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Functionalization of Low Density Polyethylene with Ethyl Crotonate and Ethyl Salicylate in the Presence of Free Radical Initiator: FTIR-RI Kinetics Study

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In this work, ethyl crotonate and ethyl salicylate esters were used for the functionalization of low density polyethylene (LDPE). The functionalization reaction was undertaken in an inert atmosphere of 160 ºC, under different experimental conditions by thermolysis method. The comprised following reaction such as functionalization, crosslinking and C=C formation were analyzed. FTIR spectral analysis was used to determine the % functionalization of LDPE and the order of functionalization reaction. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were also used to assess the thermal properties of the functionalized LDPE.

Key Words: LDPE, Functionalization, Esters, FTIR, DSC, TGA, Kinetics.

INTRODUCTION

Functionalization of polymer has generated considerable interests in the past few decades because the introduction of certain amount of functionalized short chain organic compound into polymer matrix produces environmental green polymer. Polyethylene (PE) is a non-hydrolysable polymer and hence results in environmental pollution. Polyethylene is the most widely used polymer in both packaging and automobiles sectors which possesses a fortuitous combination of many useful properties such as less weight, low cost, high chemical resistance and low dielectric constant. But its processability is confined because of environmental pollution. Such an environmental hazard can be outwitted by functionalization, which has been considered as the most desirable route for the functionalization of thermoplastic polymers. Tidjani *et al.*[1], explained the synthesis of maleic anhydride grafted polypropylene nano composite for fire applications. Ramos and coworkers[2] tested the effect of peroxide concentration on the structural modification of LLDPE. Chemical modification of polypropylene with mixture of isocynate and caprolactam was reported by Gaftarove and his research team[3]. Grafting of undecylenic acid onto ethylene octane copolymer under molten condition was reported in the literature[4]. The widely used structural modifications for polyolefins are maleic anhydride[5-9], glycidyl methacrylate[10-13], methacrylic acids and their derivatives[14-16], oxazolines[17,18] and silanes[19]. Anbarasan *et al.*[20], grafted epoxy esters onto HDPE backbone by free radical mechanism. In the present investigation, the LDPE was melt functionalized with ethyl crotonate and ethyl salicylate and their thermal properties were tested by DSC and TGA. The novelty of the present study is in calculating C=C formation during the functionalization process by FTIR study.

EXPERIMENTAL

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. Purification procedure was explained in our earlier publication[32]. Dicumyl peroxide (DCP, Ottokemi, India), 1,2-dichloro benzene (AR, Loba Chemi, India), ethyl crotonate (EC, Lancaster, UK), ethyl salicylate (ES, Ottokemi, India), dichloromethane (AR, Merck, India), Acetone (AR, Paxmy, India) and Toluene (Loba Chemi, India) used for further experimentation were used without subjecting them to any other purification.

Thermolysis reaction: Melt graft functionalization of LDPE with ethyl crotonate and ethyl salicylate was carried out through thermolysis reaction. The short procedure is illustrated further. Previously purified LDPE was taken in a 25 mL round-bottom flask along with the required amount 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 this mixing process, the solvents had been removed with the help of roto vapour under reduced pressure until a constant mass was obtained. The polymer/peroxide/ester mixture thus obtained was taken in a test tube reactor. The reactor was closed and degassed by the injection of sulphur free nitrogen gas for 0.5 h and then sealed. The reactor was heated in an oil bath at 160 ºC for 2.5 h without any stirring. When the reactants melted, the reaction started and led to various processes such as surface graft functionalization, alkenes formation and crosslinking reactions. Then the products were cut into small pieces and dissolved in DCB at 120 ºC for 2 h. During this dissolution process, the non-crosslinked (ester functionalization) part is soluble in DCB solvent whereas the crosslinked polymer is insoluble in DCB. 500 mL of acetone was added to precipitate the soluble and functionalized LDPE. The ester functionalized samples were weighed and stored in a zipper bag.

Characterization: FTIR spectroscopy plays a considerable role in research. Because of high sensitivity and low noise-to-signal ratio, FTIR spectrometer is used as a tool in various science and engineering fields. Moreover, this method is easy and in expensive. FTIR spectroscopy is used for both qualitative[21-24] and quantitative[25-28] analysis. Anbarasan and coworkers[29] reported that absorbance peak area is directly proportional to the concentration of substance. FTIR spectra of LDPE samples in the form of film before and after functionalization were recorded, using Shimadzu 8400 S FTIR spectrophotometer instrument. For FTIR film preparation, the soluble part of the modified LDPE was alone considered. Then the spectrum was recorded. The baseline correction was made carefully and the area of the peaks was determined using FTIR software. For the quantitative determination of % grafting, the area of the peaks at 1730 (due to carbonyl stretching vibration) and 1610 (C=C formation) and 720 (due to C-H out of plane bending vibration) cm^{-1} was determined and relative intensity was calculated as follows:

