

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



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

Melt grafting of metal salts onto LLDPE backbone – An FTIR study

R. Anbarasan^{a,*}, V. Dhanalakshmi^b

^a Department of Mechanical Engineering, MEMS Thermal Control Lab, National Taiwan University, Taipei – 10617, Taiwan, ROC ^b Department of Polymer Technology, KCET, Virudhunagar 626 001, Tamil Nadu, India

ARTICLE INFO

Article history: Received 16 November 2009 Received in revised form 12 February 2010 Accepted 26 February 2010

Keywords: Melt grafting Polyethylene Metal esters FTIR-RI kinetics DSC TGA HRTEM

1. Introduction

Polyolefins particularly, polyethylenes, found applications in various science and engineering fields. The widely usable fields are packaging and automobile sectors. After their better utilizations, simply they are thrown into open environment and resulted with environmental pollution. The environmental pollution of polyolefins is due to the absence of hydrolysable or polar groups in its backbone. Polyolefins are functionalized by various methods with different functional groups. In the present investigation, we are very much interested in the functionalization of LLDPE by thermolvsis method, an environmental green method, with different metal acrylates and metal methacrylates. The following is the reason for selecting the metal ester as a functional candidate. (1) Having two easily hydrolysable ester groups. (2) During the bio-degradation process there will be a chain scission process in two different places of LLDPE backbone. Recently, Walker et al. [1] reported about the synthesis and characterizations of acrylates of La, Sr and Mn. Cd acrylate core report is also available in the literature [2]. LLDPE backbone was melt grafted with tetrahydrophthalic anhydride [3], non ionic surfactants [4], maleic anhydride [5] and diethylmalonate [6] and their structure-property relationships were closely analyzed. Radiation induced graft polymerization of Mn, Cr, Co, Ni and Cu acrylate monomer onto PE was reported by Savostyanov

ABSTRACT

The melt graft functionalization of metal di(meth)acrylates onto linear low density poly(ethylene) (LLDPE) at 160 °C under inert atmosphere is reported here. The post melt grafting FTIR–RI method was used to find out the % grafting of metal salts onto LLDPE backbone. Further, DSC, TGA and HRTEM techniques were introduced to explain the results. A plausible reaction mechanism was proposed. © 2010 Elsevier B.V. All rights reserved.

et al. [7] with the basic kinetic reports. By thorough literature survey, we could not find any report based on the melt grafting of Ba, Mg and Mn di(meth) acrylates onto LLDPE backbone. In the present investigation, we took this job as a challenge and successfully grafted the same onto LLDPE backbone for the first time.

The amount of ester group chemically grafted onto the LLDPE surface can be determined by chemical as well as spectroscopy methods. The chemical method leads to the environmental pollution problem because of utilization of larger quantities of toxic and hazardous solvents. Due to these reasons we are not interested in chemical estimation method. The amount of ester group grafted onto the LLDPE backbone can be determined by the spectroscopy method but this method is an eco-friendly one. Hence, we preferred this spectroscopy method, particularly with the FTIR spectroscopy method. Moreover, this method is an economically cheaper than the chemical method with more accuracy. FTIR spectrometer is a useful tool in various science and engineering fields, because of its high sensitivity or detectivity towards traces amount of sample, low noise to signal ratio and this method is an easy and inexpensive one. FTIR spectroscopy is used for both qualitative [8–12] and quantitative [13–25] analysis. By thorough literature survey, we could not find any report based on the FTIR kinetics of melt functionalization of Ba, Mg and Mn diesters onto LLDPE backbone. In the present investigation, for the first time, we are reporting about the melt functionalization of the above-mentioned metal esters with LLDPE and further characterized by FTIR-RI kinetics.

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

^{1386-1425/\$ -} see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2010.02.042

2. Materials

2.1. Methods

Carbonates of Ba, Mg and Mn were purchased from SD Fine Chemicals, AR grade, India. Acrylic acid and methacrylic acid (CDH Chemicals, India) were purchased and used after distillation under vacuum. Linear low density poly(ethylene) (LLDPE) (Rayson, India, $M_w - 1,00,000 \text{ Da}$) was purchased and purified by the procedure followed in our earlier publication [22]. Toluene (Chemspure, AR, India) and acetone (Merck, India) were received and used without further purification. Dicumyl peroxide initiator (DCP, Across Chemicals, UK) and cyclohexane (Paxy Chemicals, AR, India) were used as received.

