

Melt Functionalization of LDPE with Thio Ester, Amino Ester, and Hydroxy Ester by Thermolysis Method—An FTIR Study

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ABSTRACT: Low density poly(ethylene) (LDPE) was melt functionalized with three different esters namely, thio ester, amino ester, and hydroxy ester under inert atmosphere at 160°C with different experimental conditions. During the functionalization reaction, crosslinking (C.L) and C=C formation are the simultaneous competitive reactions. FTIR-RI analysis method was used to determine the % functionalization onto LDPE backbone and the order

of functionalization reaction. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) were used to assess the thermal properties of the functionalized LDPE. Suitable reaction scheme was proposed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2252–2261, 2011

Key words: branched; calorimetry; crosslinking; differential scanning calorimetry (DSC); FTIR

INTRODUCTION

Applications of polyolefin's are increased day by day in the packaging and automobile sectors, but due to their nonbiodegradability their applications are restricted to greater extent. The nonbiodegradability is due to the absence of hydrolysable or polar groups in the polyolefin's backbone. Functionalization is one of the methods available for the conversion of nonbiodegradable into a biodegradable one. Functionalization of polyolefin's generated considerable interest in the past few decades because the introduction of certain amount of functionalized short chain organic compound into a polymer matrix could produce an environmental green polyolefin. Functionalization can be done by two methods namely solution and solid state method. Among these two, solid state method (thermolysis method) is an environmental green method due to the nonutilization of toxic and hazardous solvents. Polyolefin's are the most widely used polymer in the field of packaging and automobile industries, which has a fortuitous combination of many useful properties, such as light weight, low cost, high thermal resistance, and low dielectric constant. Functionalization of polyolefin's with different functionalities was reported in the literature. For example, Yamamoto et al.¹ explained the surface grafting of

PE with methyl acrylate vapor. Ramos et al.² tested the effect of peroxide concentration on the structural modification of linear low density polyethylene (LLDPE). In 2008, Zhang and Ye³ reported about the surface grafting of branched PE on silica nano particles. Grafting of undecylenic acid onto ethylene octene copolymer under molten condition was reported in the literature.⁴ Poly(ethylene)s are melt functionalized with maleic anhydride,^{5–9} glycidyl methacrylate,^{10–13} methacrylic acids and their derivatives,^{14–16} oxazolines,^{17,18} and silane.¹⁹ Dokolas et al.²⁰ reported the graft copolymerization of methyl methacrylate, styrene and 4-vinyl pyridine onto LLDPE backbone. In 2002, Pesetskii et al.²¹ studied about the dicumyl peroxide (DCP) initiated grafting of glycidyl methacrylate onto polypropylene (PP) backbone. They reported about % grafting, TG/DTG, and DSC. Moad²² reviewed the graft copolymerization by reactive extrusion of polyolefins by maleic anhydride, fumarate, maleate esters, (meth)acrylate esters, and (meth)acrylic acids. By thorough literature survey, we found very few reports are available on the functionalization of low density poly(ethylene) (LDPE) with mercapto esters, amino esters, and hydroxy esters in the presence of dicumyl peroxide as a free radical initiator. In this investigation, we took this job as a challenge and successfully carried out the functionalization of LDPE with the hydroxyl, amino, and mercapto esters by thermolysis method in the presence of DCP for the first time.

The amount of ester grafted onto LDPE backbone can be quantitatively determined by chemical method and analytical method. The chemical method requires lot of toxic and hazardous solvents and again led to environmental pollution. Analytical method,

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particularly FTIR spectroscopy method, does not require any solvent and a useful tool for various science and engineering fields, because of its low noise to signal ratio, easy operation procedure, environmentally green, and inexpensive one. FTIR spectroscopy is used for both qualitative^{23–25} and quantitative^{26–38} analysis. By thorough literature survey, we could not find any report based on the FTIR-RI kinetic method for the estimation of ester grafting of the above said systems. Moreover, during the melt functionalization reaction, C–L and C=C double bond formations are occurred and the novelty of the present study is calculating the C=C formation during the functionalization process by FTIR-RI method in a quantitative way, for the first time.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE, M_w -125,000 Da) was purchased from Ottokemi, India. Dicumyl peroxide (DCP, Ottokemi), 1,2-dichloro benzene (Loba Chemi, India), 4-ethylacetate phenol (HE, Lancaster, UK, b.pt.–298°C), 4-ethylacetate aniline (AE, Across, b.pt.–188°C), 4-ethylacetate thiophenol (ME, Aldrich b.pt. –213°C), dichloro methane (Merck, India), acetone (Paxmy, India) and toluene (Loba Chemi, India) were used for further experimentation without subjecting them to any other purification. The ester functional compounds used in the present investigations are having higher boiling points than the reaction temperature (160°C). Hence, the chance for the evaporation of functional compounds is very few.

Purification of LDPE

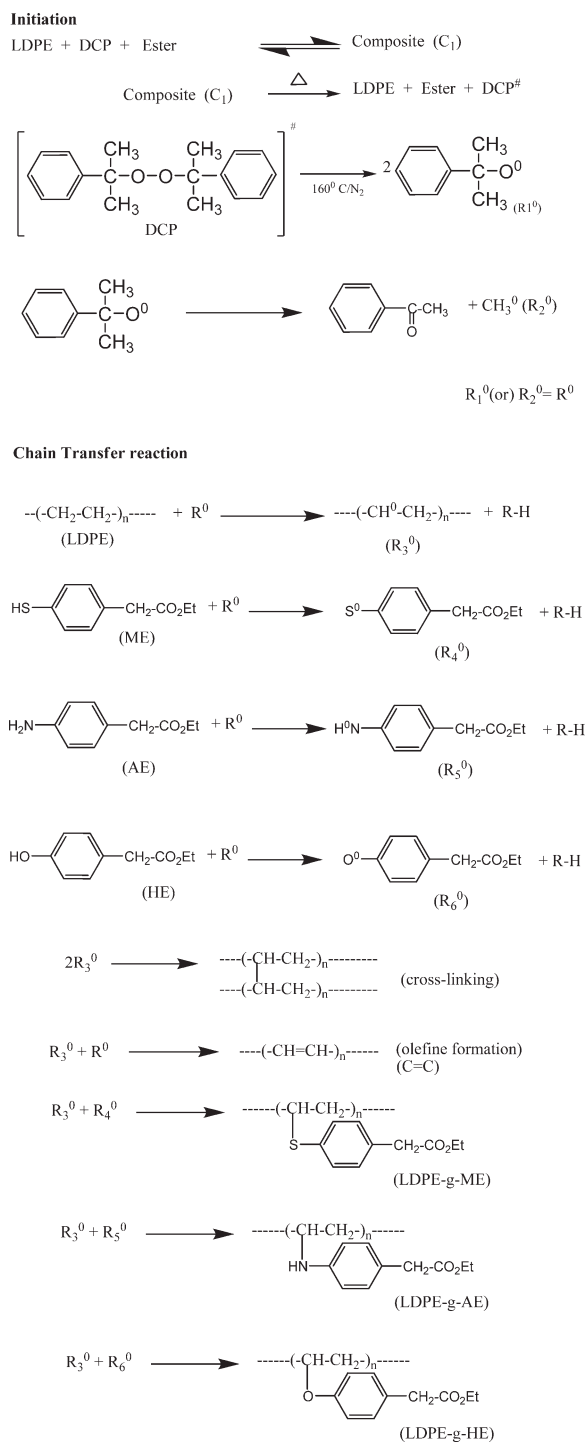
Five g of LDPE pellet sample was dissolved in 100 mL of toluene solvent in a round bottom flask at 110°C for 3 h to remove the antioxidants added during its long storage process. During the dissolution process the toluene solvent was boiled and evaporated. To avoid the loss of solvent molecules, the round bottom flask was fitted with a water condenser unit and the condenser was circulated with the ice cold water. Once all the LDPE powder samples were dissolved in toluene, then cooled it and 800 mL of acetone was added to precipitate the LDPE. The content was filtered and dried at 60°C for 24 h under vacuum. The dissolution and precipitation process were repeated 3 times to further purify the LDPE. Finally, the dried samples were weighed and stored in a zipper bag.

