

Melt Functionalization of Linear Low-Density Poly(ethylene) with Succinimide and *N*-Hydroxy Succinimide by Thermolysis Method

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ABSTRACT: Linear low-density polyethylene (LLDPE) was functionalized with succinimide under different experimental conditions like change in time, temperature, and (% weight of succinimide). The FTIR Spectrum inferred that melt grafting of succinimide onto LLDPE followed the 0.50 order of reaction with respect to (% weight of succinimide). DSC was used to analyze the (melting temperature) T_m and (crystallization temperature) T_c val-

ues of functionalized LLDPE. Free radical mechanism explained the formation of nitroxide radical during the melt functionalization of *N*-hydroxy succinimide (NHS) with LLDPE in the presence of dicumyl peroxide. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 315–323, 2010

Key words: DSC; FTIR; imide; LLDPE; melt grafting; relative intensity; TGA

INTRODUCTION

Day-by-day, the world population is increased, and the industrialists are taking efforts to meet out the daily requirements of human beings particularly in the automobile and packaging sectors.^{1,2} In these two sectors, polyolefin and poly(vinyl alcohol) (PVA) are used. PVA has one hydroxyl functional group and hence water soluble with zero environmental pollution. However, in the case of polyolefins due to the absence of functional group or hydrolysable group, it creates environmental pollution. To avoid such an environmental pollution problem due to polyolefin, they are subjected to functionalization before processing. Let us do review the available literature regarding the functionalization of different polyolefins. Chaudhary et al.³ reported the Dicumyl peroxide mediated Tetra methyl piperidinyl derivative functionalized linear low-density polyethylene (LLDPE). New aspects of the reaction of high density polyethylene (HDPE) with maleic anhydride was studied, and its thermal and mechanical properties were reported.⁴ Glycidyl methacrylate grafted

isotactic polypropylene (iPP) report was also available in the literature.⁵ Polypropylene (PP) was functionalized with peroxy esters under molten condition with simultaneous cross-linking.⁶ Benzoyl peroxide mediated functionalization of LLDPE by tetra hydro phthalic anhydride and maleic anhydride had reported by Campos et al.⁷ The carbonyl functionalization by γ -radiation dosimetry of LDPE was reported.⁸ Fodor et al.⁹ determined the carbonyl containing functional groups in the oxidized polyethylene. *N*-Vinyl pyrrolidone was grafted onto LDPE by γ -radiation.¹⁰ Epoxy functionalized polyolefin report is available in the literature.¹¹ Grafting of maleic anhydride onto various polyethylene in the presence of peroxide was studied by Clark et al.¹² *t*-Butyl cumyl peroxide initiated grafting of isocyanate onto PP was reported with decrease in T_m and enthalpy of fusion (ΔH_m) values.¹³ By thorough literature survey, we could not find any report based on succinimide (SI) and *N*-hydroxy succinimide (NHS) functionalized LLDPE.

FTIR spectrometer is a useful tool for various science and engineering fields, because of its high sensitivity or detectivity toward traces amount of substance, low noise to signal ratio and this method is an easy and inexpensive one. FTIR spectroscopy is used for both qualitative^{14–19} and quantitative^{20–30} purposes. By thorough literature survey, we could not find any report based on FTIR based kinetics of SI and NHS functionalized LLDPE. In this

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investigation, for the first time, we are reporting here about SI and NHS grafting onto LLDPE in the presence of dicumyl peroxide (DCP) as a free radical initiator by thermolysis method and characterization through FTIR kinetics method.

EXPERIMENTAL

Materials

Linear low-density polyethylene (LLDPE) was purchased from Ottokemi, India. To remove the antioxidant present in the HDPE sample, it was purified before thermolysis reaction. Succinimide (SI, Spectrochem, India), *N*-hydroxy succinimide (NHS, Spectrochem), Dicumyl peroxide (DCP, Ottokemi), 1,2-dichloro benzene (AR, Loba Chemi, India), Dichloromethane (AR, Merck, India), Acetone (AR, Paxmy, India), and Toluene (Loba Chemi) were used for experimentation without subjecting them to further purification process.

Thermolysis reaction

Graft functionalization of LLDPE with SI was done through thermolysis reaction. The short procedure is mentioned here as follows: Previously purified LLDPE (2.0 g) was taken in a 25 mL round-bottom flask and a definite quantity of SI and equal quantity of DCP were taken in a solution of 6 mL of dichloromethane (9 mL)/cyclohexane (1 mL) mixture. Mixture of solvents was used only for the uniform distribution of SI or NHS throughout LLDPE backbone, otherwise agglomeration occurred. 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/imide mixture thus obtained was placed in a Test tube reactor. The reactor was closed and degassed by the injection of sulfur 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 like graft functionalization, alkene formation, and cross-linking reactions. These reactions are possible due to thermal or over oxidation reactions. After functionalization reactions, the contents were cut into small pieces and dissolved in dichloro benzene at 110 °C for 2 h. During this process, the functionalized noncross-linked polymer was solubilized, whereas the cross-linked one was not solubilized. The solubilized functionalized polymer was reprecipitated with 750 mL of acetone. The contents were filtered and dried under vacuum at 65 °C for 24 h. Thus, obtained powdered sample was weighed and stored in a zipper bag. The same

procedure was adopted for the functionalization of LLDPE with NHS in the presence of DCP.