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

$$\text{Relative intensity of C=C formation} = \frac{A_{1610}}{A_{720}}$$

$$\text{Percentage ester grafting} = \frac{RI_{ester} \times W}{C \times 1.52} \times 100 \quad (1)$$

$$\text{Percentage C = C formation} = \frac{RI_{[C=C/C-H)} \times W}{C \times 0.35} \times 100 \quad (2)$$

where, W is the weight of non-crosslinked polymer, C is the % weight of peroxide and 1.52 and 0.35 are the calibration co-efficients taken from our earlier publication[7]. 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 ºC/min. The TGA analysis was performed under air purge at the heating rate of 10 ºC/min by using SDT 2960 simultaneous TGA and DSC, TA instruments. % cross linking was determined by using the following formula:

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

RESULTS AND DISCUSSION

For the functionalization of LDPE, two types of esters such as ethyl crotonate and ethyl salicylate were used. Equal % weight of DCP and esters were used for functionalization reaction and it was carried out under different experimental conditions such as variation of (% weight of DCP), different temperature and different intervals of thermolysis reaction time.

FTIR characterization: Fig. 1 represents the FTIR spectra of different % loading of ethyl crotonate functionalized LDPE. The important peaks are summarized below: Peaks between 3000 and 2600 cm^{-1} were related with the C-H stretching vibrations. The stretching of C=O bond could be seen at 1723 cm^{-1}. The C-H bending vibration was observed at 1490 cm^{-1}. A sharp peak at 730 cm^{-1} associated with the C-H deformations. The new peak, which appeared at the wave number of 1050 cm^{-1} was used to confirm the C-O-C ester linkage onto LDPE backbone. The peak at 1610 cm^{-1} [28,29] associated with the formation of olefin linkage (C=C) after melt functionalization reaction. The other peaks correspond to pure LDPE. Fig. 2 illustrates the FTIR spectra of ethyl salicylate functionalized LDPE under different % weight of ethyl salicylate. Here also, the above-mentioned peaks were observed. The FTIR spectra of ethyl crotonate and ethyl salicylate functionalized LDPE under different temperature and time interval were not shown here.

Effect of (Weight % of DCP) on functionalization %, crosslinking % and C=C formation: The equal ratio of both (% weight of ethyl crotonate) and DCP were used under this study. And also the concentration of ethyl crotonate was varied between 3 and 7 %. The relative intensity of [C=O/C-H] 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 ethyl crotonate onto LDPE. The universal log-log plot was used to find the order of functionalization reaction. The plot was made between log (% weight of DCP) and log ($RI_{[C=O/C-H]}$). Fig. 3(A) shows that the relative intensity