2.1.1. Synthesis of barium diacrylate (Ba DA)

10 g of BaCO₃ was dissolved in 200 mL of double distilled water (DD) in a three-necked round bottom (RB) flask. 10 mL of acrylic acid was added drop by drop to the BaCO₃ solution followed by 0.03 g of antimony trioxide, the esterification catalyst, to catalyze the metal ester formation process. The contents were sparged with nitrogen gas to create an inert atmosphere inside the flask. The RB flask was connected to a water condenser and the solution was boiled for 3 h continuously with vigorous stirring at 90 °C. Finally, the precipitate obtained {Ba DA} was washed with acetone and the sample was dried, weighed and stored in a zipper bag. The same procedure was adopted for the synthesis of other metal esters [26] and abbreviated as Ba DMA, Mg DA, Mg DMA, Mn DA and Mn DMA.

2.1.2. Purification of LLDPE

5 g of LLDPE pellet sample was dissolved in 100 mL of toluene solvent at 140 °C for 3 h in order to remove the antioxidants, added during its long storage process. Once all the LLDPE powder samples were dissolved in toluene, the contents became clear viscous solution, then cooled and 800 mL of acetone was added to precipitate the LLDPE [22]. Filtered the contents and dried at 60 °C for 24 h under vacuum. In order to confirm the complete removal of toluene from the purified LLDPE, the purified sample was weighed and compared with the amount of LLDPE pellet taken initially. Further, it can be analyzed by recording the FTIR spectrum for the purified sample. The absence of an aromatic rocking and wagging stretching in the finger print region of FTIR spectrum confirmed the absence of toluene solvent after the vacuum drying at 60 °C for 24 h. The dissolution and precipitation process were repeated for three times to further purify the LLDPE sample. Finally, the dried samples were weighed and stored in a zipper bag.

2.1.3. Synthesis of LLDPE-g-Ba DA

1 g of pure LLDPE powder sample was added with 1% weight of Ba DA in 25 mL of cyclohexane–dichloromethane (1:9 v/v)

After degassing, the temperature of the reactor was kept at 160 °C for 2.5 h without stirring. After the melt functionalization reaction was completed, the reactor was removed from the oil bath, cooled to room temperature and the functionalized LLDPE samples were collected and cut into small pieces. These were put in toluene at 140°C for 30 min for the isolation purpose. The functionalized, non-cross linked samples were dissolved in toluene while the functionalized cross-linked samples did not dissolve in toluene. The dissolved samples were re-precipitated by adding 600 mL of acetone and the cross-linked samples were isolated. The non-cross linked 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 have done with the non-cross linked, functionalized polymers. The same grafting procedure was followed for other metal esters too.

2.2. Characterizations

FTIR spectra were recorded using 8400 S Shimadzu FTIR spectrometer, Japan, by KBr pelletization method from 400 to 4000 cm⁻¹. In order to avoid the error while recording FTIR spectrum, the corrected peak area was considered. To cross check the corrected peak area values, the FTIR spectrum was recorded for the same sample disc in different parts. After proper base line correction with the aid of FTIR software, again one can get the same corrected peak area values. FTIR spectrum was recorded for three times for the same sample disc, one can get the same and repeated corrected peak area values. The FTIR spectrum was recorded without predicting the lower and upper limits of peak, because the software itself predicted exactly the lower and upper limits to nullify the errors. In such a way the errors were nullified. Further, one can cross check the efficiency of FTIR software by manually predicting the lower and upper limits and the corrected peak area was determined. In this case one can get the same corrected peak area value as reported previously (without predicting the lower and upper peak limits). For the quantitative determination of % ester grafting, the following corrected areas of the peaks, which were assigned at 1730 (C=O form) and 721 (C-H out of plane bending vibration) cm⁻¹ were determined and the relative intensity (RI) was calculated as follows:

RI of ester carbonyl
$$(RI_{[C=O/C-H]}) = A_{1730}/A_{721}$$
 (1)

% Ester grafting =
$$\frac{\text{RI}_{[C=O/C-H]} \times W}{C \times 1.5} \times 100$$
 (2)

Where, W is the weight of non-cross linked ester grafted polymer taken for FTIR study, C is the % weight of peroxide used, 1.5 is the proportionality constant as mentioned in our earlier publication [25]. The % cross-linking was determined by using the following formula:

 $% cross-linking = \frac{[Weight of polymer taken for functionalization] - [Weight of non-cross linked polymer obtained after functionalization]}{Weight of polymer taken for functionalization} \times 100$ (3)

solvent mixture in a 100 mL beaker with mild stirring. The solvent mixture was used to distribute the DCP and Ba DA onto LLDPE backbone uniformly, otherwise agglomeration occurred. Then 1% weight of DCP was mixed with the content of the beaker and the stirring was continued for 1 h. In the present investigation, both DCP and esters or Ba DA 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. The reaction mixture was transferred into a test tube reactor and de-aerated for 30 min with sulphur free nitrogen gas.

