \times 100 \quad (3)$$

The change in melting temperature of LDPE can be confirmed by DSC analysis and was recorded for the samples by using SDT 2960 simultaneous TGA and DSC instrument, TA instruments under nitrogen atmosphere at the heating rate of 10 °C/min. In order to remove the previous thermal history, the DSC was run for 2 times. The third run was considered for discussion. The TGA analysis was performed under air purge at the heating rate of 10 °C/min by using the SDT 2960 simultaneous TGA and DSC, TA instruments. Further, the functionalization can be confirmed through NMR spectra, unfortunately the LDPE sample is soluble in Toluene at 130°C. Such a facility is not available in our region and hence it is not reported here.

III. RESULTS AND DISCUSSION

For functionalization of LDPE, two types of esters such as butyl 3-mercaptopropionate and ethyl 2-mercaptopropionate were used. Equal % weight of DCP and esters were opted for this reaction. Functionalization reaction was carried out under different % weight loading of DCP at 160 °C under nitrogen atmosphere.

A. FTIR Characterization

FTIR spectra of butyl 3-mercaptopropionate functionalized LDPE with different % weight loading is showed in Fig. 1(b-f). The important peaks are described below: Peaks between 2600 and 3000 cm^{-1} are associated with the C-H stretching vibration. A sharp peak at 1723 cm^{-1} is due to the stretching of ester C=O bond. The C-H bending vibration was found at 1490 cm^{-1} . A narrow band at 730 cm^{-1} was assigned to C-H deformation vibration. The C-O-C ester linkage was confirmed by the presence of a peak at 1050 cm^{-1} . The C-S stretching appeared around 1350 cm^{-1} . Appearance of C-S stretching confirmed the chemical grafting of mercapto ester onto LDPE backbone. The remaining peaks are related to pristine LDPE (Fig. 1a). The pristine LDPE did not show any peak at 1723 cm^{-1} due to the ester carbonyl stretching vibration. Fig. 2(b-f) illustrated the FTIR spectra of ethyl 2-mercaptopropionate functionalized LDPE. Here the above-mentioned peaks are also observed. Fig. 2a represented the FTIR spectrum of pristine LDPE. The FTIR spectra of butyl 3-mercaptopropionate and ethyl 2-mercaptopropionate functionalized LDPE under different temperature and time intervals was not shown here for the sake of convenience.

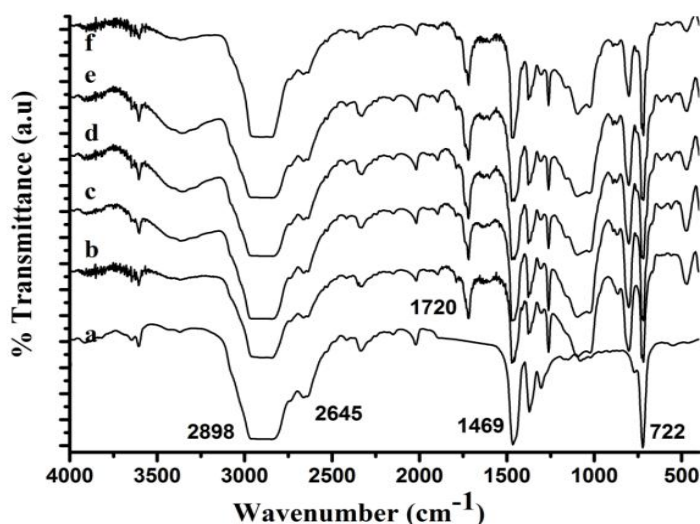


Fig. 1 FTIR spectrum of butyl 3-mercaptopropionate functionalized LDPE under different % weight of butyl 3-mercaptopropionate

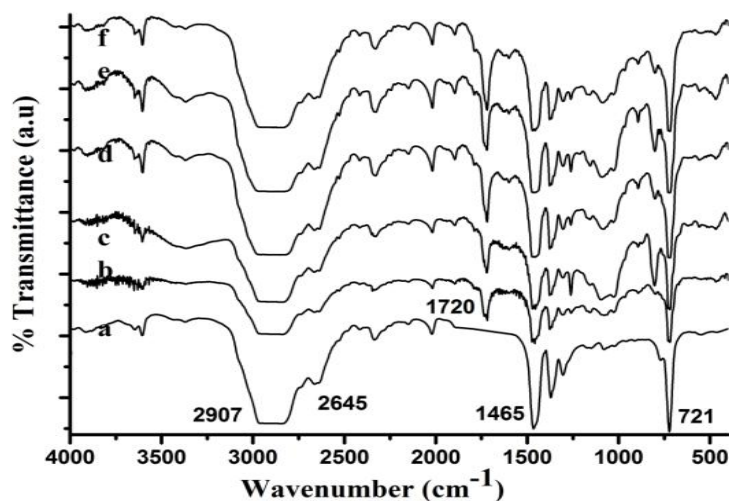


Fig. 2 FTIR spectrum of ethyl 2-mercaptopropionate functionalized LDPE under different % weight of ethyl 2-mercaptopropionate