Synthesis of LDPE-g-ME or AE or HE

One g of pure LDPE powder sample was added with 1% weight of ME in 25 mL of cyclohexane-dichloromethane (1 : 9 v/v) solvent mixture in a 100 mL beaker with mild stirring. The solvent mixture was used to distribute the DCP and ME onto LDPE backbone uniformly, otherwise agglomeration occurred. Then 3% weight of DCP was mixed with the content of the beaker and the stirring was continued for another 1 h. In the present investigation, both DCP and ME were used in equal concentrations, particularly with 1 : 1 ratio, after many trial experiments. After 1 h of mixing, the solvent was removed by rotary evaporation. After the removal of solvent mixture, the ester/peroxide mixtures were coated on the PE powder as a micro film. The reaction mixture was transferred into a test tube reactor and de-aerated for 30 min with sulfur free nitrogen gas. After degassing, the temperature of the reactor was kept at 160°C for 2.5 h without stirring. During the melting process the ester/peroxide mixtures were diffused into the PE and led to various processes like functionalization and crosslinking, etc. Once the melt functionalization reaction was completed, the reactor was removed from the oil bath, cooled to room temperature and the functionalized LDPE samples were collected and cut into small pieces. These were put in toluene at 110°C for 30 min for the isolation purpose. The functionalized, noncrosslinked samples were dissolved in toluene while the functionalized crosslinked samples did not dissolve in toluene. The dissolved samples were reprecipitated by adding 600 mL of acetone and the crosslinked samples were isolated. The noncrosslinked sample was collected and dried under vacuum at 60°C. After drying, the sample was weighed and stored in a zipper bag. FTIR spectrum was obtained and quantitative calculations were done with the noncrosslinked, ester functionalized polymer. The reactions are indicated in Scheme 1.

Characterizations

FTIR spectra of LDPE samples in the form of pellet before and after functionalization were recorded by using a Shimadzu 8400 S FTIR spectrophotometer instrument. For FTIR pellet preparation, the soluble part of the modified LDPE alone was considered. Then the FTIR spectrum was recorded. The baseline correction was made carefully and the corrected area of the peaks was determined using FTIR software. To avoid error while recording FTIR spectrum, the corrected peak area was considered and the value for the above-mentioned peak was noted. To cross check the corrected peak area values, the FTIR spectra were recorded for each sample disc in different



Scheme 1 Melt functionalization of LDPE with ME, AE, and HE.

parts for three times. On each measurement, the corrected peak area values were noted and closely analyzed. It was found that on each measurement for the same pellet, we found 1.1 to 1.3% errors in the corrected peak area values. In analytical chemistry up to 2% error is allowed. This confirmed the uniform mixing of functionalized samples in the spectral grade KBr. Now the average values are consid-

ered here for further calculations. Hence, the standard deviation plot is not necessary. 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. The FTIR spectrum was recorded without predicting the lower and upper limits of peaks, 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 % grafting, the area of the peaks at 1730 cm^{-1} (due to carbonyl stretching vibration), $\text{C}=\text{C}$ stretching at 1604 cm^{-1} and 720 cm^{-1} (due to $\text{C}-\text{H}$ out of plane bending vibration) was determined and relative intensity (RI) was calculated as follows:

$$\text{RI of carbonyl} = A_{1730}/A_{720}$$

$$\text{RI of C=C double bond} = A_{1604}/A_{720}$$

$$\% \text{ Ester grafting} = \text{RI}_{[\text{C}=\text{O}/\text{CH}]} \times W/C \times 1.52 \times 100 \quad (1)$$

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

where W is the weight of noncrosslinked polymer taken for FTIR-RI analysis, C is the % weight of peroxide and 0.35 and 1.52 are the calibration coefficients taken from our earlier publication.³⁸ DSC was recorded for the samples by using SDT 2960 simultaneous TGA and DSC, TA instruments under nitrogen atmosphere at the heating rate of $10^\circ\text{C}/\text{min}$. The TGA analysis was performed under air purge at the heating rate of $10^\circ\text{C}/\text{min}$ by using the SDT 2960 simultaneous TGA and DSC, TA instruments. The % C.L. was determined by using the following formula:

$$\% \text{crosslinking} = (\text{weight of polymer taken for functionalization} - (\text{weight of noncrosslinked polymer obtained after functionalization}) / (\text{weight of polymer taken for functionalization}) \times 100$$

RESULTS AND DISCUSSION

For the functionalization of LDPE, three types of esters such as AE, ME and HE were used. Equal % weight of DCP and ester (AE, HE and ME) were used for the functionalization reaction and was carried out under different experimental conditions such as variation in % weight of DCP, different

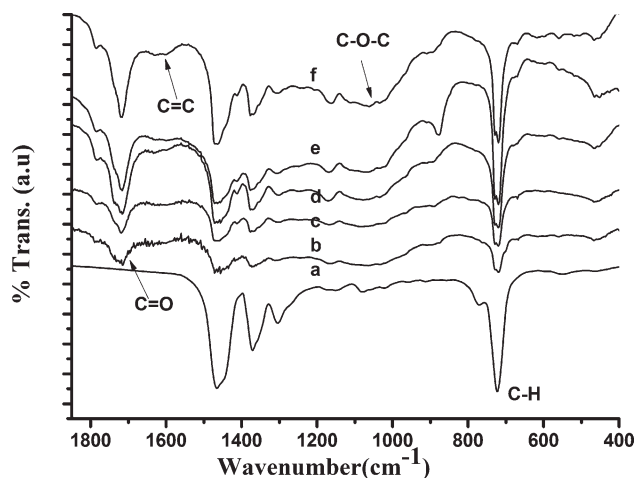


Figure 1 FTIR spectrum of LDPE loaded with ME at (a) 0% weight, (b) 3% weight, (c) 4% weight, (d) 5% weight, (e) 6% weight, (f) 7% weight.

temperature and different intervals of thermolysis reaction time. The results are presented in the order of functionalization, C.L and C=C formations for these three esters.