Characterizations

FTIR spectra of LLDPE samples in the form of neat film before and after peroxide treatment were recorded, using Shimadzu 8400 S FTIR spectrophotometer instrument. For FTIR sample preparation, the soluble part of the modified LLDPE alone considered. The baseline correction was made carefully, and the corrected area of the peaks was determined using FTIR software. For the quantitative determination of percentage grafting, the area of the peaks at 1730, 1610, and 720 cm^{-1} was determined, and relative intensity was calculated as follows:

$$\begin{aligned} \text{Relative intensity of carbonyl (RI}_{[\text{C}=\text{O}/\text{C}-\text{H}]\text{])}} \\ = A_{1730}/A_{720} \end{aligned}$$

$$\text{Relative intensity of C=C (RI}_{[\text{C}=\text{C}/\text{C}-\text{H}]\text{])} = A_{1604}/A_{720}$$

$$\% \text{ Imide grafting} = (\text{RI}_{[\text{C}=\text{O}/\text{C}-\text{H}]\text{]} \times W/C \times 1.5) \times 100 \quad (1)$$

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

where, *W* is the weight of noncross-linked imide grafted polymer taken for FTIR study, *C* is the (% weight of peroxide) used, 1.52 and 0.35 are the calibration coefficient, as mentioned in our earlier publication.²⁸ The % cross-linking was determined by using the following formula:

$$\% \text{ cross - linking} = (X - Y/X) 100 \quad (3)$$

where *X*- weight of polymer taken for functionalization, *Y*-weight of noncross-linked polymer obtained after functionalization. DSC was recorded for the samples by using SDT 2960 TA (simultaneous TGA and DSC) instrument under nitrogen atmosphere at the heating rate of 10 °C/min. TGA analysis was performed under air purge at the heating rate of 10 °C/min by using the same instrument.

RESULTS AND DISCUSSION

FTIR spectrum

Figure 1 indicated the FTIR spectrum of pristine LLDPE. The important peaks are explained below. A twin broad peak at 2654 and 2901/cm are due to the C–H symmetric and antisymmetric stretching. A small hump at 1740/cm is associated with the carbonyl stretching (due to aerial oxidation of LLDPE). CH₂ stretching is exhibited at 1475/cm. The C–H out of plane bending vibration is appeared at 726/cm.

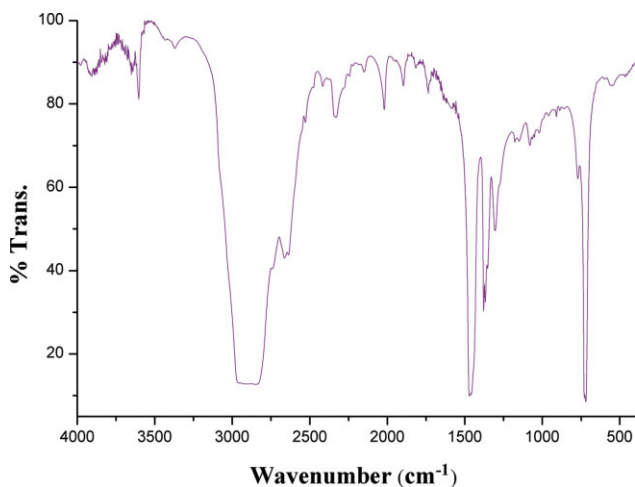


Figure 1 FTIR spectrum of pristine LLDPE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of time on relative intensity of [C=O/CH], [C=C/CH] and % cross-linking

Functionalization reaction was carried at different time interval. The time was varied between 3600 and 12,600 sec while keeping other experimental conditions as constant. The FTIR spectrum of different time interval is represented in Figure 2. The FTIR spectrum of SI grafted at different interval of time showed the same peaks as mentioned in the pristine LLDPE. Apart from those, some new peaks were appeared in the FTIR spectrum due to grafted SI. A peak at 1374/cm is due to the C—N stretching of SI. A small hump at 1612/cm accounts for the

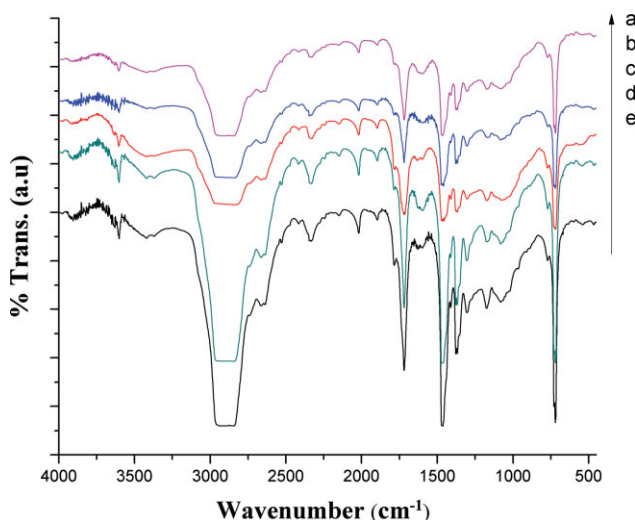


Figure 2 FTIR spectrum of LLDPE-g-SI at different time interval. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

C=C, (olefin formation). A sharp peak at 1722/cm explains the imide carbonyl stretching of SI. While increasing the reaction time, the RI of [C=O/CH] is increased. This is due to the grafting of more and more SI onto LLDPE backbone in the presence of DCP. During the long interval of reaction time, there is a chance for the interaction of SI radical with the LLDPE macro radicals, resulting with more grafting of SI onto LLDPE backbone. This is indicated in Figure 3(a) that is the plot of Time Vs RI_[C=O/CH]. (In all the FTIR overlay spectra, the y-axis is not necessary due to the normalized, arbitrary unit).