B. Effect of % weight of DCP on % Functionalization, % Crosslinking and % C=C Formation

Using DCP as a free radical initiator with butyl 3-mercaptopropionate and ethyl 2-mercaptopropionate esters as grafting agents, functionalization of LDPE was done. The % weight of DCP and butyl 3-mercaptopropionate were taken in an equal proportion. In the present investigation, the molar ratio of DCP with respect to LDPE varied from 3% to 7% weight while keeping the other experimental conditions as constant. The incremental loading of butyl 3-mercaptopropionate-DCP stimulated the % ester grafting to a greater extent. This is due to the availability of more and more free radicals derived from DCP for grafting of butyl 3-mercaptopropionate onto LDPE. This is in accordance with our recent publication [24]. The universal log-log plot method was used for the determination of order of functionalization reaction. The plot was made between $\log(\text{molar ratio of DCP})$ and $\log(\text{RI}_{\text{C=O/C-H}})$. Fig.3a shows the same with a straight line. This illustrated the increase in RI corresponding

to the increase in the molar ratio of DCP and butyl 3-mercaptopropionate. The slope value was determined as 1.71, which ensured the 1.75 order of functionalization reaction with respect to molar ratio of DCP. It means that 1.75 mol of butyl 3-mercaptopropionate is required to functionalize one mole of LDPE. While increasing the molar ratio of DCP and ethyl 2-mercaptopropionate, the RI of $[C=O/CH]$ was also increased due to the melt grafting of ethyl 2-mercaptopropionate onto LDPE backbone through hydrogen abstraction reaction. The slope value was determined from the plot of $\log(\text{molar ratio of DCP})$ Vs $\log(RI_{[C=O/CH]})$ (Fig.3b) as 1.51, which confirmed the 1.50 order of functionalization reaction with respect to molar ratio of DCP. This indicates that 1.50 mol of ethyl 2-mercaptopropionate is required to functionalize one mole of LDPE. The % ester grafting values are tabulated in Table 1.

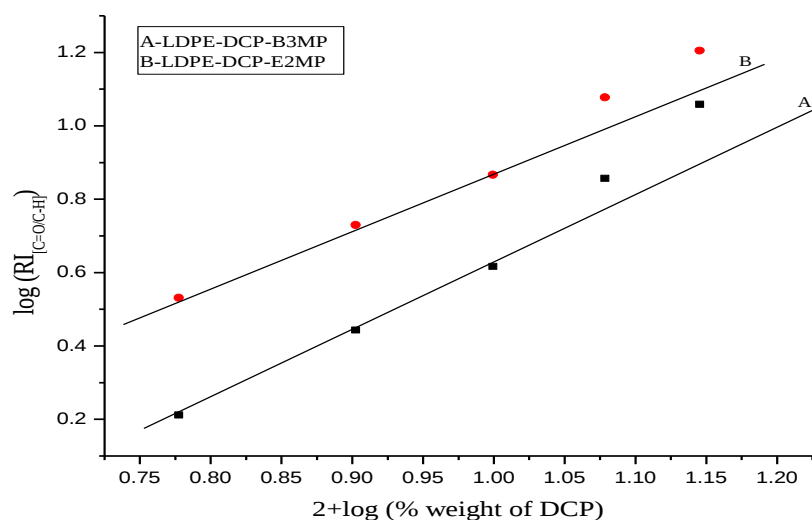


Fig. 3 Effect of % weight of DCP on RI of (a) LDPE-butyl 3-mercaptopropionate, (b) LDPE-ethyl 2-mercaptopropionate, Time = 2h, Temperature-160°C, Weight of LDPE-2.0 g

TABLE 1 EFFECT OF % WEIGHT OF DCP ON FUNCTIONALIZATION, CROSSLINKING AND C=C FORMATION

% weight of DCP	% functionalization		% crosslinking		% C=C formation	
	B3MP	E2MP	B3MP	E2MP	B3MP	E2MP
3	17.8	37.19	1.33	1.18	0.76	0.71
4	22.71	44.05	1.97	1.43	1	1.44
5	27.16	48.25	2.5	2.32	1.17	1.48
6	39.42	65.45	4.35	3.47	2.28	1.52
7	53.81	75.34	5.95	4.24	2.97	2.34

The novelty of the present investigation is the estimation of % C=C formation during the melt functionalization reaction. The C=C formation is due to the over oxidation reaction. The % C=C formation was linearly increased with the increase of molar ratio of DCP. The order of C=C formation for butyl 3-mercaptopropionate system was determined by the log-log plot method. The plot of $\log(\text{molar ratio of DCP})$ Vs $\log(RI_{[C=C/CH]})$ (Fig.4a) was drawn and the slope was determined as 1.53, which confirmed the 1.50 order of double bond formation reaction with respect to molar ratio of DCP. Similar type of plot was made for LDPE-DCP-ethyl 2-mercaptopropionate (Fig.4b) system and the slope was determined as 1.10, which recognized the 1st order double bond formation reaction with respect to molar ratio of DCP. These results indicated that 1.5 mol of DCP for butyl 3-mercaptopropionate and 1 mol of DCP for ethyl 2-mercaptopropionate are required to form 1 mol of olefin bond (C=C) in LDPE. Table 1 points out the value of % C=C formation. The second competitive reaction to the melt functionalization reaction is the crosslinking reaction. The crosslinking reaction was also increased with the increase of molar ratio of DCP. The C.L is due to the coupling of LDPE macro radicals. In order to find out the order of C.L reaction, a graph was drawn between $\log(\text{molar ratio of DCP})$ and $\log(\% \text{ C.L})$ (Fig.5a) for LDPE-DCP-butyl 3-mercaptopropionate system. The slope value was determined as 0.42, which confirmed the 0.50 order of C.L reaction with respect to molar ratio of DCP. In the case of ethyl 2-mercaptopropionate-DCP system, the slope value was determined as 0.60 from the plot of $\log(\text{molar ratio of DCP})$ Vs $\log(\% \text{ C.L})$ (Fig.5b), which revealed the 0.50 order of C.L reaction with respect to molar ratio of DCP. The rate of crosslinking reaction can be written as follows: $R_{C.L} \propto (\% \text{ weight of DCP})^{0.5}$ for both butyl 3-mercaptopropionate and ethyl 2-mercaptopropionate grafted LDPE. This inferred that 0.5 mol of DCP is required to crosslink one mole of LDPE for both systems. The % crosslinking values are represented in Table 1. The present systems showed lower % crosslinking when compared with aminoester and hydroxyester grafted HDPE systems [30]. This is due to the difference in the chain length and efficiency of hydrogen donating capability of butyl 3-mercaptopropionate. In overall comparison, the ethyl 2-mercaptopropionate system gave higher % functionalization with lower % C=C and % C.L values than the butyl 3-mercaptopropionate system due to its structural effect.