TGA was recorded using Universal V4.3A TA instrument, Japan under air atmosphere from room temperature to $800 \,^{\circ}$ C at the heating rate of $10 \,^{\circ}$ C/min. DSC of the sample was recorded using Universal V4.3A TA instrument under nitrogen atmosphere at the heating rate of $10 \,^{\circ}$ C/min from room temperature to $300 \,^{\circ}$ C. HRTEM was recorded for Mg DMA by using a TEM 3010, a product of JEOL.

3. Results and discussion

For the sake of convenience the results and discussion part is sub-divided into two parts namely, (1) synthesis and characterizations of metal containing divinyl monomers, (2) melt grafting of metal containing divinyl monomer onto LLDPE backbone.

3.1. Synthesis and characterizations of metal containing divinyl monomers

3.1.1. FTIR study

Fig. 1 shows the FTIR spectra of metal acrylates and metal methacrylates. Fig. 1a represents the FTIR spectrum of Ba DA. The important peaks are characterized below. A broad peak around 3500 cm^{-1} is due to the OH stretching of water molecules attached with the central metal ion. The C–H symmetric and anti-symmetric stretching is observed as a hump at 2909 and 2973 cm⁻¹ respectively. The C=O stretching is observed at 1721 cm⁻¹. The C=C stretch can be seen at 1647 cm⁻¹. The same peak is also corresponding to the bending vibration of water molecules as well as the CO₂-M⁺ stretching. The C–H bending vibration is observed at 1562 cm⁻¹. The metal ester linkage (C–O–M) is appeared at 1076 cm⁻¹. A twin peak appears at 637 and 600 cm⁻¹ are responsible for the C–H out of plane bending and metal oxide stretching respectively.

Fig. 1b exhibits the FTIR spectrum of Ba DMA. A sharp peak at 3561 cm^{-1} is accounted by the stretching of existence of two Ba ions in the same crystalline plane. The 2917 and 1977 cm⁻¹ peaks are corresponding to the C–H symmetric and anti-symmetric stretching of Ba DMA. A small hump appeared at 1738 cm^{-1} is responsible for the carbonyl stretching. A sharp peak at 1648 cm^{-1} is due to the C=C stretching. The metal ester linkage, C–H out of plane bending vibration and metal oxide stretching are observed at 1011, 833 and 506 cm^{-1} respectively. The shifting of peak is due to the influence of bulky methyl substituent present in the Ba DMA. Thus FTIR spectrum confirmed the presence of functional groups in Ba salts.

Fig. 1c and d represent the FTIR spectra of Mg DA and Mg DMA respectively. Here also one can observe the above-mentioned peaks. The FTIR spectrum of Mn DA and Mn DMA are given in Fig. 1e and f respectively. These systems too exhibited the same peaks as mentioned above.

3.1.2. TGA history

The TGA thermogram of Ba DA is shown in Fig. 2a. The thermogram showed a three-step degradation process. The first minor weight loss step up to 133 °C is due to the removal of physisorbed and chemisorbed water molecules. The second minor weight loss step up to 442 °C is ascribed to the dissociation of metal ester link-



Fig. 1. FTIR spectra of (a) Ba DA, (b) Ba DMA, (c) Mg DA, (d) Mg DMA, (e) Mn DA, (f) Mn DMA.



Fig. 2. TGA of (a) Ba DA, (b) Ba DMA, (c) Mg DA, (d) Mg DMA, (e) Mn DA, (f) Mn DMA.

age. The third major weight loss step is started at 450 °C and extend up to 529 °C, due to the degradation of ester linkage with simultaneous evolution of CO_2 . Above 750 °C, the system exhibited 69.9% weight residue remained due to the formation of BaO. This is similar to our earlier communication [26]. The data is mentioned in Table 1. The first minor weight loss step due to the removal of water molecule is supporting the FTIR spectrum of Ba DA.

The TGA thermogram of Ba DMA is shown in Fig. 2b. The thermogram exhibited a four-step degradation process. The first minor weight loss step before 100°C is associated with the removal of moisture and physisorbed water molecules. The chemisorbed water molecules are expelled before 210°C. In comparison, the Ba DMA had more physisorbed and chemisorbed water molecules than the Ba DA system. This can be evidenced by seeing the weight loss step below 210 °C for both the systems. This can be explained as follows: (1) during the preparation of Ba DMA, the central Ba ion might be in nano size and it should be smaller than the Ba DA. (2) Availability of more surface area for holding the physisorbed or chemisorbed water molecules. (3) Due to the presence of steric effect caused by the methyl groups, nano porous structure might be formed and which must be responsible for holding the water molecules. Further research work on HRTEM of Ba DA and Ba DMA is going on in our research lab. Third and fourth weight loss steps are corresponding to the dissociation and degradation of metal ester linkage as mentioned above. Above 750 °C, it showed 55.1% weight residue remained. The metal ester degradation was started at 393 °C. When compared with Ba DA, the present system showed a lower thermal stability due to the presence of bulky methyl substituent in Ba DMA, which caused steric effect. The data is mentioned in Table 1.