During the grafting of SI onto LLDPE backbone, the simultaneous competitive reaction is olefin formation. Olefin formation occurred due to the thermal oxidation reaction. While increasing the reaction time, the RI of [C=C/CH] is also increased [Fig. 3(b)]. The second competitive reaction is the cross-linking reaction. While increasing the time interval, the % cross-linking is also increased linearly. The cross-linking reaction is due to the coupling of LLDPE macro radicals. The plot of Time versus (% cross-linking) is shown in Figure 3(c) as a straight line. This confirmed that while increasing the reaction time the % C.L. also increased.

Table I showed the % functionalization and % C=C formation values while varying the reaction time interval. The % functionalization values increased from 25–52%, whereas the % C=C increased from 2 to 8.9%. The important point noted here is while increasing the time interval for melt functionalization reaction, both the % functionalization and % olefin formation are increased linearly.

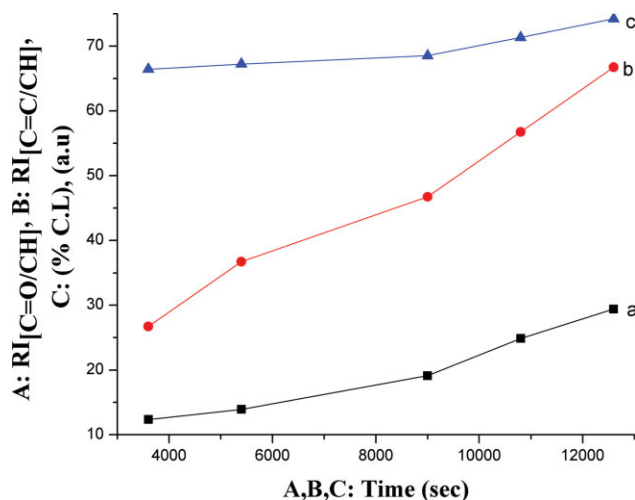


Figure 3 Effect of Time on (a) RI[C=O/CH], (b) RI[C=C/CH], (c) % C.L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Effect of Time on % Functionalisation, % C=C Formation and % C.L

System	% Funct.	% C=C
LLDPE-1% wt SI	25.25	2.0
LLDPE-2% wt SI	32.24	2.5
LLDPE-3% wt SI	41.16	3.8
LLDPE-4% wt SI	45.46	6.1
LLDPE-5% wt SI	52.45	8.9

Effect of % weight of SI on the RI of [C=O/CH], [C=C/CH] and % cross-linking

Figure 4 showed the FTIR spectrum SI grafted LLDPE at different % loading of SI. Here also the aforementioned peaks are appeared. Appearance of C—N stretching peak confirmed the chemical grafting of SI onto LLDPE backbone. The % weight of SI was varied between 1 and 5% weight. When the % weight of SI was increased, the RI of [C=O/CH] was increased from 0.83 to 1.53. This is due to the grafting of more amount of SI onto LLDPE backbone. To find out the order of functionalization reaction, the plot of $\log(\% \text{ weight of SI})$ versus $\log(\text{RI}_{[\text{C}=\text{O}/\text{CH}]})$ [Fig. 5(a)] was made and the slope value was determined as 0.45, which confirmed the 0.50 order of functionalization reaction with respect to % weight of SI. It indicated that 0.50 mol of SI was grafted onto 1 mol of LLDPE backbone. In our earlier communication, we have reported that mercaptoester functionalized HDPE, in which the % functionalization was very high due to ready hydrogen releasing nature of thio group.²⁸ The present system showed somewhat lower % functionalization

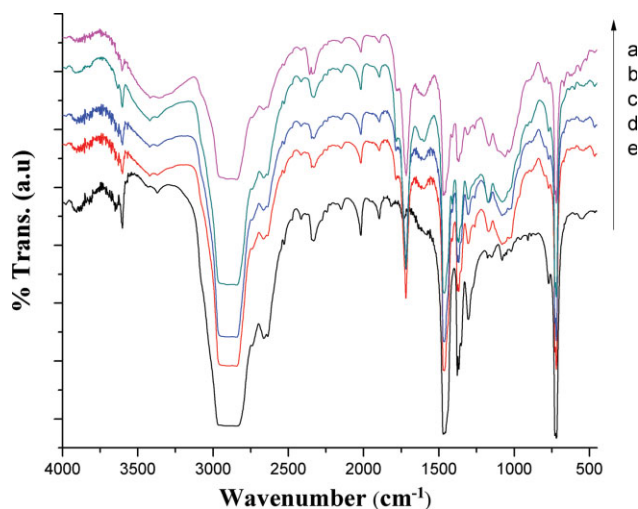


Figure 4 FTIR spectrum of LLDPE loaded with SI at (a) 1% weight, (b) 2% weight, (c) 3% weight, (d) 4% weight, (e) 5% weight. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