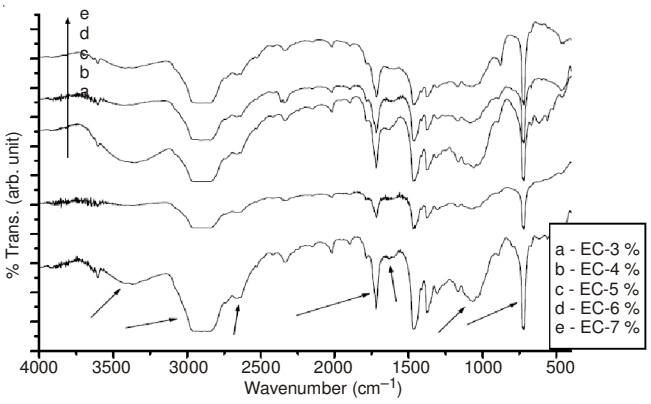

Fig. 1. FTIR spectrum of LDPE-DCP-ethyl crotonate system

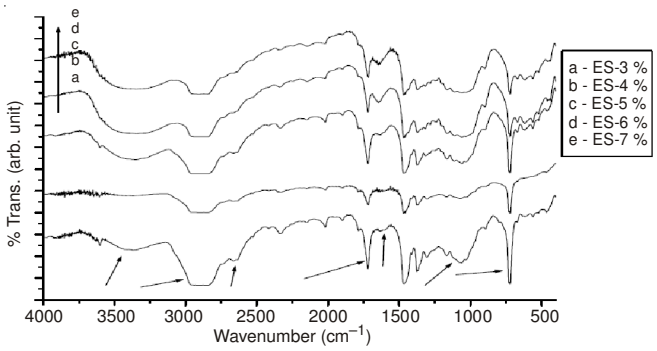

Fig. 2. FTIR spectrum of LDPE-DCP-ethyl salicylate system

increases with the increase of (% weight of DCP). The slope value was obtained as 1.35, which confirmed the 1.25 order of functionalization reaction with respect to (% weight of DCP). The rate of functionalization (R_f) can be written as follows: $R_f \alpha$ (% weight of DCP)$^{1.25}$. It means that 1.25 mol of DCP is required to functionalize one mole of LDPE. Under the same experimental conditions, another ester ethyl salicylate was melt functionalized with LDPE. The result obtained for ethyl salicylate is also more relevant with the ethyl crotonate functionalized LDPE. While increasing the % weight of DCP, the relative intensity of [C=O/C-H] is increased in a linear manner as shown in Fig. 3(B). Fabris *et al.*[30] reported that the relative intensity of A_{958}/A_{2020} was increased linearly with the increase of % weight of vinyltriethoxysilane during the functionalization reaction. The slope value was determined as 1.46 which confirmed 1.50 order of functionalization reaction with respect to (% weight of DCP). The rate of functionalization (R_f) can be written as follows: $R_f \alpha$ (% weight of DCP)$^{1.50}$. It means that 1.50 mol of DCP is required to functionalize one mole of LDPE. The % of ester grafting was determined by using eqn. 1 and the values are given in Table-1. During the melt functionalization reaction, crosslinking and olefin formation are competitive. The coupling between LDPE macroradicals led to the crosslinking reaction. Anbarasan *et al.*[28] reported the % crosslinking of HDPE during the functionalization reaction in the presence of different thioesters. It was observed that % crosslinking increased in a linear manner and is given in Fig. 4(A). A plot was made, (% weight of DCP) *versus* (log % crosslinking) and the slope value was found to be 0.42. This confirmed the 0.50 order of crosslinking reaction with respect to (% weight of DCP). The rate of crosslinking ($R_{C.L}$) reaction can be written as follows: $R_{C.L} \alpha$ (% weight of DCP)$^{0.50}$. It infers that 0.50 mol of DCP is required to crosslink one mole of LDPE. This system showed higher % crosslinking when compared with mercaptoester[32] system. Another ester ethyl salicylate grafted LDPE also showed that % crosslinking increased with respect to (% weight of DCP) as shown in Fig. 4(B). The slope value was determined as 0.22 which confirmed the 0.25 order of crosslinking reaction with respect to (% weight of DCP). $R_{C.L}$ reaction can be written as follows: $R_{C.L} \alpha$ (% weight of DCP)$^{0.25}$. It explained that 0.25 mol of DCP is required to crosslink one mole of LDPE. The % crosslinking values are listed in Table-1. In FTIR spectrum, there is one new peak around 1610 cm^{-1} and is related with olefin linkage. So the determination of olefin formation was essential during the graft functionalization reaction. Actually, it reduces the

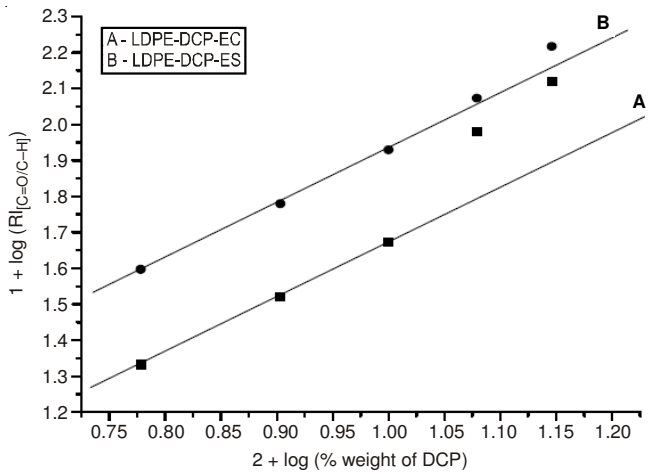

Fig. 3. Effect of % weight of DCP on RI of (A) LDPE-ethyl crotonate, (B) LDPE-ethyl salicylate time 2 h, temperature-160 ºC, weight of LDPE-2.0 g

TABLE-1
EFFECT OF % WEIGHT OF DCP ON FUNCTIONALIZATION, CROSS LINKING AND C=C FORMATION

Weight (%) of DCP	Functionalization (%)		Cross linking (%)		C=C formation (%)	
	EC	ES	EC	ES	EC	ES
3	25.64	27.86	53.5	46	1.71	0.74
4	27.45	49.74	60.5	54	2.65	1.94
5	31.61	55.90	63.0	60	3.05	2.94
6	52.49	65.09	68.5	64	3.51	5.74
7	61.91	78.45	72.5	70	4.20	9.88