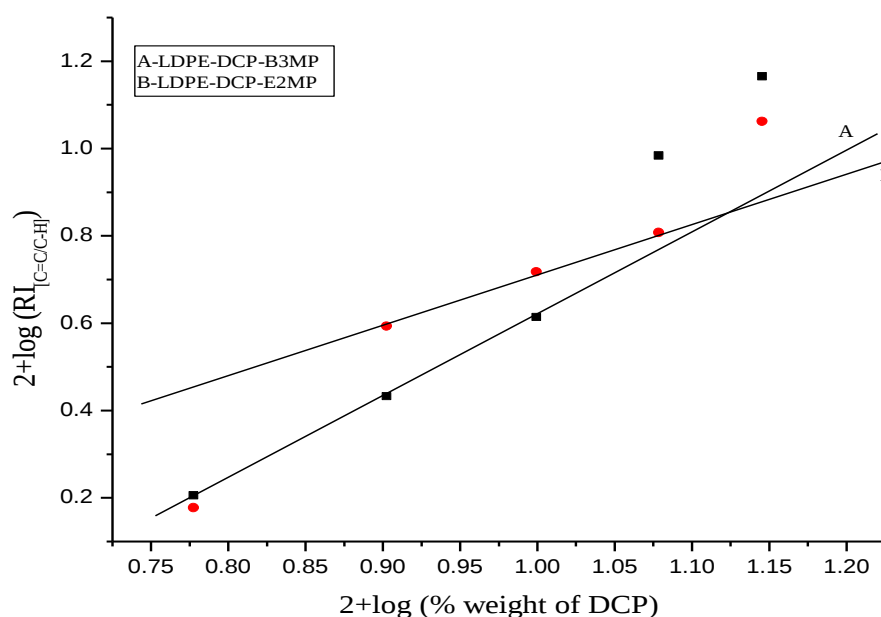


Fig. 4 Effect of % weight of DCP on C=C formation (a) LDPE- butyl 3-mercaptopropionate, (b) LDPE-ethyl 2-mercaptopropionate, Time-2 h, Temperature-160°C, Weight of LDPE-2.0 g

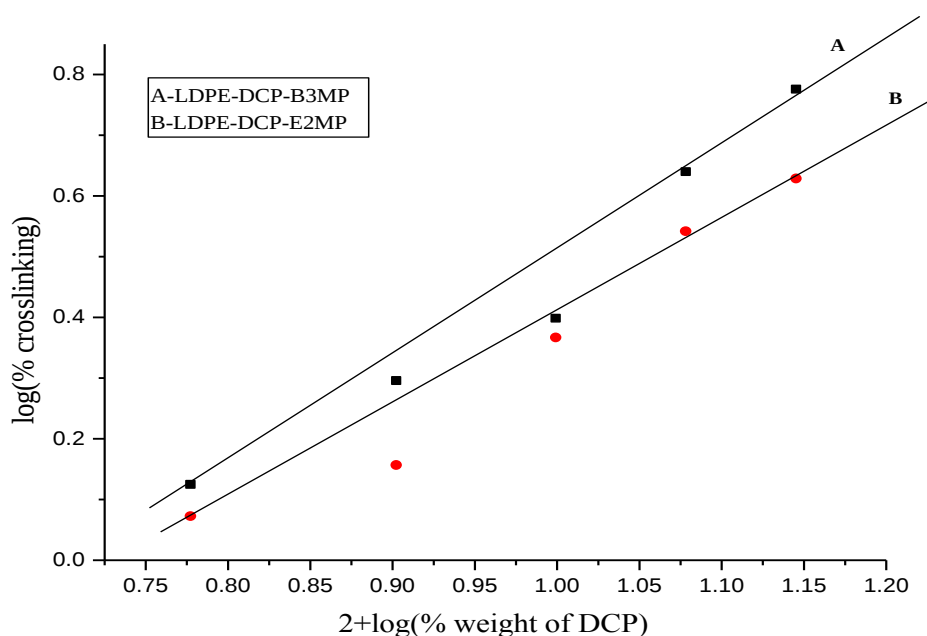


Fig. 5 Effect of % weight of DCP on crosslinking of (a) LDPE-butyl 3-mercaptopropionate, (b) LDPE-ethyl 2-mercaptopropionate, Time-2 h, Temperature-160°C, Weight of LDPE-2.0