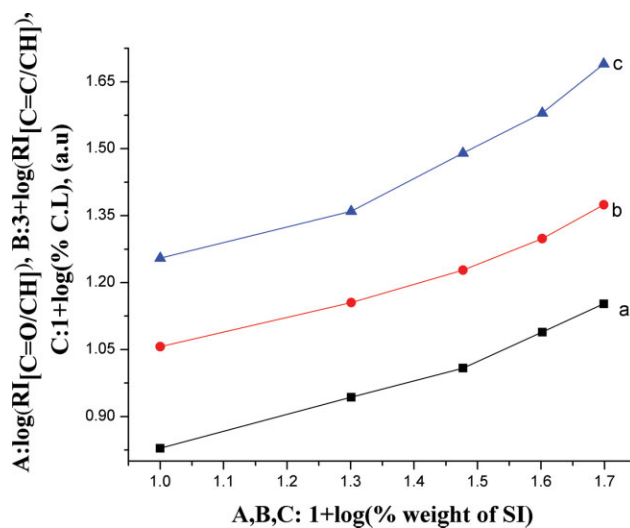


Figure 5 Effect of (% weight of SI) on (a) $\text{RI}_{[\text{C}=\text{O}/\text{CH}]}$, (b) $\text{RI}_{[\text{C}=\text{C}/\text{CH}]}$, (c) % C.L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

due to slight difficulty in the removal of hydrogen from the imide group.

The other possible reaction during the functionalization reaction is olefin formation reaction. It was noted that while increasing the % weight of SI the RI of [C=C/CH] was also increased from 1.05 to 1.37. The order of olefin formation reaction was determined by plotting $\log(\% \text{ weight of SI})$ versus $\log(\text{RI}_{[\text{C}=\text{C}/\text{CH}]})$ [Fig. 5(b)] and the slope value was calculated as 0.44. This confirmed the 0.50 order of olefin formation reaction with respect to (% weight of SI). This concluded that olefin formation linearly propagated with (% weight of SI).

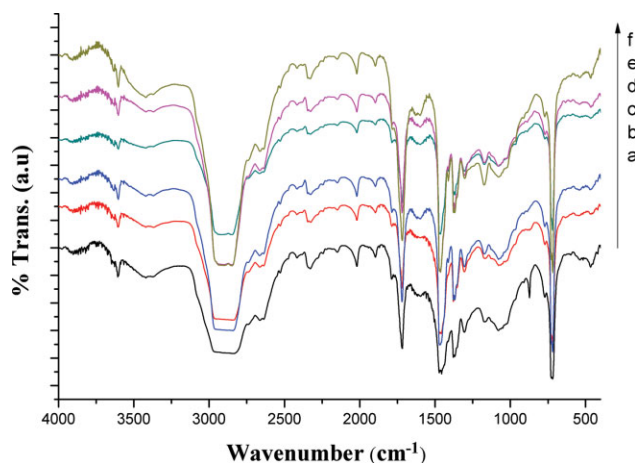


Figure 6 FTIR spectrum of LLDPE-g-SI at different temperature. (a) 1300 °C, (b) 1400 °C, (c) 1500 °C, (d) 1600 °C, (e) 1700 °C, (f) 1800 °C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Effect of (% Weight of SI) on % Functionalization, % C=C Formation and % C.L

System	% Funct.	% C=C	% C.L
LLDPE-1% wt SI	51.35	0.74	1.81
LLDPE-2% wt SI	68.61	3.16	2.46
LLDPE-3% wt SI	72.99	4.95	3.11
LLDPE-4% wt SI	78.13	6.14	3.98
LLDPE-5% wt SI	81.74	7.36	4.85

The C.L is the next possible reaction parallel to the functionalization reaction. While varying the (% weight of SI) the % C.L is increased linearly. During the loading of reactants for melt functionalization process, equal concentration of both DCP and SI were taken. The excess, unreacted DCP activated the formation of more and more HDPE macro radicals, which resulted with the cross-linking reactions. A graph was drawn between $\log(\% \text{ weight of SI})$ and $\log(\% \text{ C.L})$ [Fig. 5(c)] to find out the order of reaction. The plot showed a straight line with a slope value of 0.61. This informed us that the C.L reaction followed the 0.50 order of reaction with respect to (% weight of SI). Again this C.L reaction proved the linear propagation with (% weight of SI) that is coupling of LLDPE macro radicals were increased with the increase of (% weight of SI). In our Ref.²⁸, we have reported about the almost negligible % C.L values, exhibited by the thioester functionalization of HDPE.