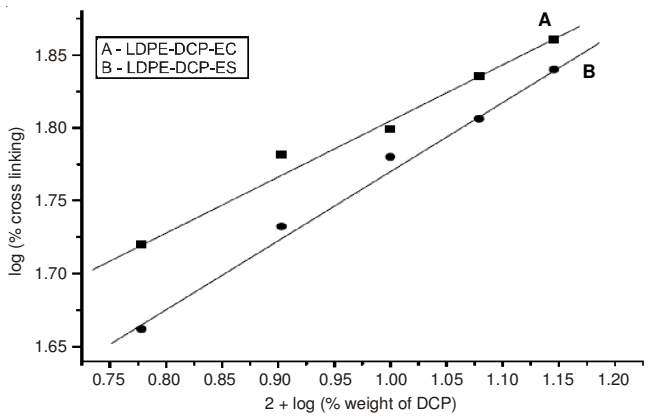

Fig. 4. Effect of % weight of DCP on cross linking of (A) LDPE-ethyl crotonate, (B) LDPE-ethyl salicylate time 2 h, temperature 160 ºC, weight of LDPE-2.0 g

molecular weight and restricts the chain rotation process. The obtained result showed that the % olefin formation was increased with the increase of (% weight of DCP) during the melt functionalization reaction for both ethyl crotonate and ethyl salicylate grafted LDPE systems. In order to find the order of olefin formation, the plot log (% weight of DCP) *versus* log ($RI_{[C=C/C-H]}$) was made and is shown in Fig. 5(A) for ethyl crotonate grafted system. The slope value was found to be 1.31 which confirmed 1.25 order of olefin formation with respect to (% weight of DCP). The rate of double bond formation ($R_{D.B}$) reaction can be written as follows: $R_{D.B} \alpha$ (% weight of DCP)$^{1.25}$. It infers that 1.25 mol of DCP is required to crosslink 1 mol of LDPE. From Fig. 5(B) the slope value was

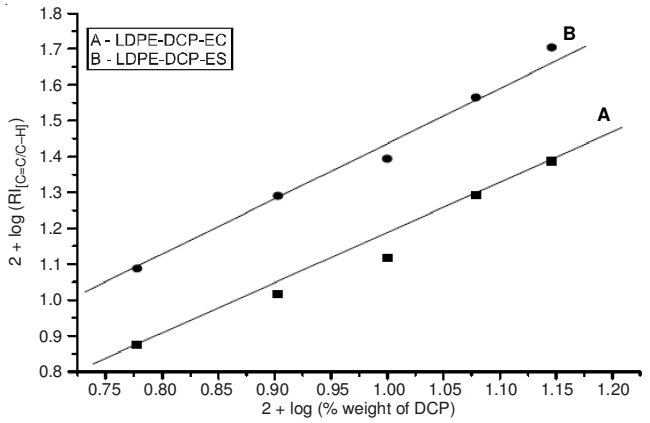

Fig. 5 Effect of % weight of DCP on C=C formation (A) LDPE-ethyl crotonate, (B) LDPE-ethyl salicylate time 2 h, temperature 160 ºC, weight of LDPE-2.0 g

obtained as 1.58 which confirmed 1.50 order of olefin formation with respect to (% weight of DCP) for ethyl salicylate grafted system. The rate of double bond formation ($R_{D.B}$) reaction can be written as follows: $R_{D.B} \alpha$ (% weight of DCP)$^{1.50}$. It infers that 1.50 mol of DCP is required to crosslink one mole of LDPE. Parthasarathy *et al.*[32] have reported the formation of olefin linkage during the melt graft functionalization reaction. The % olefin formation values were listed in Table-1.

Effect of temperature on % functionalization, % crosslinking and % double bond formation: Ethyl crotonate and ethyl salicylate esters were grafted onto LDPE at various temperatures ranging from 413-453 K, while keeping (% weight of DCP) and reaction time as constant. Energy of activation (E_a) has been studied for functionalization, crosslinking and olefin formation during melt graft functionalization reaction for both ester grafted systems. It was observed that $RI_{[C=O/C-H]}$ was increased upto 160 ºC then it was decreased for ethyl crotonate grafted LDPE. It revealed that formation of undesired by products at higher temperature with high activation energy. Similar trend was noticed and reported in earlier publication[31]. In order to find out activation energy (E_a) for functionalization reaction, the log-log plot was made between 1/T and log ($RI_{[C=O/C-H]}$) as given in Fig. 6(A). The slope value was determined and E_a was calculated as 436 kJ/mol. Fig. 6(B) showed the plot of 1/T *versus* log ($RI_{[C=O/C-H]}$) for ethyl salicylate grafted LDPE. The E_a value was calculated as 380 kJ/mol from the obtained slope value for ethyl salicylate functionalized LDPE. The % functionalization values are given in Table-2. Among these two systems, ethyl crotonate consumes more amount of heat energy for functionalization than ethyl salicylate. Here the lower E_a value supported higher % grafting of ethyl salicylate onto LDPE. The other possible reaction *i.e.*, crosslinking was increased with the increase of reaction temperature. Fig. 7(A) represented the plot of 1/T *versus* log (% crosslinking) from which the slope value was determined and E_a was calculated as 358 kJ/mol for ethyl crotonate grafted LDPE. In a similar fashion, E_a value was calculated as 400 kJ/mol for ethyl salicylate grafted LDPE as shown in Fig. 7(B). This concluded that ethyl crotonate grafted system consumes less amount of heat energy for crosslinking reaction than ethyl salicylate grafted system. The lower E_a value led to higher % crosslinking for ethyl crotonate than ethyl salicylate. The % crosslinking