Fig. 2c exhibits the TGA thermogram of Mg DA. It showed a four-step degradation process, as mentioned above. Here the metal ester degradation was started at 421 °C and above 750 °C it showed 18.2% weight residue remained. Fig. 2d reveals the thermogram of Mg DMA. It showed a three-step degradation process. The third major weight loss step and dissociation of metal ester were started at 458 °C. Above 750 °C, it yielded 15.6% weight residue remained. The data is mentioned in Table 1. In comparison, the Mg DA system showed the higher % weight residue remained above 750 °C whereas the Mg DMA system exhibited a higher metal ester degradation temperature. In comparison with previous Ba system, the metal ester degradation temperature is higher for Mg system whereas the % weight residue remained above 750 °C is higher for Ba system. This is due to the smaller size of Mg ion ($3s^2$ level configuration) [27].

Table 1		
TGA and DSC da	ata of metal	ester

System	Metal ester degradation temperature (°C)	% weight residue remained above 750°C	Removal of physisorbed water (°C)	Removal of chemisorbed water (°C)
Ba DA	450	69.9	88.3	119.1
Ba DMA	392	55.1	79.6	110.4
Mg DA	429	18.2	90.6	130.2
Mg DMA	458	15.6	116.7	153.6
Mn DA	413	26.7	97.9	-
Mn DMA	278	25.1	81.6	110.7

Fig. 2e reveals the TGA thermogram of Mn DA. This system exhibited a four-step degradation process as explained for previous systems. The metal ester degradation was started at 413 °C and it showed 26.7% weight residue remained above 750 °C. The TGA thermogram of Mn DMA is shown in Fig. 2f with four-step degradation process. The metal ester degradation was started at 278.6 °C and above 750 °C it showed 25.1% weight residue remained. The data is mentioned in Table 1. In comparison, the Mn DA showed higher thermal stability than the Mn DMA. This can be explained on the basis of steric repulsion. In the case of Mn DMA, the bulky size methyl substituent caused steric effect and de-stabilized the thermal stability of Mn DMA.

In overall comparison, the Mn DMA system exhibited lower metal ester degradation temperature due to $3d^5 4s^2$ configuration [27] whereas the Ba DA showed higher % weight residue remained above 750 °C due to the $6s^2$ configuration level. The TGA thermogram also supported the FTIR spectrum for the presence of water molecules attached with the central metal ion.

3.1.3. DSC profile

The FTIR spectrum showed the attachment of water molecules with the central metal ion. Further, it was supported by TGA analvsis. The DSC profile confirmed the presence of water molecules in the metal esters. Fig. 3 shows the DSC thermogram of various metal esters. Fig. 3a represents the DSC heating scan of Ba DA. It showed two endothermic peaks at 88.3 and 119.1 °C corresponding to the removal of physisorbed and chemisorbed water molecules. Fig. 3b indicates the DSC heating scan of Ba DMA. This system too exhibited two endothermic peaks at 79.6 and 110.4 °C (Table 1) due to the both physisorbed and chemisorbed water molecules respectively. Appearance of these two endothermic peaks confirmed the presence of water molecules attached with the central metal ion [26]. In comparison, the Ba DMA system showed lower de-watering temperature $(T_{d.w.})$ than the Ba DA system. The decrease in $T_{d.w.}$ of Ba DMA can be explained as follows. (1) Presence of bulky methyl substituent de-stabilize the thermal stability as well as phase transition



Fig. 3. DSC of (a) Ba DA, (b) Ba DMA, (c) Mg DA, (d) Mg DMA, (e) Mn DA, (f) Mn DMA.

temperature. (2) While introducing a methyl substituent in the acrylate group which has not only increased the molecular weight but also improved the hydrophobic character (non-homogeneity). Hence, due to these two reasons the water molecules were removed from the central metal ion at lower temperature.

The DSC heating scan of Mg DA and Mg DMA is indicated in Fig. 3c and d respectively. The $T_{d,w}$ of Mg system is higher than that of Ba system (Table 1). This can be explained as follows. During the synthesis of Mg DA or Mg DMA, the size of central metal ion was reduced to the nano size. When the size of the metal ion is reduced to smaller and smaller, the inorganic phase of metal ion is transferred to organic phase. This concept is similar to that of dissolution of Ag nano particles in both water and toluene medium [28]. The same principle is applied to the present system. The reduction in size of central metal ion led to the formation of homogeneity (i.e.) organic phase. The formation of homogeneity can be further confirmed with Mg DMA. While introducing a bulky methyl substituent in the acrylate, which further increased the hydrophobic character with the simultaneous reduction in size of Mg²⁺ ion. The reduction in size (i.e.) nano size of Mg²⁺ ion can be confirmed by observing the topography of the same. Fig. 4 represents the HRTEM images of Mg DMA. Fig. 4a indicates the ordered structure of Mg ions with the length of 3 nm. Fig. 4b represents the nano hexagon and with distorted spherical morphology of central Mg ions. Fig. 4 confirms the nano size of the central metal ion. The nano sized Mg²⁺ ion expelled the water molecules at somewhat higher temperature due to its larger surface area. The surface area of nano sized Mg ion is responsible for holding the water molecules.