C. Effect of Temperature on % Functionalization, % Crosslinking and C=C Formation

While increasing the temperature, relative intensity of carbonyl ester increased upto 160 °C and then decreased further. This was due to the formation of unwanted by-products at higher temperature with very high activation energy. Arrhenius plot was drawn to calculate the activation energy (E_a) for the functionalization of butyl 3-mercaptopropionate onto LDPE. The plot was made between $1/T$ Vs $\log(RI_{C=O/C-H})$ as shown in Fig.6a. The slope value was determined and the E_a value was estimated as 92 kJ/mol. For ethyl 2-mercaptopropionate grafted system, the calculated activation energy (E_a) was 80 kJ/mol (Fig. 6b). This concluded that butyl 3-mercaptopropionate consumed more amount of heat energy for functionalization than ethyl 2-mercaptopropionate. The lower E_a value supported the higher % functionalization for ethyl 2-mercaptopropionate system. Fig.7a visualized the effect of % (weight of DCP) on crosslinking reaction for butyl 3-mercaptopropionate grafted LDPE. The E_a value was calculated as 105 kJ/mol. Similar trend was followed for ethyl 2-mercaptopropionate system as shown in Fig.7b. The slope value was determined and the E_a value was estimated as 125 kJ/mol. These results indicated that ethyl 2-mercaptopropionate system consumed more amount of heat energy than butyl 3-mercaptopropionate for crosslinking of LDPE. The lower E_a value supported the higher % crosslinking for butyl 3-mercaptopropionate than ethyl 2-mercaptopropionate. The %

crosslinking values are listed in Table 2. The C=C formation was also analyzed for both esters by FTIR-RI method. Fig.8a represented the plot of $1/T$ Vs $\log(RI_{[C=C/C-H]})$ for butyl 3-mercaptopropionate system and the E_a value was 101.7 kJ/mol. In the same way, another plot was made for ethyl 2-mercaptopropionate system as shown in Fig.8b. The E_a value was determined as 121 kJ/mol. This confirmed butyl 3-mercaptopropionate system consumed less amount of heat energy for olefin formation than ethyl 2-mercaptopropionate. The lower E_a value supported higher % olefin formation for butyl 3-mercaptopropionate than ethyl 2-mercaptopropionate system. The % C=C formation values are displayed in Table 2. In overall comparison ethyl 2-mercaptopropionate consumed more amount of heat energy for functionalization reaction whereas butyl 3-mercaptopropionate consumed more amount of heat energy for crosslinking and C=C formation reaction. This is in accordance with our earlier publication [24].

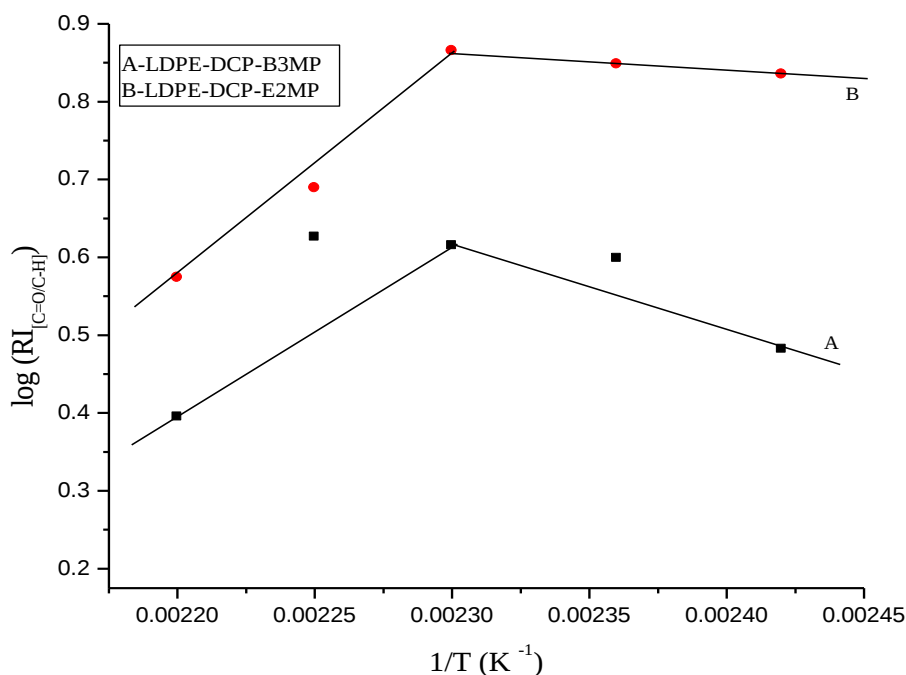


Fig. 6 Effect of temperature on functionalization (a) LDPE-butyl 3-mercaptopropionate, (b) LDPE-ethyl 2-mercaptopropionate, Time-2 h, % weight of DCP-5%, weight of LDPE-2.0 g