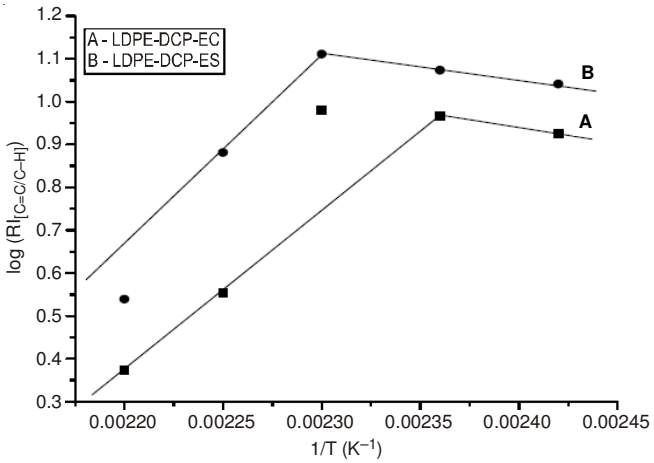

Fig. 6. Effect of temperature on functionalization (A) LDPE-ethyl crotonate, (B) LDPE-ethyl salicylate time 2 h, % weight of DCP-5 %, weight of LDPE-2.0 g

TABLE-2
EFFECT OF TEMPERATURE ON FUNCTIONALIZATION, CROSS LINKING AND C=C FORMATION

Temperature (K)	Functionalization (%)		Cross linking (%)		C=C formation (%)	
	EC	ES	EC	ES	EC	ES
413	55.44	72.46	59.5	53.0	3.00	2.14
423	60.87	77.94	65.2	59.0	4.40	4.14
433	62.85	85.08	70.0	66.5	4.65	5.57
443	23.57	50.04	76.0	71.3	5.37	7.20
453	15.52	22.78	81.5	75.0	6.54	8.17

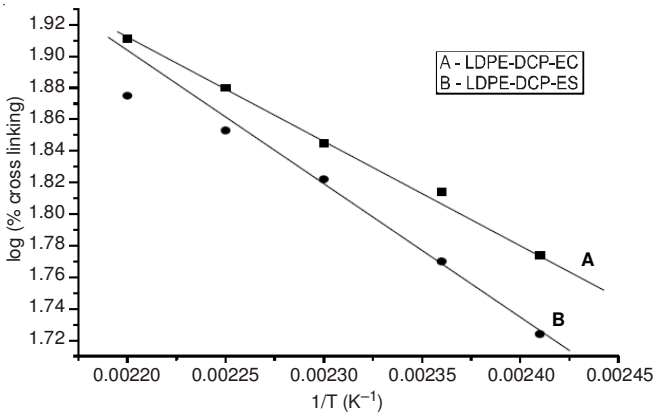

Fig. 7. Effect of temperature on cross linking of (A) LDPE-ethyl crotonate, (B) LDPE-ethyl salicylate time 2 h, % weight of DCP-5 %, weight of LDPE-2.0 g

values are given in Table-2. The C=C formation was increased linearly when the reaction time was increased. The plot between 1/T and log ($RI_{[C=C/C-H]}$ were used to find E_a of C=C formation for ethyl salicylate grafted system as shown in Fig. 8(A). It was calculated as 345 kJ/mol from the slope value. From Fig. 8(B) the activation energy of C=C formation was calculated as 302 KJ/mol for ethyl salicylate grafted LDPE. By our observation, ethyl salicylate system consumed less energy than ethyl crotonate grafted system and this resulted with higher % C=C formation for ethyl salicylate grafted system. The % C=C formation values are listed in Table-2.