The DSC heating scan of Mn DA and DMA is given in Fig. 3e and f respectively. Fig. 3e (Mn DA) shows only one endothermic peak (94.5 °C), corresponding to the removal of physisorbed water molecules from the central metal ion. Fig. 3f represents the DSC heating scan of Mn DMA with two endothermic peaks, corresponding to the removal of physisorbed (82 °C) and chemisorbed (112 °C) water molecules. The Mn DMA system showed a lower $T_{d.w.}$ due to the increase in hydrophobicity. In 2004, Walker et al. [1] reported about the DSC and TGA of various metal acrylates. An endothermic peak appeared around 125 °C in DSC analysis was explained well by them based on the removal of superficial and structural water molecules. Further, the water removal from the metal salt was confirmed through TGA method. Our report is co-inside with them [1].

In overall comparison, the Mg salts particularly Mg DMA exhibited higher $T_{d,w}$ due to its nano size with larger surface area. The water molecules were adsorbed on the surface of the central metal ion strongly and yielded higher $T_{d,w}$. The DSC heating scan of metal esters confirmed the presence of water molecules attached with the central metal ion.

3.2. Melt grafting of metal containing divinyl monomers onto LLDPE backbone

3.2.1. FTIR study

Fig. 5 indicates the FTIR spectra of 1–5% weight Ba DA loaded LLDPE systems. Fig. 5a reveals the FTIR spectrum of pristine LLDPE.



Fig. 4. HRTEM of Mg DMA, (a) ordered nano structure, (b) nano hexagon morphology.

Та

The important peaks are characterized below. A broad peak around 2896 cm⁻¹ is due to the anti-symmetric stretching. The C-H symmetric stretching vibration is observed at 2655 cm⁻¹. The C-H bending and out of plane bending vibration are seen at 1460 and 721 cm^{-1} respectively. Fig. 5 (b–f) indicates the FTIR spectra of 1–5% weight Ba DA loaded LLDPE. The spectra showed some new peaks apart from the peaks of pristine LLDPE. They are characterized below. A broad peak around 3500 cm⁻¹ is ascribed to the OH stretching of water molecules attached with Ba DA. Two molecules of water are attached with the central Ba metal ion. This is in accordance with our earlier publication [26]. The ester grafting can be confirmed by representing a peak at 1721 cm⁻¹ due to the ester carbonyl group. The bending vibration of water and CO₂-M⁺ stretching are merged and observed as a broad peak at 1556 cm⁻¹. A broad peak around 1038 cm⁻¹ is responsible for the metal ester, C-O-M linkage. The Ba–O stretching is seen at 553 cm⁻¹. Appearance of these new peaks confirmed the chemical grafting of Ba DA onto LLDPE backbone.

The interesting point observed here is while increasing the % weight loading of Ba DA, the RI of [C=O/C-H] is also increased. This argued that the chemical grafting increased with the increase of % weight loading of Ba DA. We know that the metal esters are hav-



Fig. 5. FTIR spectra of LLDPE loaded with Ba DA at (a) 0% weight, (b) 1% weight, (c) 2% weight, (d) 3% weight, (e) 4% weight, (f) 5% weight.



Fig. 6. Effect of (% weight of DCP) on $RI_{[C=O/C-H]}$ of (a) Ba DA, (b) Ba DMA, (c) Mg DA, (d) Mg DMA, (e) Mn DA, (f) Mn DMA systems.

ing the melting temperature above 400 °C and the grafting reaction is occurred through the dissolution of metal esters in the molten state of LLDPE. In the present investigation, the DCP and Ba DA were used in equal concentration. Fig. 6a shows the plot of log(% weight of DCP) vs. log(RI_{IC=O/C-H1}). The normalized values are presented in Fig. 6. The plot showed a straight line with the slope value of 1.93, which declared the 2.0 order dependence of grafting reaction with respect to % weight of DCP. It means that 2 mol of DCP are required to functionalize 1 mol of LLDPE. The rate of functionalization reaction (R_f) can be written as follows: $R_f \alpha$ (% weight of DCP)^{1.93}. The second order of functionalization reaction inferred that the termination reaction occurred through the bi-molecular termination mechanism. The % grafting values are mentioned in Table 2. Recently, Parthasarathi et al. [25] found similar type of results during the melt graft functionalization of mercapto esters