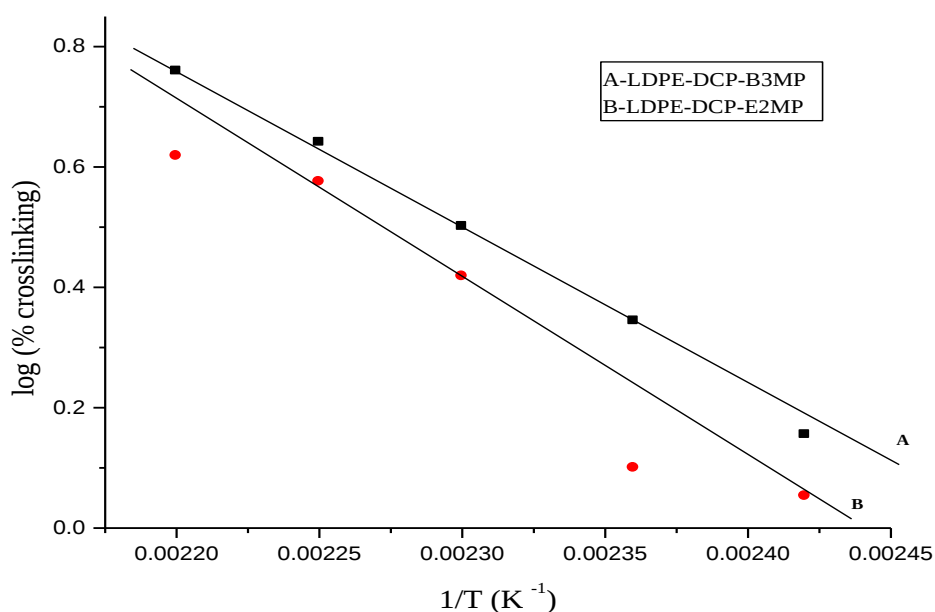


Fig. 7 Effect of temperature on crosslinking of (a) LDPE-butyl 3-mercaptopropionate, (b) LDPE-ethyl 2-mercaptopropionate, Time-2 h, % weight of DCP-5%, weight of LDPE-2.0 g

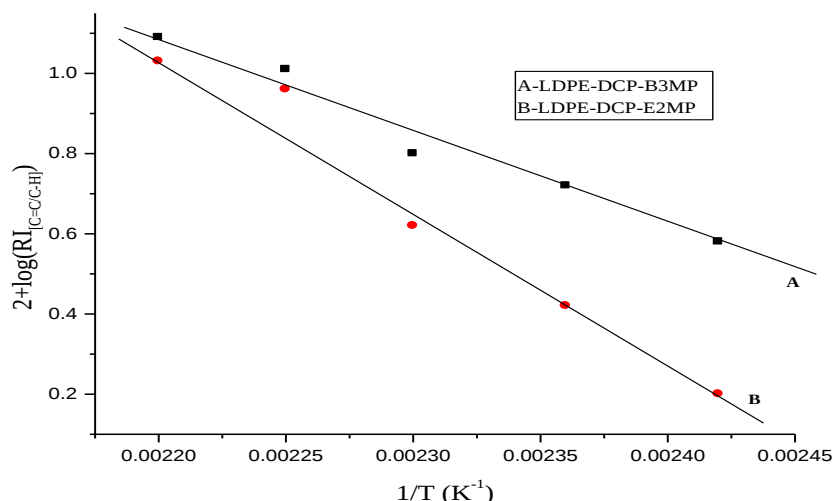


Fig. 8 Effect of temperature on C=C formation of (a) LDPE- butyl 3-mercaptopropionate, (b) LDPE-ethyl 2-mercaptopropionate, Time-2 h, % weight of DCP-5%, weight of LDPE-2.0 g

TABLE 2 EFFECT OF TEMPERATURE ON FUNCTIONALIZATION, CROSSLINKING AND C=C FORMATION

Temperature (K)	% functionalization		% crosslinking		% C=C formation	
	B3MP	E2MP	B3MP	E2MP	B3MP	E2MP
413	19.98	45.07	1.43	1.13	0.94	0.42
423	26.13	46.45	2.21	1.26	1.31	0.71
433	27.16	48.25	3.17	2.62	1.48	1.17
443	27.81	32.17	4.38	3.76	2.65	2.5
453	16.34	23.23	5.75	4.15	3.42	3.08

D. Effect of Time on % Functionalization, % Crosslinking and C=C Formation

The functionalization of LDPE with esters was achieved by changing the reaction time. Fig.9a showed the effect of time on $RI_{[C=O/C-H]}$ for butyl 3-mercaptopropionate system. The obtained straight line slope confirmed that the % ester grafting (i.e increase of $RI_{[C=O/C-H]}$) was increased with the increase in reaction time. Increase in reaction time made a possible interaction between LDPE macro radicals and butyl 3-mercaptopropionate radicals during the melt functionalization process resulting with higher % ester grafting. A similar plot was made for ethyl 2-mercaptopropionate system also as shown in Fig.9b. Here also, the RI of carbonyl ester was increased with the increase of reaction time. Figs.10a and b showed the plot of Time Vs (% crosslinking) for both butyl 3-mercaptopropionate and ethyl 2-mercaptopropionate grafted LDPE. From this, one can observe that % crosslinking was increased with the increase of reaction time. Effect of time on C=C formation was also investigated for butyl 3-mercaptopropionate and ethyl 2-mercaptopropionate system as shown in Figs.11a and b respectively. Increase in the reaction time uplifted the % C=C formation in a linear manner. This may be due to the thermal oxidation process. Table 3 critically compared the % functionalization, crosslinking and C=C formation values.