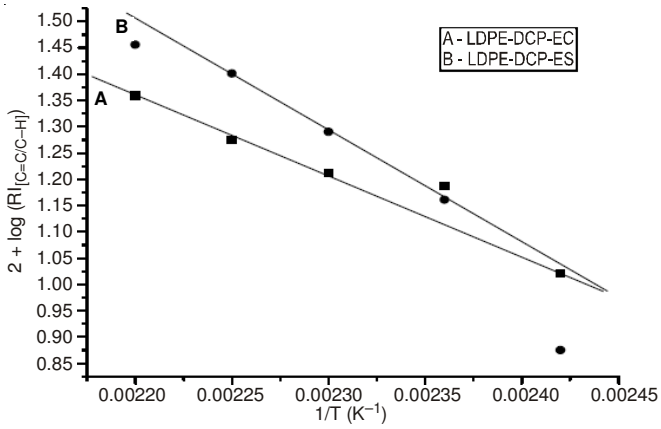

Fig. 8. Effect of temperature on C=C formation of (A) LDPE-ethyl crotonate, (B) LDPE-ethyl salicylate time 2 h, % weight of DCP-5 %, weight of LDPE-2.0 g

Effect of time on % functionalization, % crosslinking and % C=C formation: For this experimental condition, the reaction time was varied between 3600 and 12600 s by keeping other experimental conditions such as temperature (160 ºC) and (% weight of DCP) as constant. The $RI_{[C=O/C-H]}$ was increased linearly for ethyl crotonate grafted LDPE in accordance with an increase in reaction time. This is in accordance with our earlier publication[32]. It was observed from the plot of time *versus* log ($RI_{[C=O/C-H]}$) as shown in Fig. 9(A). Similar trend was observed for ethyl salicylate grafted LDPE system also. Fig. 9(B) revealed that $RI_{[C=O/C-H]}$ increased linearly. Table-3 highlighted the % functionalization values for both systems. The % crosslinking and % olefin formation were also increased with the increase of reaction time for both ethyl crotonate and ethyl salicylate grafted systems. This was confirmed from the plot time *versus* log ($RI_{[C=O/C-H]}$) as shown in Fig. 10(A,B) and 11(A,B). The % crosslinking and % olefin formation values are also given in Table-3.

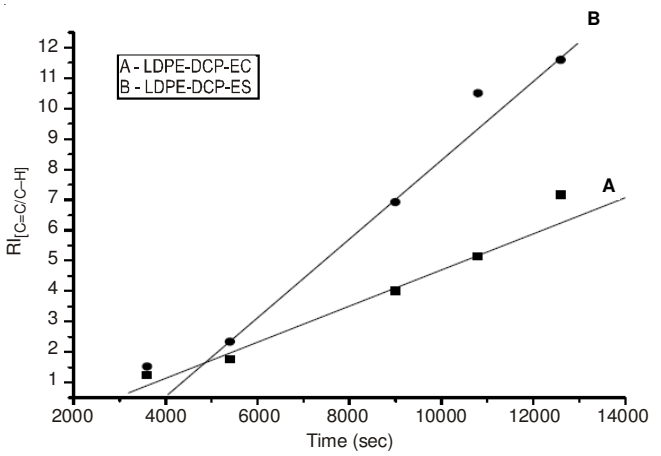

Fig. 9. Effect of time on functionalization of (A) LDPE-ethyl crotonate, (B) LDPE-ethyl salicylate temperature = 160 ºC, % weight of DCP-5 %, weight of LDPE-2.0 g

DSC profiles: Melt functionalization of LDPE with different esters such as ethyl crotonate and ethyl salicylate led to the change in physical and chemical properties of LDPE. Fig. 12 shows the DSC of different % loading of ethyl crotonate functionalized LDPE. While increasing the % weight of ethyl

TABLE-3
EFFECT OF TIME ON FUNCTIONALIZATION, CROSS LINKING AND C=C FORMATION

Time (s)	Functionalization (%)		Cross linking (%)		C=C formation (%)	
	EC	ES	EC	ES	EC	ES
3600	8.21	10.03	44.0	42	1.71	0.74
5400	11.63	15.37	51.1	48	2.05	1.85
9000	26.37	45.51	64.0	55	2.66	2.94
10800	29.88	69.09	71.5	68	3.53	5.74
12600	47.12	76.27	83.0	77	4.28	9.88

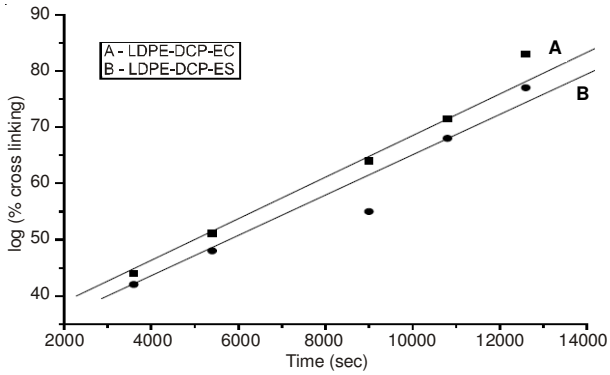

Fig. 10. Effect of time on cross linking of (A) LDPE-ethyl crotonate, (B) LDPE-ethyl salicylate temperature = 160 ºC, % weight of DCP-5 %, weight of LDPE-2.0 g