FTIR study

Figure 1 represents the FTIR spectra of LDPE before and after functionalization reactions. Figure 1(a) indicates the FTIR spectrum of pristine LDPE. The important peaks are characterized below: A sharp peak at 730 cm^{-1} is associated with the C—H out of plane bending vibration. A peak at 1459 cm^{-1} is corresponding to the C—H bending vibration of LDPE. Figure 1 (b–f) indicates the FTIR spectra of 3,4,5,6, and 7% weight of ME loaded LDPE, respectively. The new peaks corresponding to the ester grafting is

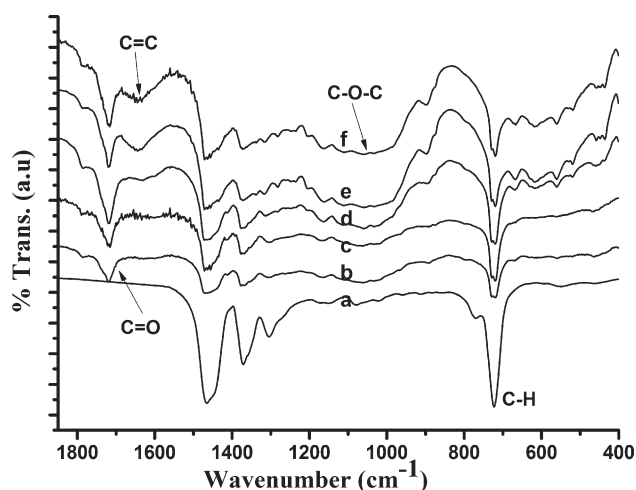


Figure 2 FTIR spectrum of LDPE loaded with AE at (a) 0% weight, (b) 3% weight, (c) 4% weight, (d) 5% weight, (e) 6% weight, (f) 7% weight.

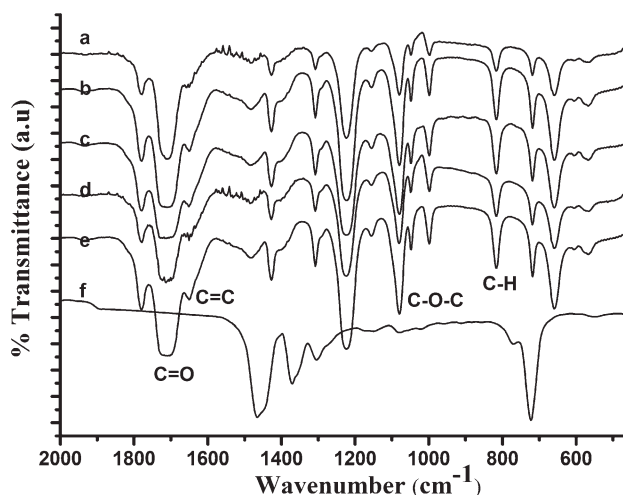


Figure 3 FTIR spectrum of LDPE loaded with HE at (a) 3% weight, (b) 4% weight, (c) 5% weight, (d) 6% weight, (e) 7% weight.

mentioned below. A broad peak appeared at the wave number of 1050 cm^{-1} is used to confirm the C—O—C ester linkage due to ester grafting reaction. The stretching of C=O bond is seen at 1723 cm^{-1} . The C=C stretching vibration is observed at 1660 cm^{-1} as a weak band. This is due to the negligible C=C formation reaction. The C—S bond is appeared at 672 cm^{-1} as a small hump. Appearance of these new peaks confirmed the chemical grafting of ME onto the LDPE backbone.

Figure 2 indicates the FTIR spectra of LDPE before and after functionalization with AE. Figure 2(a) confirms the FTIR spectrum of pristine LDPE. The important peaks were characterized above. Figure 2(b–f) declares the FTIR spectra of 3,4,5,6, and 7% weight AE loaded LDPE, respectively. Here also the above said peaks are observed. The C—N stretching is appeared at 1375 cm^{-1} . Thus, the FTIR spectrum confirmed the presence of an amino ester group on the LDPE backbone via thermolysis reaction. Figure 3(a–e) indicates the FTIR spectra of LDPE loaded with HE at 3,4,5,6, and 7% weight, respectively. The peaks corresponding to ester (1723 cm^{-1}), C—H out of plane bending vibration (730 cm^{-1}), C=C stretching (1490 cm^{-1}) and C—O—C linkage (1050 cm^{-1}) are observed and confirmed the chemical grafting of HE onto LDPE backbone by thermolysis reaction. For the sake of comparison, the FTIR spectrum of pristine LDPE is given in Figure 3(f). The important peaks of pristine LDPE were already discussed well.

Effect of time on FTIR-RI of functionalization, olefine formation, and C.L

LDPE was allowed to ester grafting reaction in the presence of DCP and AE at different intervals of

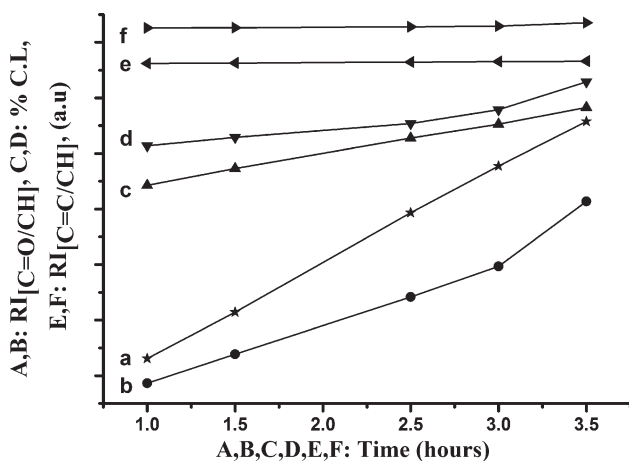


Figure 4 Effect of Time on (a) $RI_{[C=O/CH]}$, (c) (% C.L), (e) $RI_{[C=C/CH]}$ of LDPE-DCP-AE system and (b) $RI_{[C=O/CH]}$, (d) (% C.L), (f) $RI_{[C=C/CH]}$ of LDPE-DCP-HE system, % weight of DCP = 5%, % weight of ester = 5%, Temperature-160°C, weight of LDPE-2.0 g

reaction time. The reaction time was varied between 1.0 and 3.5 h, while the other experimental conditions were kept constant. Figure 4a represents the effect of time on $RI_{[C=O/CH]}$ for LDPE-DCP-AE system. While increasing the reaction time intervals, the RI of ester carbonyl is increased. Figure 4(a) shows a straight line and infers that increase in reaction time leads to increase in % ester grafting. Longer reaction time is responsible for the possible interaction between LDPE macro radicals with AE radicals, resulting in higher FTIR-RI of $[C=O/C-H]$. Similar phenomenon is also observed for HE and ME esters, which represents as the linear relationship in Figures 4(b) and 5(a), respectively.