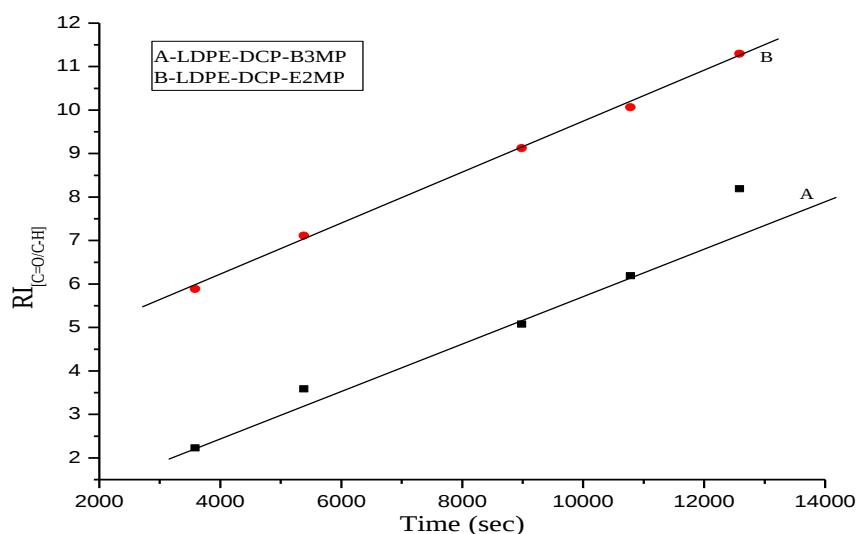


Fig. 9 Effect of time on functionalization of (a) LDPE-butyl 3-mercaptopropionate, (b) LDPE-ethyl 2-mercaptopropionate, temperature = 160⁰ C, % weight of DCP-5%, weight of LDPE-2.0 g

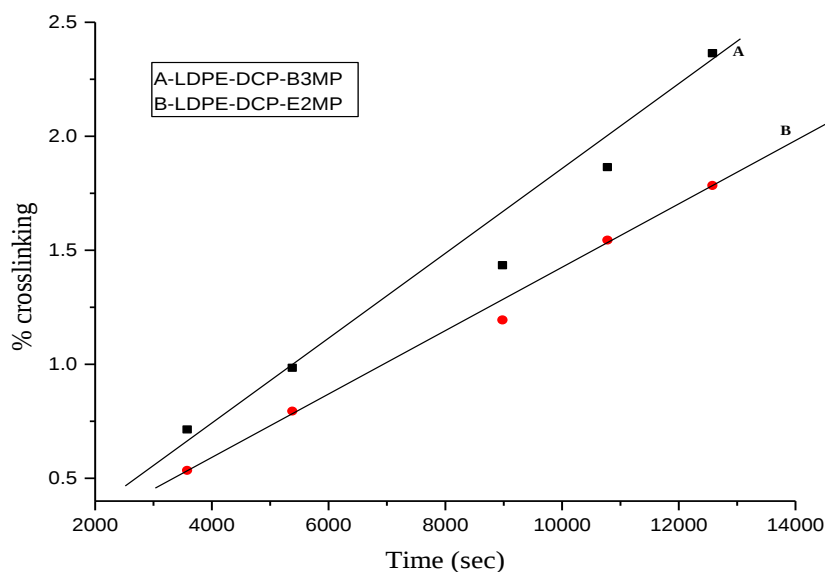


Fig. 10 Effect of time on crosslinking of (a) LDPE-butyl 3-mercaptopropionate, (b) LDPE-ethyl 2-mercaptopropionate, temperature = 160⁰ C, % weight of DCP-5%, Weight of LDPE-2.0 g

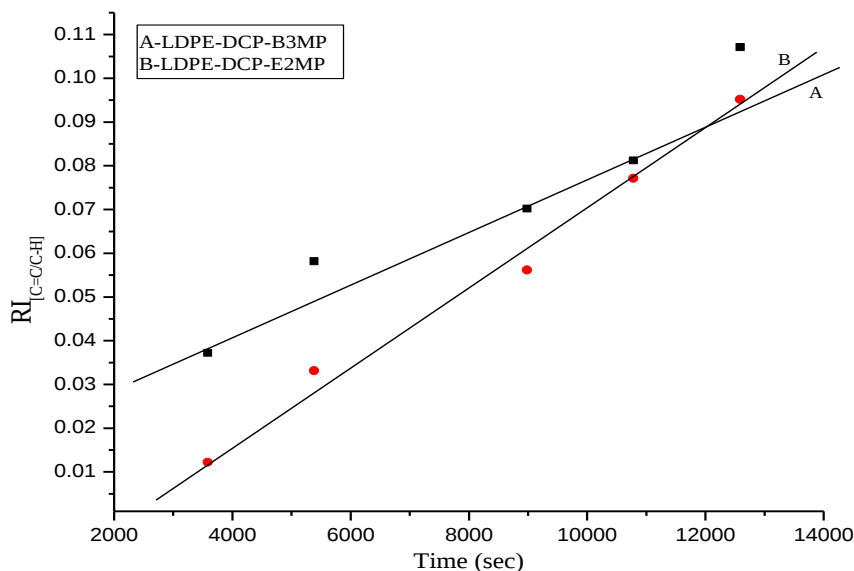


Fig. 11 Effect of time on C=C formation of (a) LDPE-butyl 3-mercaptopropionate, (b) LDPE-ethyl 2-mercaptopropionate, temperature = 160⁰ C, % weight of DCP-5%, weight of LDPE-2.0 g

TABLE 3 EFFECT OF TIME ON FUNCTIONALIZATION, CROSSLINKING AND C=C FORMATION

Time (sec)	% functionalization		% crosslinking		% C=C formation	
	B3MP	E2MP	B3MP	E2MP	B3MP	E2MP
3600	14.53	38.61	0.71	0.53	1.05	0.34
5400	23.48	46.66	0.98	0.79	1.65	0.94
9000	33.3	59.91	1.43	1.19	1.85	1.6
10800	40.61	66.09	1.86	1.54	2.31	2.2
12600	53.75	74.2	2.36	1.78	3.05	2.71