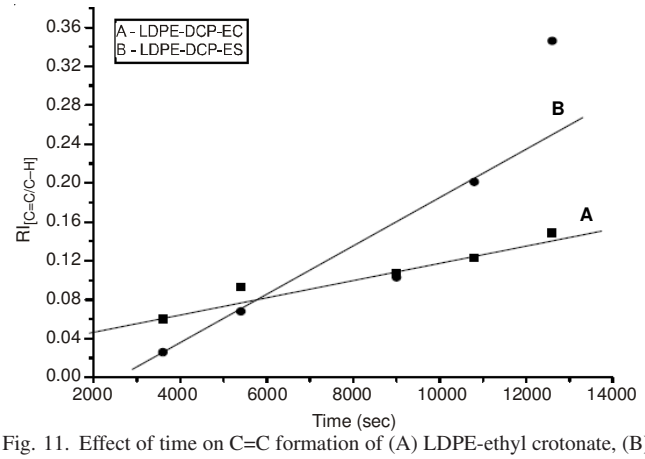

Fig. 11. Effect of time on C=C formation of (A) LDPE-ethyl crotonate, (B) LDPE-ethyl salicylate temperature = 160 ºC, % weight of DCP-5 %, weight of LDPE-2.0 g

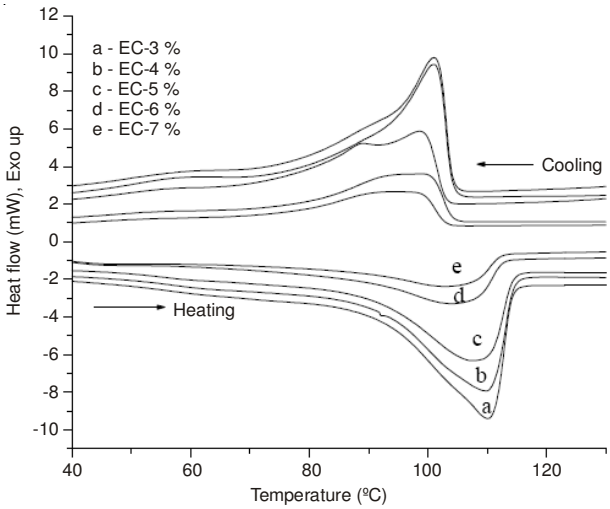

Fig. 12. DSC of LDPE-DCP-ethyl crotonate system

crotonate, the T_m value was suppressed by the grafted ethyl crotonate. Menyhard *et al.*[33] reported that the T_m of PP-g-MAH was found to be decreased with the increase of % content of MAH in its backbone. Our results are coinciding with their reports. On cooling, the T_c value was slightly shifted towards lower temperature. The reasons are as follows: (1) The change in the micro structure appearance of LDPE (α or β or γ form) slightly modifies during the melt functionalization process 2) This may be due to the chain scission of LDPE with terminal double bonds 3) Chain scission process accompanied with decrease in molecular weight accounts for the reduction in T_m 4) The formation of double bond in the middle of LDPE chain is one of the possibilities. Fig. 13 shows the DSC of different % weight loading of ethyl salicylate functionalized LDPE system. Here also, the decreased T_m and T_c values were recorded while increasing the % weight of ethyl salicylate. Parthasarathy *et al.*[32], reported decrease in T_m value for fuctionalized HDPE with amino and hydroxyl esters. Further research work on GPC measurement is going on in our laboratory.