On comparison, the LDPE-ME system yielded higher FTIR-RI of $[C=O/C-H]$ values. This accounted the structural entity of ME. The ME contains one active thiol group and it is an active hydrogen donating group. One hydrogen atom can be easily donated by the active thiol group and readily participated in the melt grafting reaction. In the case of AE, withdrawal of a hydrogen atom from the amino group is little bit difficult due to the electron rich nature of amino group. In the case of HE, one hydrogen atom can be easily removed from the hydroxyl group of HE and the resulting phenoxy radical involved in the resonance stabilization with the benzene ring. It formed a semiquinone like structure which destabilized the active participation of HE radical in the functionalization process. In 2009, Anbarasan et al.³⁸ reported the melt grafting reaction of mercapto esters with HDPE in the presence of DCP as a free radical initiator. Also, they reported that the mercapto ester yielded a maximum ester grafting with negligible C.L reaction. When compared with the mercapto ester, the present system particularly the HE gave a low

$RI_{[C=O/CH]}$ values, because the mercapto esters are good hydrogen donors.

C.L is the simultaneous reaction during the melt functionalization reaction. C.L is the first competitive reaction to the functionalization reaction. While increasing the reaction time intervals, the % C.L was increased slowly for LDPE-DCP-AE system. This is due to the very low coupling reaction between LDPE macro radicals. In the case of LDPE-DCP-HE system, the % C.L was increased in a linear manner. Figure 4(c,d) and 5(b) indicate a plot of time versus % C.L for LDPE-AE, LDPE-HE and LDPE-ME systems respectively. Figure 4(d) indicates a straight line whereas Figure 5(b) shows a horizontal line. The plots, Figure 4(c) and d indicate that while increasing the reaction time interval the % C.L values are increased in a linear manner. On comparison, the ME system produced the lowest % C.L than the AE and HE systems. This is due to the following reasons. (1)ME has a thiol group which is a ready hydrogen donor. (2)HE is readily donating one hydrogen atom from the hydroxyl group and which is involved in the resonance stabilization with benzene ring of HE. (3)AE produced amino radical cation in a slow manner. When compared with mercapto esters, the AE and HE systems yielded higher % C.L values due to their structural effect during the melt functionalization reaction. This is in accordance with literature report.³⁸

The second competitive reaction during the melt functionalization reaction is the C=C double bond formation reaction. This is ascribed to the oxidative degradation reaction, led by the DCP at higher temperature. While increasing the reaction time intervals, the RI of double bond formation is increased very slowly. Figure 4(e,f) and Figure 5(C) indicate a plot of time versus $RI_{[C=C/CH]}$ for AE, HE and ME

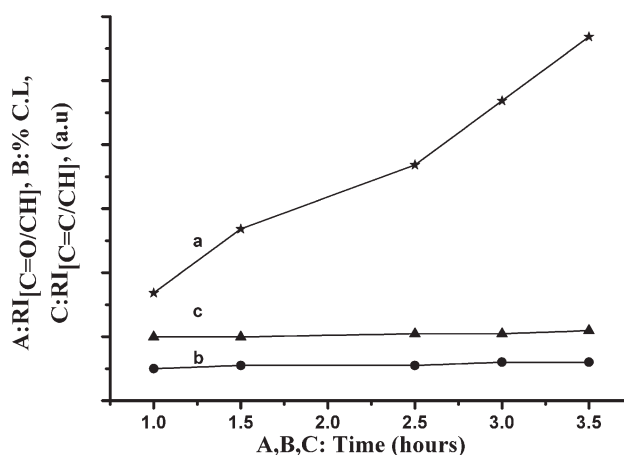


Figure 5 Effect of Time on (a) $RI_{[C=O/CH]}$, (b) (% C.L), (c) $RI_{[C=C/CH]}$ of LDPE-DCP-ME system, % weight of DCP = 5%, % weight of ME = 5%, Temperature-160°C, weight of LDPE-2.0 g

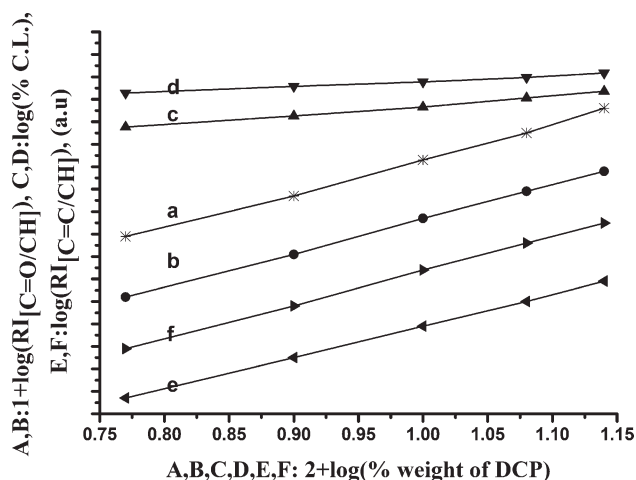


Figure 6 Effect of (% weight of DCP) on (a) $RI_{[C=O/CH]}$, (c) (% C.L), (e) $RI_{[C=C/CH]}$ of LDPE-DCP-AE system and (b) $RI_{[C=O/CH]}$, (d) (% CL), (f) $RI_{[C=C/CH]}$ of LDPE-DCP-HE system, Time-2 h, Temperature-160°C, weight of LDPE-2.0 g

systems, respectively. In comparison, the AE and HE systems yielded higher $RI_{[C=C/CH]}$ values due to the slower generation of free radicals from AE and HE, respectively. In over all comparison, the ME yielded higher $RI_{[C=O/CH]}$ values³⁸ whereas the AE and HE gave a higher $RI_{[C=C/CH]}$ and % C.L values respectively, due to their structural effect. From our earlier publications^{36,37} we optimized the experimental conditions for the present system. Thermolysis reaction time of more than 2.5 h led to the very high C.L value and found nonprocessable. The main aim of the present investigation is to obtain a maximum % functionalization with minimum or negligible C.L or olefin formation.