Table II showed the % functionalization, % C=C formation and % C.L while varying the % weight of SI. The % functionalization varied between 51.3 and 81.7% while varying the % weight of SI from 1–5%

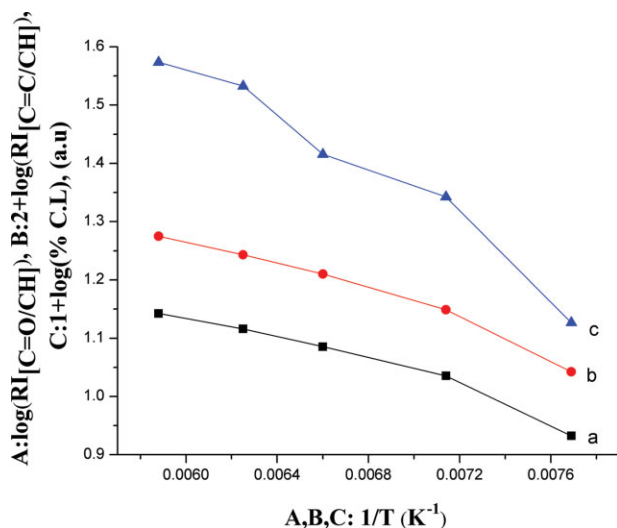


Figure 7 Effect of temperature on (a) $\text{RI}[\text{C}=\text{O}/\text{CH}]$, (b) $\text{RI}[\text{C}=\text{C}/\text{CH}]$, (c) % C.L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Effect of Temperature on % Functionalization, % C=C Formation and % C.L

System	% Funct.	% C=C	% C.L
LLDPE-1% wt SI	24.06	1.75	0.92
LLDPE-2% wt SI	35.11	2.64	1.57
LLDPE-3% wt SI	59.52	3.53	2.74
LLDPE-4% wt SI	75.54	5.97	4.26
LLDPE-5% wt SI	86.79	8.32	10.86

weight. The % C=C is varied from 0.74 to 7.36%, whereas the % C.L varied between 1.81 and 4.85%. While increasing the % weight of SI, the RI of functionalization and olefin formation are increased with the simultaneous increase of % C.L, and they followed the 0.50 order of reaction with respect to % weight of SI.

Effect of temperature on the RI of $[\text{C}=\text{O}/\text{CH}]$, $[\text{C}=\text{C}/\text{CH}]$ and % cross-linking

Effect of temperature plays a vital role in the determination of energy of activation (E_a) for melt grafting reaction (Fig. 6). While increasing the temperature the RI of $[\text{C}=\text{O}/\text{CH}]$ and $[\text{C}=\text{C}/\text{CH}]$ are increased linearly. Similar trend was followed by the % C.L reaction. E_a values can be determined from the famous Arrhenius equation. The E_a values for the functionalization, olefin formation and C.L reactions were determined from $1/T$ versus $\log(\text{RI}_{[\text{C}=\text{O}/\text{CH}]})$ [Fig. 7(a)], $1/T$ versus $\log(\text{RI}_{[\text{C}=\text{C}/\text{CH}]})$ [Fig. 7(b)] and $1/T$ versus $\log(\% \text{ C.L})$ [Fig. 7(c)] as 260.37, 290.22, and 318.75 kJ/mol respectively. The above E_a values indicated that functionalization was the most

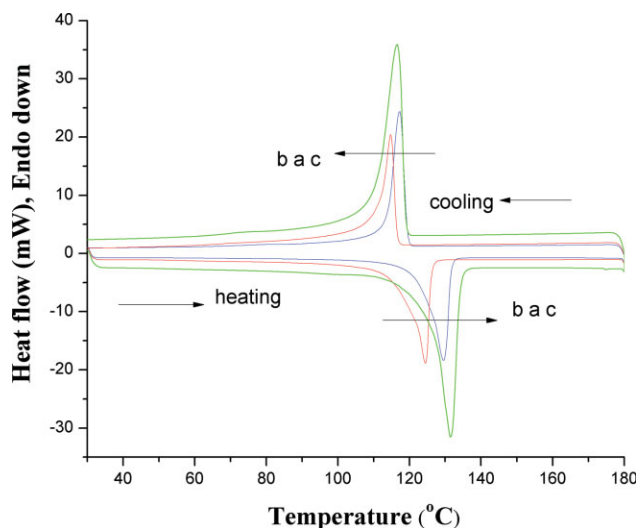


Figure 8 DSC of (a) Pristine LLDPE, (b) LLDPE-DCP thermolyzed, (c) LLDPE-thermolyzed. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

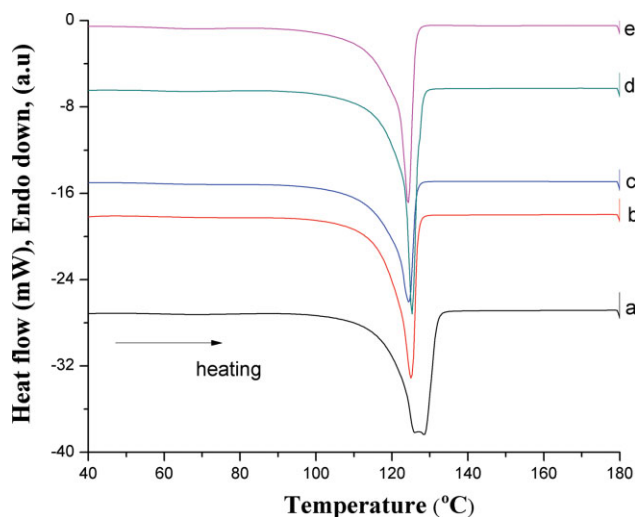


Figure 9 DSC heating scan of LLDPE loaded with SI at (a) 1% weight, (b) 2% weight, (c) 3% weight, (d) 4% weight, (e) 5% weight. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

feasible reaction, whereas C.L reaction consumed more amount of heat energy, and hence it was least favorable reaction. This is explained as follows: (1) at higher temperature the formation of SI radical was accelerated. (2) production of more amounts of free radicals from DCP at higher temperature was activated. (3) at higher temperature coupling of SI radical and LLDPE macro radicals were activated because of low consumption of heat energy for their coupling.