E. DSC Profiles

Functionalization of LDPE with two different esters such as butyl 3-mercaptopropionate and ethyl 2-mercaptopropionate induced some changes in physical and chemical properties of LDPE. These changes were analyzed intensively with the help of DSC and TGA thermograms. Fig. 12 (b-f) represents the DSC heating scans of butyl 3-mercaptopropionate functionalized LDPE system. The T_m values were slightly increased with the increase of % weight loading of DCP or mercaptoester. The basic reason is explained as follows: 1) the micro structural rearrangement of LDPE (α form into β form) slightly increased the

T_m of LDPE after functionalization with mercapto ester. 2) due to the melt grafting of ester side chain [24]. 3) the melt grafted mercaptoester side chain will restrict the C-C rotation and resulted with more conformational energy which alternatively increased the T_m of LDPE. 4) crosslinking process might increase the molecular weight of LDPE which accounted the increase in T_m . Our DSC reports are coinciding with the literature report [30]. For the sake of comparison, the DSC heating scan of pristine LDPE is shown in Fig.12a. In comparison, the T_m value of butyl 3-mercaptopropionate functionalized LDPE showed higher values than the pristine one. Moreover, the peaks were more sharpened while increasing the % weight loading of butyl 3-mercaptopropionate. This confirmed the increase in crystallinity of the LDPE after melt functionalization with butyl 3-mercaptopropionate. Fig.13(b-f) shows the DSC heating scan of ethyl 2-mercaptopropionate functionalized LDPE system. Here the above mentioned trend was also observed. Table 4 exhibits the T_m values of LDPE before and after functionalization with butyl 3-mercaptopropionate and ethyl 2-mercaptopropionate systems.

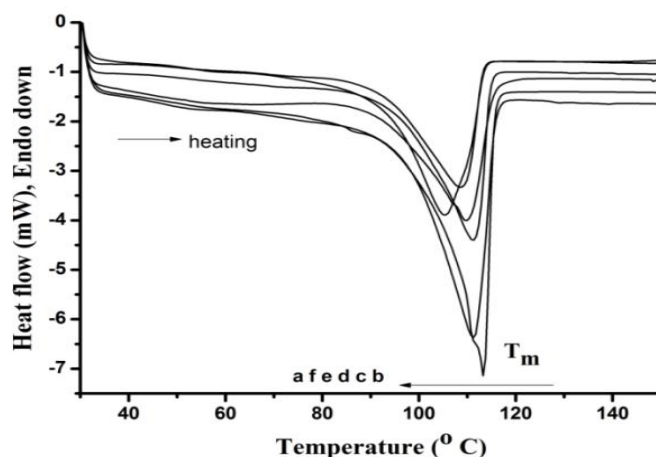


Fig. 12 a) DSC of Pristine LDPE, b-f) DSC of butyl 3-mercaptopropionate functionalized LDPE at different % weight of butyl 3-mercaptopropionate

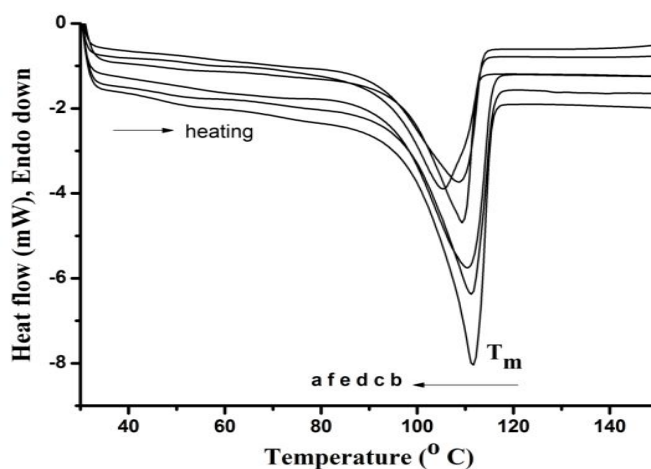


Fig. 13 a) DSC of pristine LDPE, b-f) DSC of ethyl 2-mercaptopropionate functionalized LDPE at different % weight of ethyl 2-mercaptopropionate

TABLE 4 DSC AND TGA DATA OF LDPE GRAFTED BUTYL 3-MERCAPTOPROPIONATE AND ETHYL 2-MERCAPTOPROPIONATE SYSTEMS

System	T_m (°C)	% wt. at 350°C
LDPE	105.1	98.2
LDPE-3% wt. B3MP	113.1	95.5
LDPE-4% wt. B3MP	111.2	94.8
LDPE-5% wt. B3MP	110.9	94
LDPE-6% wt. B3MP	109.6	89.1
LDPE-7% wt. B3MP	108.4	85.5
LDPE-3% wt. E2MP	111.5	97.8
LDPE-4% wt. E2MP	111.2	97.5
LDPE-5% wt. E2MP	110.5	96.7
LDPE-6% wt. E2MP	109.3	95.9
LDPE-7% wt. E2MP	108.4	93.6