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

The % weight composition of DCP and AE were kept in an equal concentration during the entire study. In this work, AE or DCP concentration was varied between 3 and 7% weight. During the variation of % weight of DCP, the other experimental conditions like temperature and time were maintained as constant. The increment in the % loading

of AE-DCP increased the $RI_{[C=O/CH]}$. The reason is explained as follows: (1) due to the availability of enormous free radicals^{35,39} derived from homolytic decomposition of DCP, which led to the grafting of AE onto LDPE. The universal log-log plot was used to find out the order of functionalization reaction (i.e.) $\log(\% \text{ weight of DCP})$ versus $\log(RI_{[C=O/CH]})$ [Fig. 6(a)]. Figure 6(a) represents the same with a straight line. The RI of $[C=O/CH]$ was increased with increase in the % weight of DCP and AE. The slope value was determined from the above plot as 1.38, which confirmed the 1.50 order of functionalization reaction with respect to % weight of DCP. It means that 1.50 mol of AE is required to functionalize one mol of LDPE. The rate of functionalization (R_f) reaction can be written as follows: $R_f \propto (\% \text{ weight of DCP})^{1.38}$. The % grafting values are indicated in Table I. Under the identical experimental conditions LDPE was melt functionalized with HE and ME too. The order of functionalization reaction can be determined by plotting $\log(\% \text{ weight of DCP})$ versus $\log(RI_{[C=O/CH]})$ [Figs. 6(b), 7(a)]. The plot was found to be a straight line with the slope values of 1.46 and 1.59, which explained the 1.50 order of functionalization reaction for HE and ME respectively. $R_f \propto (\% \text{ weight of DCP})^{1.46}$ and 1.59 for HE and ME systems, respectively. The % grafting values are indicated in Table I. The functionalization queue is as follows: ME > AE > HE. In comparison, the ME system yielded higher % ester grafting values due to the above said reasons. When compared with mercapto ester, the AE and HE system yielded the lower % functionalization values because the former readily donated the hydrogen atom toward the functionalization reaction.³⁸

The first competitive reaction to the functionalization reaction is the C.L reaction. Although increasing the % weight loading of DCP, the C.L is also increased slightly at higher % weight loading of DCP. In the case of LDPE-AE system, the slope value was determined from the plot of $\log(\% \text{ weight of DCP})$ versus $\log(\% \text{ C.L})$ [Fig. 6(c)] as 0.42. The rate of C.L ($R_{C.L}$) can be written as $R_{C.L} \propto (\% \text{ weight of DCP})^{0.42}$. This value confirmed the 0.50 order of C.L reaction with respect to % weight of DCP. Figures 6(d) and 7(b) indicate the plots of $\log(\% \text{ weight$

TABLE I
Effect of (% weight of DCP) on % Functionalization, % C.L and % C=C Formation

% weight of DCP	% Functionalization			% C.L			% C=C formation		
	ME	AE	HE	ME	AE	HE	ME	AE	HE
3	80.1	63.8	46.2	0.10	3.01	10.4	0.09	5.02	8.12
4	84.9	67.4	53.2	0.76	5.45	12.8	1.78	7.11	11.5
5	90.6	71.5	59.3	1.15	7.11	15.1	2.51	9.42	16.8
6	93.4	79.8	68.7	1.78	9.98	18.3	3.05	12.4	21.6
7	98.9	84.6	75.1	2.11	12.9	22.4	3.91	15.8	26.3

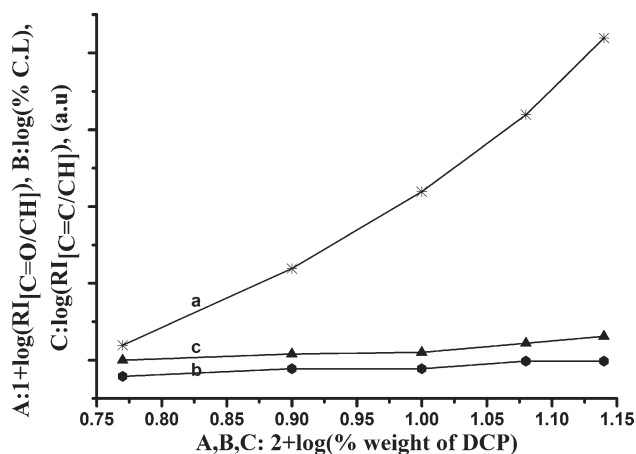


Figure 7 Effect of (% weight of DCP) on (a) $RI_{[C=O/CH_2]}$, (b) (% C.L.), (c) $RI_{[C=C/CH_2]}$ of LDPE-DCP-ME system, Time-2 h, Temperature-160°C, weight of LDPE-2.0 g

of DCP) versus $\log(\% \text{ C.L.})$ with slope values of 0.35 and 0.52, for LDPE-HE and LDPE-ME systems, respectively. This indicated that the C.L. reaction occurred through the 0.50 order of reaction with respect to % weight of DCP. $R_{C.L.} \propto (\% \text{ weight of DCP})^{0.35}$ and 0.52 . The % C.L. values are mentioned in Table I. In comparison, the ME yielded the lowest % C.L. values, whereas the HE gave the highest % C.L. values. It means that ME is more suitable for functionalization than HE. The % C.L. queue is as follows: HE > AE > ME.

The second competitive reaction to the functionalization reaction is C=C double bond formation reaction. Although increasing the % weight loading of DCP, the RI of C=C formation is increased. This is due to the availability of more and more DCP, leads to the oxidative degradation reaction. Figure 6(e) indicates a plot of $\log(\% \text{ weight of DCP})$ versus $\log(RI_{[C=C/CH_2]})$ for LDPE-AE system. Although increasing the % weight loading of DCP, the RI of double bond formation was also increased. The slope value was calculated as 1.15. This conformed the 1.0 order of C=C double bond formation with respect to % weight of DCP during the functionalization reaction. The rate of olefin formation (R_O) can be written as follows: $R_O \propto (\% \text{ weight of DCP})^{1.15}$. The increase in % of C=C double bond formation is associated with the oxidative degradation reaction. The % C=C double bond formation values are tabulated in Table I.

The plot of $\log(\% \text{ weight of DCP})$ versus $\log(RI_{[C=C/CH_2]})$ [Fig. 6(f), 7(c)] was made for LDPE-HE and LDPE-ME systems and the slope values were calculated as 0.95 and 1.31, which confirmed the 1.0 and 1.25 order of olefin formation reaction with respect to % weight of DCP for HE and ME systems, respectively. The $R_O \propto (\% \text{ weight of DCP})^{0.95}$ and 1.31 . The % C=C double bond values are mentioned in Table I. On comparison, the ME

system yielded the lowest % C=C formation values whereas the HE produced the highest % C=C values. The values are entered in Table I. The following is the olefin formation queue: HE > AE > ME. In over all comparison, the HE system exhibited higher % C=C values than the ME and AE systems due to its structural influence.