Table III showed the % functionalization, %C=C formation and % C.L values with respect to change in temperature. The % functionalization values

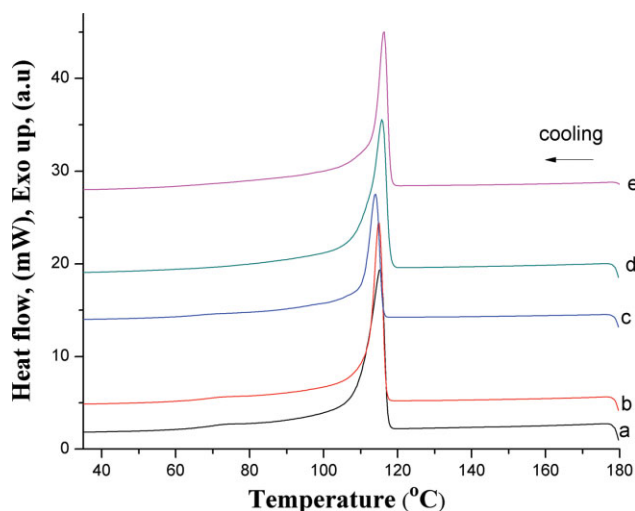


Figure 10 DSC cooling scan of LLDPE loaded with SI at (a) 1% weight, (b) 2% weight, (c) 3% weight, (d) 4% weight, (e) 5% weight. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
DSC Data of LLDPE-g-SI

System	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
LLDPE	119.58	79.24	106.99	60.50
LLDPE-1% wt SI	118.62	77.50	107.76	66.57
LLDPE-2% wt SI	117.24	76.73	107.80	70.67
LLDPE-3% wt SI	115.95	72.47	107.55	66.95
LLDPE-4% wt SI	115.45	70.28	106.61	63.89
LLDPE-5% wt SI	112.30	67.43	104.69	61.66

increased up to 86.7%, whereas the %C=C increased up to 8.32%. Temperature variation showed higher % C.L (0.92–10.86%).

DSC study

Figure 8 explained the DSC of LLDPE. DSC of pristine LLDPE is shown in Figure 8(a). Figure 8(a) showed the T_m and T_c values at 129.6 and 117.13 °C, respectively. Figure 8(b) represented the DSC of LLDPE after thermolysis reaction in the presence of DCP with the T_m and T_c values of 124.45 and 114.56 °C, respectively. Figure 8(c) exhibited the DSC of LLDPE after thermolysis reaction in the absence of DCP with the T_m and T_c values of 131.75 and 116.69 °C, respectively. The DSC results indicated that the thermolyzed LLDPE in the absence of DCP showed better T_m and T_c results with sharp peaks.

The DSC heating scan of SI functionalized samples are mentioned in Figure 9. The T_m of 1% weight SI mediated LLDPE was appeared at 127.35 °C, whereas the 5% weight SI mediated one showed the same at 124.15 °C. While increasing the (% weight of SI), the T_m and ΔH_m values of LLDPE are decreased

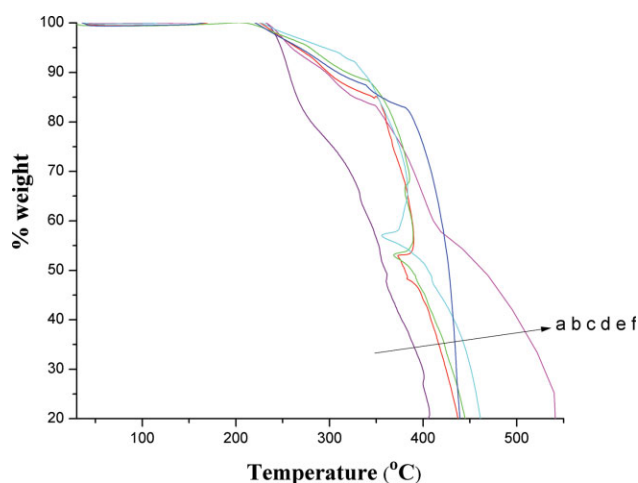


Figure 11 TGA of LLDPE loaded with SI at (a) 0% weight, (b) 1% weight, (c) 2% weight, (d) 3% weight, (e) 4% weight, (f) 5% weight. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
TGA Data of LLDPE-g-SI

System	% wt at 250 °C	% wt at 300 °C	% wt at 350 °C	% wt at 400 °C	% wt at 450 °C	% wt at 500 °C
LLDPE	93.13	75.61	57.28	28.66	—	—
LLDPE-1% wt SI	93.68	89.11	82.53	65.24	—	—
LLDPE-2% wt SI	97.45	90.28	87.62	43.79	—	—
LLDPE-3% wt SI	98.04	92.65	88.92	46.82	—	—
LLDPE-4% wt SI	97.58	94.12	82.43	51.08	30.55	—
LLDPE-5% wt SI	95.22	91.84	84.78	75.91	52.71	40.78

(Table IV). The reasons are: (1) hydrophilic SI is grafted onto hydrophobic LLDPE. (2) there may be reduction in molecular weight of LLDPE. (3) due to the olefin formation. (4) change in the internal microstructure of LLDPE during the melt grafting of SI. Our results are in accordance with Ref.¹³.