F. TGA History

The thermal stability of functionalized LDPE was analyzed with the help of TGA instrument. The TGA thermogram was recorded at the heating rate of 10 °C/min under air atmosphere. Fig. 14 (b-f) exhibits the TGA thermograms of butyl 3-mercaptopropionate functionalized LDPE system. The thermogram showed a two-step degradation process. The first, minor weight loss was started around 320 °C and extended up to 360 °C. Then, the second, major weight loss was started and extended up to 460 °C, which accounted the complete degradation of LDPE backbone. At higher % weight loading of butyl 3-mercaptopropionate, the thermal stability of LDPE was not affected. These results revealed that the initial degradation temperature (T_{id}) of LDPE was increased. Due to the random grafting of butyl 3-mercaptopropionate onto LDPE backbone, the extra thermal stability due to the grafted side chain was not observed. For the sake of comparison, the thermogram of pristine LDPE is shown in Fig.14a. The thermogram showed a one-step degradation process. In comparison, the butyl 3-mercaptopropionate functionalized LDPE showed slightly higher thermal stability than the pristine LDPE. Fig. 15(b-f) shows the TGA of ethyl 2-mercaptopropionate functionalized LDPE and the thermal stability was increased with the increase of % weight loading of ethyl 2-mercaptopropionate. Due to the random grafting of ethyl 2-mercaptopropionate onto LDPE backbone the extra thermal stability due to the grafted ethyl 2-mercaptopropionate was not observed. This concluded that after melt functionalization reaction with mercaptoesters the initial degradation temperature of LDPE was increased slightly. The T_{id} values of mercaptoester functionalized LDPE were compared with the literature value [31]. This inferred that after functionalization with mercaptoester, the LDPE showed slight increase in T_{id} value. The TGA thermogram of pristine LDPE is included as Fig.15a. The ethyl 2-mercaptopropionate system exhibited higher thermal stability than the pristine LDPE. This is because of random grafting of ethyl 2-mercaptopropionate onto LDPE backbone.

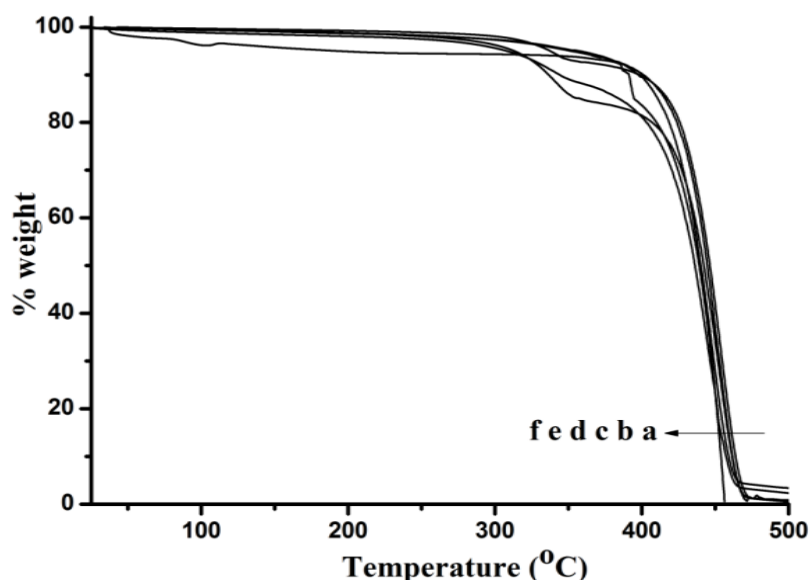


Fig. 14 a) TGA of Pristine LDPE, b-f) TGA of butyl 3-mercaptopropionate functionalized LDPE at different % weight of butyl 3-mercaptopropionate

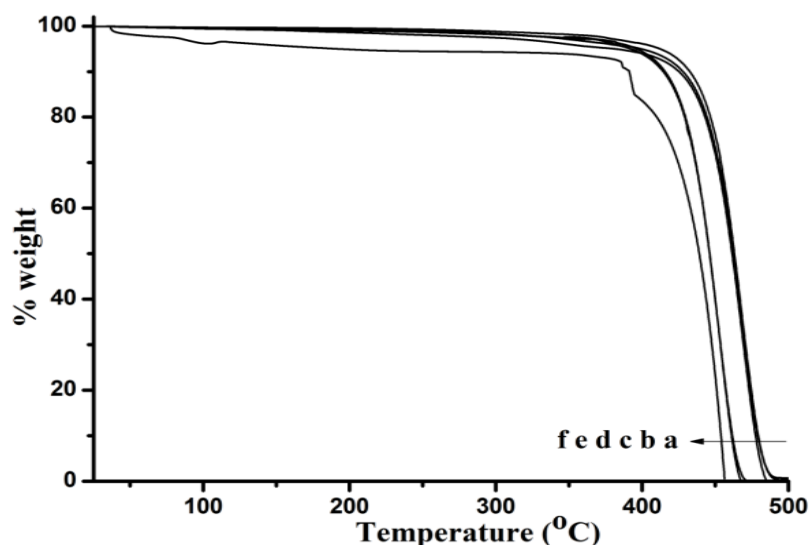


Fig. 15 a) TGA of Pristine LDPE, b-f) TGA of ethyl 2-mercaptopropionate functionalized LDPE at different % weight of ethyl 2-mercaptopropionate

IV. CONCLUSIONS

- 1) The area of C=O peak increased with the increase of % ester grafting.
- 2) The % functionalization was higher for ethyl 2-mercaptopropionate than butyl 3-mercaptopropionate.
- 3) Butyl 3-mercaptopropionate showed higher % crosslinking and C=C formation than ethyl 2-mercaptopropionate.
- 4) Butyl 3-mercaptopropionate consumed more amount of heat energy for functionalization than ethyl 2-mercaptopropionate.
- 5) Ethyl 2-mercaptopropionate consumed less amount of heat energy for crosslinking and C=C formation than butyl 3-mercaptopropionate.
- 6) DSC concluded the increase in T_m and T_c value for both systems.
- 7) TGA explored the increase in initial degradation temperature for both butyl 3-mercaptopropionate and ethyl 2-mercaptopropionate grafted LDPE.

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