Effect of temperature on the FTIR-RI of functionalization, olefin formation, and C.L

LDPE was functionalized with ME, AE, and HE in the presence of DCP at different reaction temperature. The reaction temperature was varied between 413 and 453 K while the other experimental conditions were kept constant. Here, the ester or DCP concentration was maintained as 5% weight. 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 LDPE moieties are 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. The energy of activation (E_a) required for the functionalization reaction can be determined from the famous Arrhenius plot. The plot of $1/T$ versus $\log(RI_{[C=O/CH_2]})$ [Figs. 8(a,b) and 9(a)] was drawn for LDPE-AE, LDPE-HE and LDPE-ME systems, respectively. The E_a for the functionalization of AE, HE, and ME onto LDPE was determined as 274.3 kJ/mol, 305.6 kJ/mol and 253.8 kJ/mol, respectively. In comparison, the HDPE-DCP-ME consumed lower E_a value, and hence, activated the functionalization reaction.³⁸

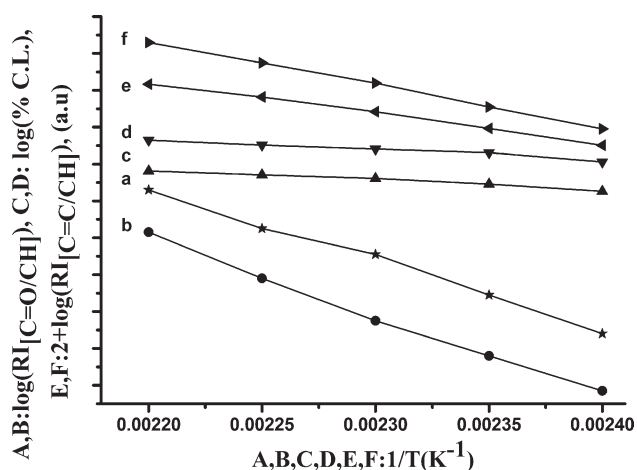


Figure 8 Effect of Temperature on (a) $RI_{[C=O/CH_2]}$, (c) (% C.L.), (e) $RI_{[C=C/CH_2]}$ of LDPE-DCP-AE system and (b) $RI_{[C=O/CH_2]}$, (d) (% C.L.), (f) $RI_{[C=C/CH_2]}$ of LDPE-DCP-HE system, Time-2 h, % weight of DCP = 5%, % weight of ester = 5%, weight of LDPE = 2.0 g

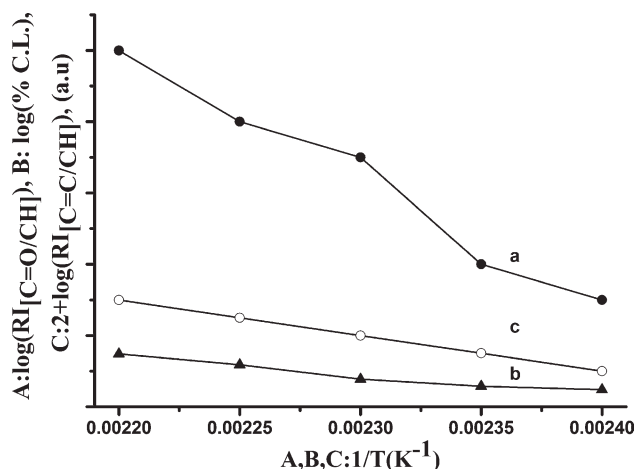


Figure 9 Effect of Temperature on (a) $RI_{[C=O/CH]}$, (b) (% C.L.), (c) $RI_{[C=C/CH]}$ of LDPE-DCP-ME system, Time-2 h, % weight of DCP = 5, % weight of ester = 5, weight of LDPE = 2.0 g

The role of temperature on % C.L of LDPE in the presence of DCP and ester was also tested. The plot of $1/T$ versus $\log(\% \text{ C.L.})$ was made for LDPE-DCP-AE and indicated as in Figure 8(c). The E_a value was calculated as 268.7 kJ/mol. The E_a value for the C.L of LDPE-DCP-HE and LDPE-DCP-ME systems were calculated from Figures 8(d) and 9(b), respectively, as 278.1 kJ/mol and 286.4 kJ/mol. On comparison, the LDPE-ME system consumed higher amount of heat energy for C.L reaction and resulted with lower % C.L values. This is due to the ready hydrogen donating nature of ME.

Effect of temperature on % C=C formation was also tested. While increasing the temperature, the RI of $[C=C/CH]$ was also increased. The plot of $1/T$ versus $\log(RI_{[C=C/CH]})$ [Fig. 8(e)] was made for LDPE-AE system and the E_a value was calculated as 260.9 kJ/mol. In the case of LDPE-DCP-HE and LDPE-DCP-ME systems, the same type of plot was made [Figs. 8(f) and 9(c)] and the E_a were calculated as 264.7 kJ/mol 293.6 kJ/mol, respectively. In comparison, the LDPE-ME system consumed higher amount of heat energy for C=C formation and resulted with lower amount of % C=C formation than the LDPE-AE and LDPE-HE systems. 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. In over all comparison, the ME system consumed lower amount of energy for functionalization reaction and consumed higher amount of heat energy for C.L and C=C formation reactions.

DSC Profiles

Melt functionalization of LDPE with different esters, such as ME and AE lead to the change in physical

and chemical properties of LDPE. Figure 10 shows the DSC heating scan of different % weight ME loaded LDPE. While increasing the % weight of ME, the T_m value moved toward lower temperature, (i.e.) the T_m value was suppressed. This can be explained as follows: (1) formation of C=C double bond led to the reduction in molecular weight of LDPE. (2) because of grafting reaction, internal micro structural arrangement occurred. (3) the grafted ester side chain led to the steric effect and it destabilized the conformational energy of LDPE. (4) because of grafting reaction, the % crystallinity value of LDPE were depressed. This is in accordance with literature report.³⁵ In this investigation we observed a decrement of T_m values due to melt grafting of esters. Figure 11 exhibits the DSC heating scan of different % weight of AE loaded LDPE system. Here also, the decrease in T_m value was recorded while increasing the % weight of AE. Again, this is due to the aforementioned reasons. Further research work on GPC measurement is going on in our laboratory.