The DSC cooling scan of SI functionalized LLDPE is shown in Figure 10. The 1% weight SI mediated functionalization of LLDPE showed the T_c value at 115.11 °C whereas the 5% weight SI mediated one showed the same at 115.95 °C. This indicated that while increasing the (% weight of SI) the T_c and ΔH_c values of LLDPE were slightly shifted to higher temperature and then decreased (Table IV). This is associated with the induced crystallization (by the grafted SI units) and change in the internal microstructure of LLDPE after grafting with SI.

TGA profile

Thermal stability of LLDPE before and after functionalization reaction is represented in Figure 11. Figure 11(a) indicated the thermo gram of pristine LLDPE with single step degradation process (Table V). Up to 232 °C, there is a no change in thermal stability of pristine LLDPE, on further increase in temperature leads to the degradation of LLDPE backbone and the degradation extends up to 405 °C. Figure 11(b-f) indicated the thermo gram of SI functionalized LLDPE with two-step degradation process. The first minor weight loss step is associated with the degradation of grafted SI units, whereas the second major weight loss step is linked with the degradation of LLDPE backbone. The important point noted here is while increasing the (% weight of SI) the % of mass remain is increased. At 400 °C, the pristine LLDPE showed the % weight residue of 25.17%. The SI grafted LLDPE (1–5% weight) showed the % weight residue at 400 °C is 44.21, 45.06, 51.02, 65.23, and 75.17%, respectively (Table V). This concluded that the SI functionalized LLDPE showed improved thermal stability than the pristine LLDPE. Currently Qi and research team reported about the TGA of maleic anhydride grafted PEC, in which the initial degradation temperature (T_{id}) was increased with the % grafting of MAH.³¹

For the sake of comparison, the melt functionalization reaction of LLDPE was carried out with NHS at different % weight loading under similar experimental conditions used for SI case. Figure 12 exhibited the FTIR spectrum of LLDPE grafted with NHS at different % weight. The important peaks are characterized below. A broad peak around 3500/cm explains the OH stretching of water molecules associated with NHS. A small hump at 2832 and 2944/cm accounts for the C–H symmetric and antisymmetric stretching vibration, respectively. The imide carbonyl is appeared at 1722/cm. A peak at 1651/cm indicates the C=C stretching. Peaks at 1437 and 1487/cm are corresponding to C–N and C–O–N stretching vibration respectively. The C–H out of plane bending vibration is appeared at 815/cm. Remaining peaks in the finger print region are due to wagging, scissoring and rocking of C–H stretch.

The order of reaction for functionalization, olefin formation and C.L reactions can be determined by plotting $\log(\% \text{ weight of NHS})$ versus $\log(\text{RI}_{[C=O/CH]})$ [Fig. 13(a)], $\log(\% \text{ weight of NHS})$ versus $\log(\text{RI}_{[C=C/CH]})$ [Fig.13 (b)] and $\log(\% \text{ weight of NHS})$ versus $\log(\% \text{ C.L})$ [Fig. 13(c)] as 0.25, 0.50, and 1.25, respectively. This system behaved entirely

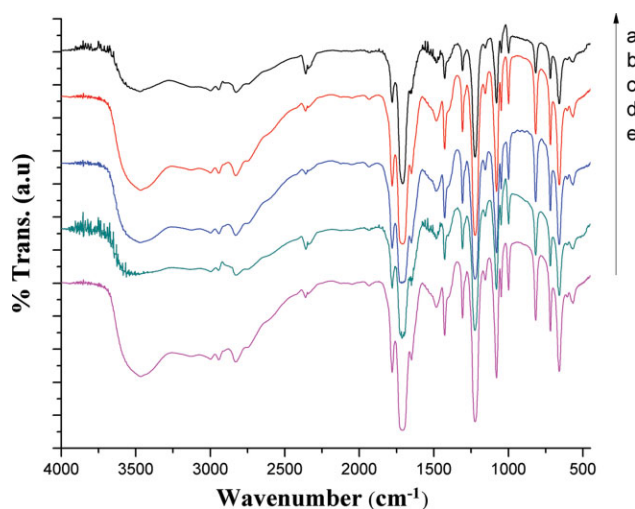


Figure 12 FTIR spectrum of LLDPE loaded with NHS at (a) 1% weight, (b) 2% weight, (c) 3% weight, (d) 4% weight, (e) 5% weight. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