Table 2
Effect of Ba DA and Ba DMA on % functionalization and % cross-linking

% weight loading	Ba DA		Ba DMA	
	% funct.	% C.L.	% funct.	% C.L.
1	46.7	30.8	33.8	36.2
2	49.5	38.2	37.5	45.7
3	53.1	51.5	41.3	61.4
4	57.5	65.7	48.7	72.8
5	62.6	80.1	55.1	85.3



Fig. 7. FTIR spectra of LLDPE loaded with Ba DMA at (a) 1% weight, (b) 2% weight, (c) 3% weight, (d) 4% weight, (e) 5% weight.

with HDPE. The Ba DA contains two C=C double bonds. A broad peak at 1571 cm⁻¹ is due to the combination of OH bending vibration and $CO_2^-M^+$ stretching vibrations. Hence the grafting of Ba DA onto LLDPE backbone occurred through the cleavage of C=C double bonds. The competitive reaction during the melt graft functionalization reaction is the C.L reaction. C.L is due to the coupling between LLDPE macro radicals. Table 2 indicates the % C.L values. The % C.L values increased with the increase of % weight loading of Ba DA.

Fig. 7 explains the FTIR spectra of 1-5% weight Ba DMA loaded LLDPE system. The DCP concentration and metal ester concentration was varied equally. Here also one can observe the above-mentioned peaks. While increasing the % weight loading of DCP, the RI of [C=O/C-H] is also increased. This is due to the more and more chemical grafting of Ba DMA onto LLDPE backbone. In order to find out the order of functionalization reaction, the following universal log-log plot was made. Fig. 6b shows the plot of log(% weight of DCP) vs. $log(RI_{[C=O/C-H]})$. The plot showed a straight line with the slope value of 1.98. $R_f \alpha$ (% weight of DCP)^{1.98}. This claimed the 2.0 order of melt functionalization reaction. The Ba DMA system also yielded the bi-molecular termination reaction. In the case of Ba DMA, 2 mol of Ba DMA are required to functionalize 1 mol of LLDPE. The % grafting values and % C.L values are included in Table 2. In critical comparison, Ba DA system exhibited higher % grafting values due to the absence of steric effect. The Ba DMA system revealed the higher % C.L. values due to slow rate of formation of Ba DMA radicals.

The FTIR spectra of 1-5% weight Mg DA loaded LLDPE is shown in Fig. 8. While increasing the % weight of Mg DA, the RI of [C=O/C-H] is also increased. At higher % weight of loading of Mg DA, the carbonyl stretching and the bending vibration of water molecules were merged and the carbonyl peak was observed like a hump. The remaining peaks are similar to that of Ba DA-LLDPE system. The order of functionalization reaction can be determined by plotting log(% weight of DCP) vs. log(RI_[C=O/C-H]) (Fig. 6c). The plot exhibited a straight line with a slope value of 0.63, which concluded the 0.50 order of functionalization reaction (i.e.) $R_f \alpha$ (% weight of DCP)^{0.63}. 0.50 mol of Mg DA is required to functionalize 1 mol of LLDPE. This is in accordance with literature report [26]. The % grafting and % C.L. values are mentioned in Table 3. Fig. 9 exhibits the FTIR spectra of 1-5% weight Mg DMA loaded LLDPE system. The RI of [C=O/C-H] is increased with the simultaneous increase of % weight loading of Mg DMA. Fig. 6d indicates the plot of log(% weight of DCP) vs. $log(RI_{[C=O/C-H]})$. The plot showed a straight line with the



Fig. 8. FTIR spectra of LLDPE loaded with Mg DA at (a) 1% weight, (b) 2% weight, (c) 3% weight, (d) 4% weight, (e) 5% weight.

Table 3 Effect of Mg DA and Mg DMA on % functionalization and % cross-linking			
% weight loading	Mg DA	Mg DMA	

% weight loading	Mg DA	Mg DA		Mg DMA	
	% funct.	% C.L.	% funct.	% C.L.	
1	50.1	10.4	42.6	16.2	
2	56.4	14.6	48.5	22.1	
3	65.3	19.3	57.3	27.6	
4	74.8	25.7	66.8	32.6	
5	85.7	29.8	75.6	38.4	

slope value of 1.05. $R_f \alpha$ (% weight of DCP)^{1.05}. 1 mol of Mg DMA is required to functionalize 1 mol of LLDPE. The % functionalization and % C.L values are represented in Table 3. In comparison, the % grafting values are greater than that of % C.L. Mg DA system exhibited a higher % functionalization values due to the absence of steric effect and the Mg DMA system revealed the higher % C.L. due to the presence of steric effect and slow production of Mg DMA radicals. Even though, the Mg DMA maintained the homogeneity with LLDPE in its molten condition, due to the presence of bulky size methyl substituent that led to the steric effect and resulted with lower % grafting. By comparing Ba and Mg systems, the Mg system



Fig. 9. FTIR spectra of LLDPE loaded with Mg DMA at (a) 1% weight, (b) 2% weight, (c) 3% weight, (d) 4% weight, (e) 5% weight.