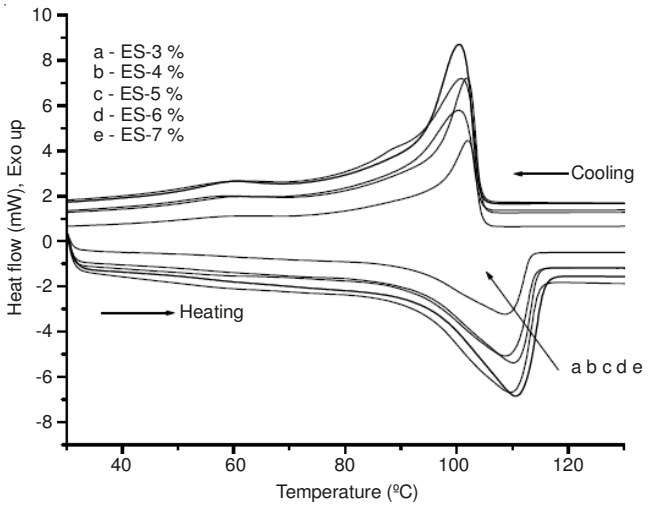

Fig. 13. DSC of LDPE-DCP-ethyl salicylate system

Thermogravimetric analysis: The thermal stability of functionalized LDPE was tested with the help of TGA instrument. The TGA was recorded at the heating rate of 10ºC/min under air atmosphere. The TGA of ethyl crotonate functionalized LDPE is shown in Fig. 14. The thermogram showed a single step degradation process. Upto 450 ºC, there was no change in the structure of LDPE. The major weight loss started around 460 ºC and extended upto 500 ºC. This accounted for the main chain scission or degradation. While increasing the % weight of ethyl crotonate, the thermal stability of LDPE was slightly affected. Due to the random grafting of ethyl crotonate onto LDPE, the extra thermal stability due to grafted side chain was not observed. The point to be noted here is while increasing the % weight of ethyl crotonate the T_{id} (initial degradation temperature) shifted towards lower temperature with slight decrease in degradation temperature of LDPE. Mostafa[34] 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. 15 show the TGA of ethyl salicylate functionalized LDPE. Here also, there was almost no change in thermal stability due to the random functionalization of ethyl salicylate in the presence of DCP. Due to the random grafting of ethyl salicylate onto LDPE, with very low % of ethyl salicylate used for functionalization process, the extra thermal stability due to grafted ethyl salicylate was not observed. But there was change in the T_{id} of ethyl salicylate functionalized LDPE. At higher % weight of ethyl salicylate, LDPE showed a considerable decrease in thermal stability.

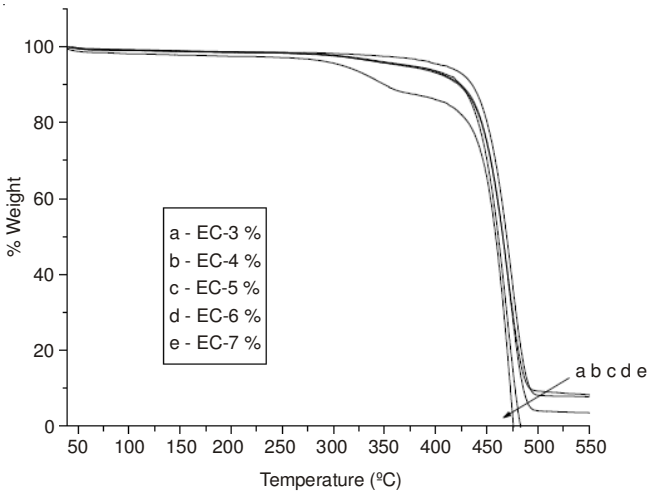

Fig. 14. TGA of LDPE-DCP-ethyl crotonate system

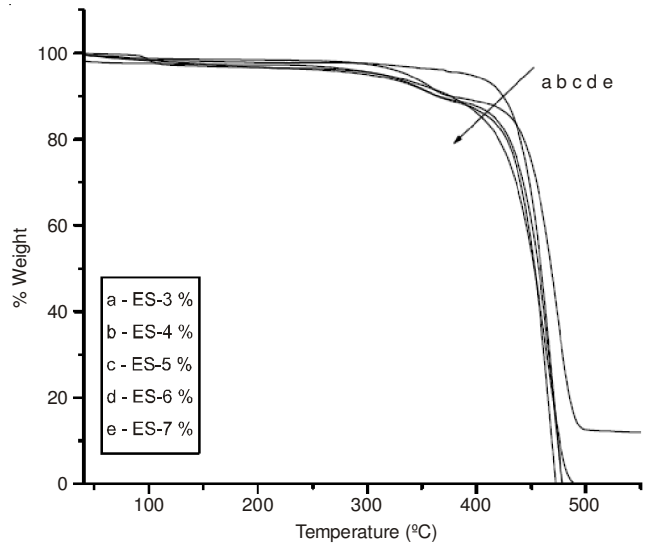

Fig. 15. TGA of LDPE-DCP-ethyl salicylate system

Conclusion

From the above FTIR-RI based kinetic study the important points were presented here as conclusion: (1) The relative intensity of C=O peak increased with increase in % weight loading of ethyl crotonate and ethyl salicylate onto LDPE. (2) ethyl crotonate showed higher % crosslinking and lower % olefin formation values than ethyl salicylate. (3) ethyl salicylate consumed lower amount of heat energy for functionalization than ethyl crotonate. (4) ethyl salicylate showed 1.50 order of functionalization reaction whereas ethyl crotonate exhibited 1.25 order of functionalization reaction with respect to (% weight of DCP). (5) DSC revealed that the decreased T_m and

T_c values for functionalized LDPE by both esters. (6) TGA witnessed the decrease in T_{id} for both ester grafted LDPE.

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