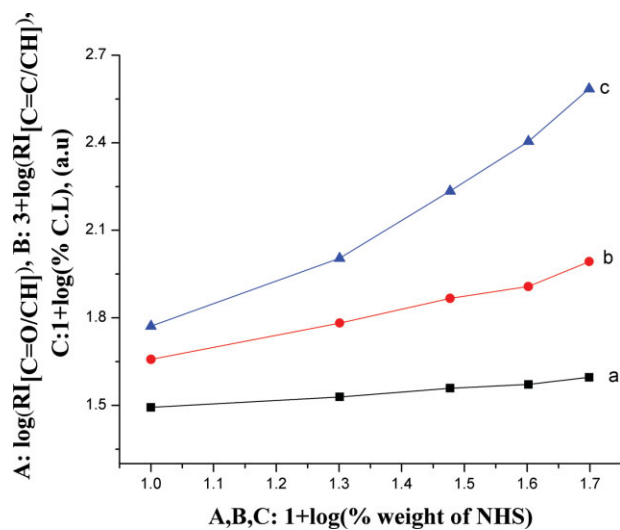


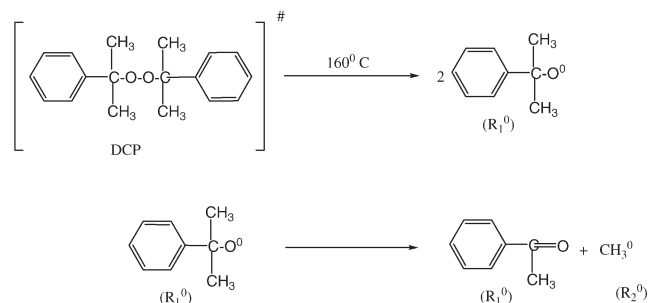
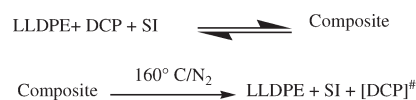
Figure 13 Effect of (% weight of NHS) on (a) RI[C=O/CH], (b) RI[C=C/CH], (c) % C.L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

different from SI system. This is due to the formation of nitroxide radical from NHS. On comparison, the SI system showed higher functionalization value than NHS system. However, the NHS system showed higher olefin formation and % C.L values (Table VI).

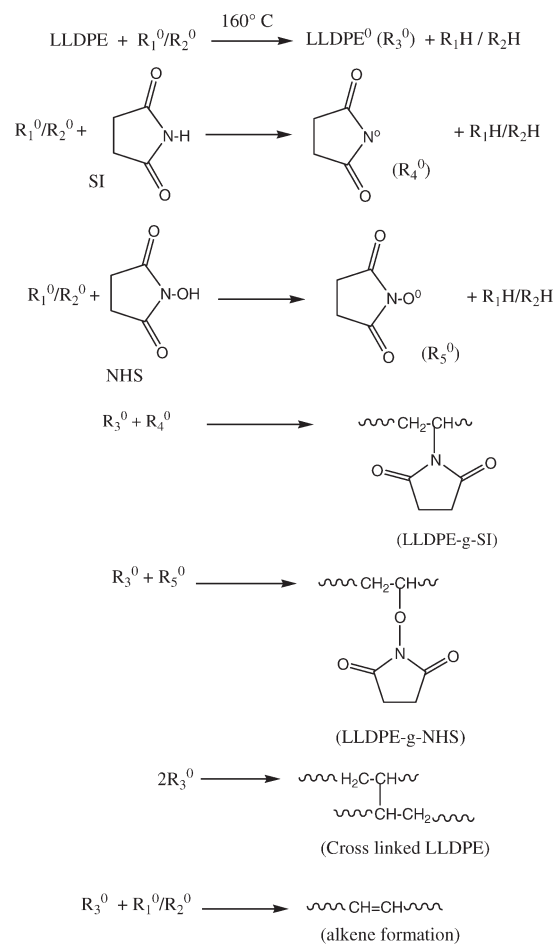
Grafting mechanism

In 2005, Anbarasan et al.²⁸ explained the mechanism of free radical grafting of thioester onto HDPE backbone. Similar type of mechanism is applied here. Melt functionalization reaction proceeds via free radical reaction. Free radical reactions precede through three steps namely initiation, propagation, and termination reactions. The mechanism is represented below:

Initiation



Propagation



CONCLUSIONS

From the above FTIR based kinetic study the important points are summarized here as conclusions. (1) The RI of both functionalization and olefin formation were increased with the increase of reaction time interval due to the coupling between LLDPE macro radical and SI or NHS radicals. (2) The SI variation showed 0.50 order of reaction for functionalization, olefin formation, and C.L. (3) The temperature

TABLE VI
Effect of (% Weight of NHS) on % functionalisation, % C=C Formation and % C.L

System	% Funct.	% C=C	% C.L
LLDPE-1% wt NHS	28.62	3.41	3.09
LLDPE-2% wt NHS	36.95	5.84	5.12
LLDPE-3% wt NHS	43.87	7.46	8.91
LLDPE-4% wt NHS	56.53	12.22	13.43
LLDPE-5% wt NHS	67.94	16.33	19.82

variation gave the E_a values for functionalization, olefin formation, and C.L were as 260.37, 290.22, and 318.75 kJ/mol. (4) DSC confirmed that both the T_m and ΔH_m were decreased, whereas T_c and ΔH_c values were initially increased and then decreased. (5) TGA concluded the increase in thermal stability for SI functionalized LLDPE. (6) NHS showed higher % C.L and % C=C values. (7) The free radical melt grafting mechanism confirmed the formation of nitroxide radical during the functionalization of LLDPE with NHS.

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