TGA history

The thermal stability of ester functionalized LDPE was tested with the help of TGA instrument. The TGA was recorded at the heating rate of $10^\circ\text{C}/\text{min}$ under air atmosphere. The TGA of ME functionalized (from 3 to 7% weight loading) LDPE is mentioned in Figure 12. The thermogram showed a two step degradation process. Up to 250°C , there was no change in the structure of LDPE. The ester degradation occurred around 350°C , as a minor weight loss step. The major weight loss started around 400°C and extended up to 500°C . This accounted the main chain scission or degradation. The important point noted here is, while increasing the % weight of ME,

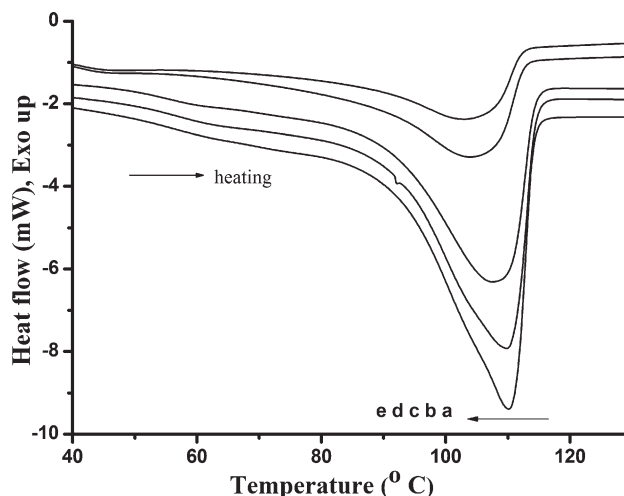


Figure 10 DSC of LDPE loaded with ME at (a) 3% weight, (b) 4% weight, (c) 5% weight, (d) 6% weight, e) 7% weight

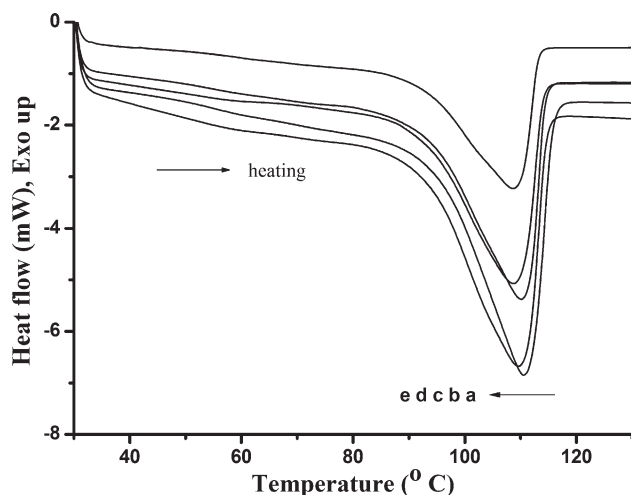


Figure 11 DSC of LDPE loaded with AE at (a) 3% weight, (b) 4% weight, (c) 5% weight, (d) 6% weight, (e) 7% weight

the thermal stability of LDPE was slightly increased around 500°C. At lower % weight loading of ester random grafting occurs and may not affect the thermal stability that much. So that the thermograms at lower and higher % weight loading of ester are not similar to each other. The point to be noted here is while increasing the % weight of ME, the initial degradation temperature (T_{id}) was shifted toward higher temperature. This is in accordance with our earlier publication.^{35,38} This suggested that the thermal stability of LDPE after melt functionalization reaction depended on the nature and structure of ester functionality. Figure 13 shows the TGA of AE functionalized LDPE. Here also, the above said trend was observed. The % weight residue remained above 450°C was increased with the increase of % weight ester loading. This suggested that the ther-

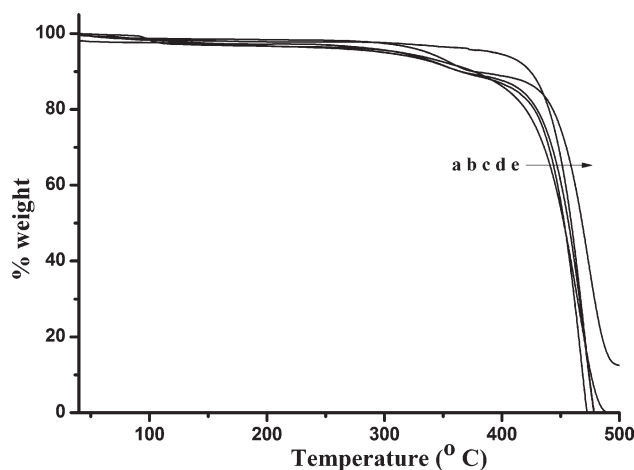


Figure 12 TGA of LDPE loaded with ME at (a) 3% weight, (b) 4% weight, (c) 5% weight, (d) 6% weight, (e) 7% weight

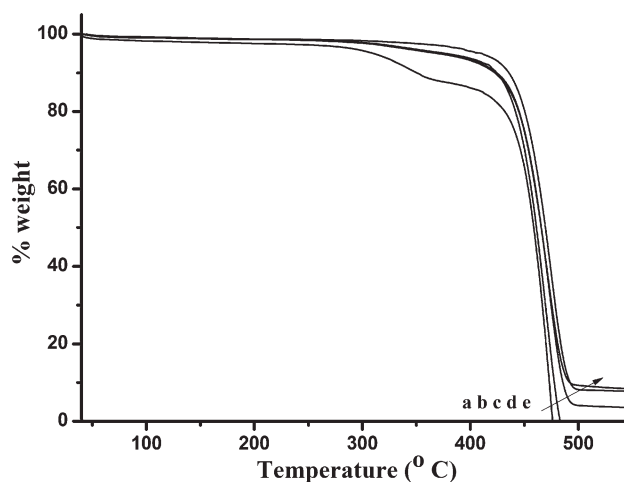


Figure 13 TGA of LDPE loaded with AE at (a) 3% weight, (b) 4% weight, (c) 5% weight, (d) 6% weight, (e) 7% weight

mal stability of LDPE was slightly increased after melt functionalization reaction with ME and AE.

Mechanism of melt functionalization reaction

Anbarasan et al.^{36–38} explained the mechanism of free radical grafting of thioester onto HDPE backbone. Similar type of mechanism is applied to the present system. Melt functionalization reaction proceeds via free radical reaction. DCP, the free radical initiator, produced two cumyloxy radicals on heating at 160°C under inert atmosphere with normal dissociation rate. Formations of free radicals are the initiation step of melt functionalization reaction. The formed free radicals interacted with LDPE and other ester led to the various processes. Because of the electro negative character nature of mercapto, amino and hydroxyl esters there will be a formation of mercapto radical, amino radical, and hydroxyl radicals. On any account benzyl radical will not form at 160°C under nitrogen atmosphere. If benzyl radical is formed during the melt functionalization reaction there will be a liberation of CO_2 with the degradation of ester structure, then FTIR will not show a peak around 1725 cm^{-1} due to the ester carbonyl stretching. Hence, benzyl radical is absent here. To confirm the functionalization mechanism FTIR spectral analysis is a right tool because the ester carbonyl stretching and C—O—C ester linkages are observed around 1725 and 1100 cm^{-1} , respectively, after the melt functionalization reaction. The parent LDPE did not show any peak around 1725 and 1100 cm^{-1} due to the ester group stretching. The change in the thermal property of functionalized samples also supported the chemical grafting of esters onto LDPE backbone. In this investigation, we used 1 : 1 : 1 ratio of LDPE, ester and DCP. In general, one mol of DCP is required to initiate one mol of LDPE and one

mol of ester. Hence, we used the equal concentrations of DCP and ester. Meanwhile, coupling of LDPE macro radicals led to the C.L reaction. Reactions are mentioned in Scheme 1.