Fig. 10. FTIR spectra of LLDPE loaded with Mn DA at (a) 1% weight, (b) 2% weight, (c) 3% weight, (d) 4% weight, (e) 5% weight.

yielded higher % functionalization and the Ba system gave higher % C.L. values.

Fig. 10 represents the FTIR spectra of 1-5% weight Mn DA loaded LLDPE system. Here also the RI of [C=O/C-H] was increased with

Initiation

LLDPE + DCP + Metal ester

Table 4

Effect of Mn DA and Mn DMA on % functionalization and % cross-linking.

% weight loading	Mn DA		Mn DMA	
	% funct.	% C.L.	% funct.	% C.L.
1	54.5	24.6	48.9	32.8
2	59.8	36.1	52.5	44.5
3	63.4	47.4	57.3	52.1
4	68.7	56.7	62.8	62.4
5	74.9	65.8	68.7	73.7

the increase of % weight of Mn DA. This confirmed the chemical grafting of Mn DA onto LLDPE backbone. The order of functionalization reaction can be determined by drawing a plot of log(% weight of DCP) vs. log(RI_[C=O/C-H]) (Fig. 6e). The plot yielded a straight line with the slope value of 1.56. $R_f \alpha$ (% weight of DCP)^{1.56}. The slope value confirmed the 1.50 order of functionalization reaction with respect to % weight of DCP. The % grafting and % C.L. values are mentioned in Table 4. Fig. 11 shows the FTIR spectra of 1–5% weight Mn DMA loaded LLDPE system. The order of functionalization reaction was determined by plotting log(% weight of DCP) vs. log(RI_[C=O/C-H]) (Fig. 6f) as 1.70. $R_f \alpha$ (% weight of DCP)^{1.70}. This inferred that 1.75 mol of Mn DMA was required to functionalize 1 mol of LLDPE. On comparison, the Mn DA system gave higher % grafting due to smaller in size without steric effect and Mn DMA system yielded higher % C.L values due to the presence of steric effect



- Composite (C₁)

Scheme 1. Melt functionalization of metal ester with LLDPE.



Fig. 11. FTIR spectra of LLDPE loaded with Mn DMA at (a) 1% weight, (b) 2% weight, (c) 3% weight, (d) 4% weight, (e) 5% weight.

[26] and slow production of Mn DMA radicals. Table 4 exhibits the % grafting as well as % C.L values.

In overall comparison, Mg DA monomer yielded higher % grafting due to the nano size, better miscibility with LLDPE in its molten condition and the absence of steric effect. The Ba containing monomers gave higher % C.L values due to the presence of steric effect and very slow production of radicals with nonhomogeneity. These results inferred that both grafting and C.L efficiency depended on the size and homogeneity (miscibility) of monomer with LLDPE in its molten state.

3.2.2. Melt grafting mechanism

Parthasarathi et al. [25] explained the mechanism of free radical grafting of thioester onto HDPE backbone. Similar type of mechanism is applied to the present system. However, the presence of two double bonds at the end of metal ester leads to different possible reactions. Melt functionalization reaction proceeds via free radical reaction. Free radical reactions occurred through three-steps namely initiation, propagation and termination reactions.

DCP, the free radical initiator, produced two cumyloxy radicals while heating at 160 °C under inert atmosphere with normal dissociation rate. The secondary formation of aggressive methyl radical at 160 °C is minimum in DCP system. The minimum side product with normal generation of cumyl oxyradicals with normal dissociation rate of DCP urged us to use DCP as a free radical initiator for the current investigation. Formations of free radicals are the initiation step of melt functionalization reaction. The formed free radicals interacted with LLDPE and other esters led to the various processes. In the present investigation, we used 1:1:1 ratio of LLDPE, esters and DCP. In general, 1 mol of DCP is required to initiate 1 mol of LLDPE and 1 mol of ester. Hence, we used the equal concentrations of DCP and ester. The experimental results indicated that the ester functionalization process followed the 2.0 order of reaction with respect to % weight of DCP particularly in the case of Ba salts. The Mg DA system followed the 0.50 order of functionalization reaction. Meanwhile, the coupling of LLDPE macro radicals led to the C.L reaction. By this way, the experimental results obtained through various chemical reactions and proposed reactions scheme are matching with each other. Reactions are mentioned in Scheme 1.