In overall comparison, the ME performed well toward the functionalization reaction with LDPE backbone whereas the HE performed well toward the C.L and olefin formation reactions of LDPE. The ME readily donates one hydrogen atom and forms ME radical whereas the HE produces the same at slower rate because of resonance stabilization with the phenyl ring of HE. The AE produces the AE radical in a normal rate.

CONCLUSIONS

From the above FTIR-RI study the important points are presented here as conclusions. (1) The LDPE-ME system showed higher % functionalization values than the LDPE-AE and LDPE-HE systems. (2) The corrected area of C=O and C=C peaks were increased with increase in % weight of DCP. (3) The functionalization reaction followed the 1.50 order of reaction for LDPE-ME, LDPE-AE, and LDPE-HE systems with respect to % weight of DCP. (4) The LDPE-ME system consumed lower amount of heat energy for functionalization reaction than LDPE-AE and LDPE-HE systems. (5) The DSC concluded the decrease in T_m for both ME and AE functionalized LDPE systems. (6) The TGA declared the increase in T_{id} of LDPE after the melt functionalization reaction with ME and AE. (7) ME performed well toward the functionalization reaction with LDPE backbone.

References

1. Yamamoto, F.; Yamakawa, S. *J Polym Sci Polym Chem Ed* 1980, 18, 2257.
2. Ramos, V. D.; Costa, H. M.; Pereira, A. O.; Gomes, A. S. *Polym Bull* 2005, 54, 117.
3. Zhang, Y.; Ye, Z. *Macromolecules* 2008, 41, 6331.
4. He, P.; Huang, H.; Zhang, Y.; Liu, C. *React Funct Polym* 2005, 62, 25.
5. Braun, D.; Silvis H.C.; Kramer, I. *Angew Makromol Chem* 1997, 251, 37.
6. Roove, D.; Devaux, J.; Legras, R. *J Polym Sci A Polym Chem* 1996, 34, 1195.
7. Roove, D.; Sclavons, M.; Carlier, V. *J Polym Sci A Polym Chem* 1995, 33, 829.
8. Gaylord, N. G.; Mishra, M. K. *J Polym Sci C Polym Lett* 1983, 21, 23.
9. Minoura, Y. J.; Veda, M.; Mizunuma, S. *J Appl Polym Sci* 1969, 13, 1625.
10. Cartier, H.; Hu, G. H. *J Polym Sci Part A Polym Chem* 1998, 36, 1053.
11. Chandranupap, P.; Bhattacharya, S. N. *J Appl Polym Sci* 2000, 78, 2405.
12. Huang, H.; Liu, N. C. *J Appl Polym Sci* 1957 1998, 67.
13. Sun, Y. J.; Hu, G. H.; Lambla, M. *Angew Makromol Chem* 1995, 229, 1.
14. Srinivasa, R. G. A.; Choudhary, M. S.; Naqvi, M. K. *Eur Polym Mater* 1996, 32, 625.
15. Ghosh, P.; Chattopadhyay, B.; Sen, A. K. *Polymer* 1998, 39, 193.
16. Pavlinec, J.; Lazar, M.; Manazek, Z. *J Polym Sci* 1967, 16, 1113.
17. Vanio, T.; Hu G. H.; Lambla, M. *J Appl Polym Sci* 1996, 61, 843.
18. Liu, N. C.; Baker, W. E. *Polymer* 1994, 35, 988.
19. Liu, N. C.; Yao, G. P.; Huang, H. *Polymer* 2000, 41, 4537.
20. Dokolas, P.; Looney, M. G.; Solomon, D. H. *Polymer* 2000, 41, 3137.
21. Pesetskii, S. S.; Jurkowski, B.; Makarenko, O. A. *J Appl Polym Sci* 2002, 86, 64.
22. Moad, G. *Prog Polym Sci* 1999, 24, 81.
23. Svegl, F.; Orel, B. *Mat Tech* 2003, 37, 29.
24. Copikova, J.; Synytsya, A.; Novotna, M. *Czech J Food Sci* 2001, 19, 51.
25. Wang, J. S.; Shi, J. S.; Wu, J. G. *World J Gastro* 2003, 9, 1897.
26. Rathika, S.; Baskaran, I.; Anbarasan, R. *J Mater Sci* 2009, 44, 3542.
27. Duraimurugan, K.; Rathika, S.; Anbarasan, R. *Chin J Polym Sci* 2008, 26, 393.
28. Saule, M.; Navarre, S.; Babot, O.; Maillard, B. *Macromolecules* 2003, 36, 7469.
29. Saule, M.; Navarre, S.; Babot, O.; Maillard, B. *Macromolecules* 2005, 38, 77.
30. Gandhi, S.; Dhanalakshmi, V.; Anbarasan, R. *J Mater Sci* 2010, 45, 1688.
31. Parveen, M. F.; Dhanalakshmi, V.; Anbarasan, R. *J Mater Sci* 2009, 44, 5852.
32. Parveen, M. F.; Dhanalakshmi, V.; Anbarasan, R. *NANO* 4:147 2009.
33. Yelilarasi, A.; Dhanalakshmi, V.; Anbarasan, R. *Spectrochim Acta A* 2009, 74, 1229.
34. Yelilarasi, A.; Dhanalakshmi, V.; Anbarasan, R. *Polym Polym Compos* 2009, 17, 397.
35. Anbarasan, R.; Kanchana, S.; Dhanalakshmi, V. *J Appl Polym Sci* 2010, 115, 315.
36. Anbarasan, R.; Babot, O.; Maillard, B. *J Appl Polym Sci* 2005, 97, 761.
37. Anbarasan, R.; Babot, O.; Dequil, M.; Maillard, B. *J Appl Polym Sci* 2005, 97, 766.
38. Parthasarathi, V.; Dhanalakshmi, V.; Anbarasan, R. *Polym Eng Sci* 2010, 50, 474.
39. Anbarasan, R.; Anusuya, M.; Dhanalakshmi, V. *J Appl Polym Sci* 2010, 115, 2582.