4. Conclusions

From the above kinetic study the important points are presented here as conclusions. (1) The DAs yielded the higher % functionalization and DMAs produced the higher % C.L. values. (2) The Mg salts exhibited the higher $T_{d,w}$ and % functionalization values due to the homogeneity with LLDPE in its molten state. (3) The Mg DA showed the 0.50 order of functionalization reaction whereas the Mg DMA exhibited the 1.0 order of functionalization reaction with respect to % weight of DCP. (4) Ba DA showed 69.9% weight residue remained above 750 °C in TGA analysis. (5) The $RI_{[C=O/C-H]}$ was increased with the increase of % weight of metal salts due to more and more chemical grafting onto LLDPE backbone in the presence of DCP under inert atmosphere at 160 °C. (6) The kinetics of Ba salts declared that the melt functionalization reaction occurred through the bi-molecular termination reaction.

Acknowledgement

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

References

- [1] E.H. Walker Jr., A.W. Apblett, R. Walker, A. Zachary, Chem. Mater. 16 (2004) 5336–5343.
- [2] N. Duxin, F. Liu, H. Vali, a. Eisenberg, J. Am. Chem. Soc. 127 (2005) 10063-10069.
- [3] P.G.S. Compos, M.C.A. Fantini, D.F.S. Petri, J. Braz. Chem. Soc. 15 (2004) 532–540.
- [4] L. Li, J. Yin, G. Costa, P. Stagnaro, J. Appl. Polym. Sci. 111 (2009) 1268–1277.
- [5] L.P. Huang, X.P. Zhou, W. Cui, X.L. Xie, S.Y. Tong, J. Mater. Sci. 43 (2008) 4290–4296.
- [6] J.G. Fatou, B.R. de Gascue, Polym. Bull. 44 (2000) 285-292.
- [7] V.S. Savostyanov, A.D. Pomogailo, D.A. Kritskaya, A.N. Ponotarev, J. Polym. Sci. Part A Polym. Chem. 27 (1989) 1935–1956.
- [8] J.S. Wang, J.S. Shi, J.G. Wu, World J. Gastroenterol. 9 (2003) 1897-1899.
- [9] I. Xueref, F. Domine, Atmos. Chem. Phys. 3 (2003) 1779-1789.
- [10] S.F. Hamed, M.A. Allam, J. Appl. Polym. Sci. 2 (2006) 27-33.
- [11] S. Chakraborty, S. Bandyopadhyay, A.S. Dueri, Polym. Test 26 (2007) 38–41.
- [12] F. Svegl, B. Orel, Mat. Tech. 37 (2003) 29-31.
- [13] S. Rathika, I. Baskaran, R. Anbarasan, J. Mater. Sci. 44 (2009) 3542-3555.
- [14] K. Duraimurugan, S. Rathika, R. Anbarasan, Chin. J. Polym. Sci. 26 (2008) 393-398.
- [15] M. Saule, S. Navarre, O. Babot, B. Maillard, Macromolecules 36 (2003) 7469-7476.
- [16] M. Saule, S. Navarre, O. Babot, B. Maillard, Macromolecules 38 (2005) 77-85.
- [17] S. Navarre, B. Maillard, J. Polym, Sci. Part A Polym, Chem, 38 (2000) 2957–2963.
- [18] M.F. Parveen, V. Dhanalakshmi, R. Anbarasan, J. Mater. Sci. 44 (2009) 5852-5860.
- [19] M.F. Parveen, V. Dhanalakshmi, R. Anbarasan, NANO 4 (2009) 147-156.
- [20] A. Yelilarasi, J. Juliat Latha Jayakumari, V. Dhanalakshmi, R. Anbarasan, Spectrochim. Acta A 74 (2009) 1229–1234.
- [21] A. Yelilarasi, J. Juliat Latha Jayakumari, R. Anbarasan, Polym. Polym. Compos. 17 (2009) 397-407.
- [22] R. Anbarasan, S. Kanchana, S. Gayathri, T. Jayalakshmi, V. Dhanalakshmi, J. Appl. Polym. Sci. 115 (2010) 315–323.
- [23] R. Anbarasan, O. Babout, B. Maillard, J. Appl. Polym. Sci. 97 (2005) 761–765.
- [24] R. Anbarasan, O. Babout, M. Dequil, B. Maillard, J. Appl. Polym. Sci. 97 (2005)
- 766–774.
 [25] V. Parthasarathi, B. Sundaresan, V. Dhanalakshmi, R. Anbarasan, Polym. Eng. Sci. 50 (2010) 474–483.
- [26] R. Anbarasan, V. Dhanalakshmi, K. Rajasulochana, M. Sudha, T. Jayalakshmi, M. Anusuya, J. Appl. Polym. Sci. 115 (2010) 2582–2590.
- [27] N. Gupta, A.K. Srivastava, Macromolecules 28 (1995) 827-832.
- [28] A. Panacek, M. Kolar, R. Vecerora, L. Kvitek, Biomaterials 30 (2009) 6333-6340.