

Synthesis, characterization and melt functionalization of high density poly (ethylene) with zinc salt

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Zinc dimethacrylate (Zn DMA) was synthesized by a chemical method and characterized by different analytical tools like Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) analysis, differential scanning calorimetry (DSC) and high resolution transmission electron microscopy (HRTEM). Synthesized Zn DMA was melt-functionalized with high density polyethylene (HDPE) at 160 °C in nitrogen atmosphere. For melt functionalization reaction, dicumyl peroxide initiator (DCP) and Zn DMA were used in 1:1 ratio. FTIR spectroscopy was used to confirm the quantitative chemical grafting of Zn DMA onto HDPE backbone. FTIR-Relative Intensity (FTIR-RI) method was used to find out the order of melt functionalization reaction. The results were analyzed and critically compared with literature reports. HRTEM report confirmed the chemical grafting of Zn DMA onto HDPE backbone. A plausible reaction mechanism was proposed.

Key Words: Zinc dimethacrylate, FTIR, DSC, HRTEM, Melt functionalization

INTRODUCTION

Recently, many astonishing industrial developments have been registered particularly in the engineering plastic field because of the rapidly increasing use of plastics in varied applications in the automobile and packaging sectors. However, plastics are inactive towards bio-degradability due to the absence of functional groups in their backbone thus causing environmental pollution. Melt grafting is a way to minimize the undesired properties by introducing additional functions in a polymer. By using the melt functionalization method, functional compounds are chemically grafted onto the backbone of polyolefins to make them environment friendly, i.e., to make them active towards the bio-degradation process. Different techniques are available for the functionalization process. For example, Garmabi and co-workers [1] reported the free radical grafting of glycidyl methacrylate onto HDPE by the response surface method. PE backbone was modified with heparin for the improvement of antithrombogenicity [2]. HDPE was grafted with acrylic acid [3], chloromethyl styrene [4], epoxide [5] ethylmercapto propionate [6], butyl-3-mercapto propionate and ethyl-2-mercapto propionate [7]. Currently, melt grafting of metal salts onto the polyolefin backbone is a fascinating field of

research because of their ester functionalization and active double bond present as a side chain for further structural modification. The recent literature indicates that different metal salts were synthesized, characterized and grafted onto polyolefin backbone [8, 9]. In 2005, Sadeghi [10] reported on the synthesis and characterization of Zn salts containing polymerizable double bond. Poly(siloxane)-Zn DMA composites were prepared and characterized by various analytical tools [11]. Other authors also reported on the synthesis, characterization and application of Zn DMA [12-15]. The thorough literature survey did not reveal, however, reveal any report on the synthesis, characterization and melt grafting of zinc dimethacrylate (Zn DMA) onto HDPE backbone in the presence of dicumyl peroxide as a free radical initiator. In the present investigation, we successfully synthesized, characterized and grafted Zn DMA onto HDPE in the presence of dicumyl peroxide (DCP) as a free radical initiator at 160 °C in nitrogen atmosphere.

After the melt functionalization process, the amount of Zn DMA grafted onto HDPE backbone can be determined by chemical or instrumental analytical methods. Generally, the chemical methods cause environmental pollution because of the utilization of toxic and hazardous solvents. The instrumental analytical methods are eco-friendly and inexpensive and provide more accurate results. For these reasons, we preferred the FTIR

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spectroscopy method to find out the amount of ester grafted onto HDPE backbone. FTIR spectroscopy is used for both qualitative [16,17] and quantitative [18-25] analysis. Recently, Kaith *et al.* [26] and Chauhan *et al.* [27-29] explained the thermal properties of structurally modified polymers.

No report was found in the literature on the FTIR-RI based determination of kinetics of melt functionalization of Zn DMA onto HDPE backbone. The novelty of the present investigation is the conversion of non-biodegradable HDPE into biodegradable, processable and eco-friendly HDPE by a simple melt functionalization reaction. Moreover, metal salts are also eco-friendly. The FTIR-RI method was used to determine the amount of melt grafted Zn DMA onto HDPE backbone. In such a way, environmental issues related to the plastic pollution can be solved.

MATERIALS AND METHODS

Zinc carbonate (SD Fine Chemicals, AR grade, India) and methacrylic acid (MA, SD Fine Chemicals) were used as received. High density poly(ethylene) (HDPE, Rayson, India, of average molecular weight 1,25,000 Da) was purified by the procedure followed in our earlier publication [5]. Toluene (Chemspure, AR, India) and acetone (Merck) were used without further purification. Dicumyl peroxide (DCP, Across Chemicals, UK) and cyclohexane (Paxy chemicals, AR, India) were used as received.

Purification of HDPE

5g of HDPE powder sample was dissolved in 100 mL of toluene at 130 °C for 3h in order to remove antioxidants added during its long period of storage. During the dissolution process, the toluene solvent was boiled and evaporated. In order to avoid the loss of solvent molecules, the condenser unit was circulated with cold water. After dissolving the HDPE powder samples in toluene, 800 mL of acetone was added to precipitate the HDPE [5]. The contents were filtered and dried at 60 °C for 24 h under vacuum. The dissolution and precipitation processes were repeated thrice to further purify the HDPE. Finally, the dried samples were weighed and stored in a zipper bag.

Synthesis of zinc dimethacrylate (Zn DMA)

10g ZnCO₃ was dissolved in 100 mL of 0.01M HCl solution in a three-necked round bottom (RB) flask. 10 mL of methacrylic acid was dropwise added to the acidified ZnCO₃ solution followed by 0.03 g of antimony trioxide, the esterification catalyst, to catalyze the metal salt formation

process. The contents were sparged with nitrogen gas to create an inert atmosphere inside the RB flask. The latter was connected to a water condenser and the solution was boiled with vigorous stirring at 90 °C for 3h. There is a chance for the polymerization of MA under these conditions, but due to the dominant reaction of zinc chloride with methacrylic acid, the double bond remains unaltered. During this reaction, HCl is obtained as a by-product. Zn DMA thus formed is insoluble in water and was hence purified from HCl by repeated washing with doubly distilled water. Finally, the Zn DMA was washed with acetone and the sample was dried, weighed and stored in a zipper bag. Synthesis of Zn DMA and melt functionalization with HDPE are the novel contributions of the present investigation.

Synthesis of HDPE-g-Zn DMA

1g of pure HDPE powder sample was mixed with 1% w/w of Zn DMA in 25 mL of cyclohexane-dichloromethane (1:9 v/v) solvent mixture in a 100 mL beaker under mild stirring. Then 1% w/w of DCP was added to the contents of the beaker and the stirring was continued for further 1h. The solvent mixture was used to distribute the DCP and Zn DMA onto HDPE backbone uniformly, otherwise agglomeration would occur. In the present investigation, both DCP and ester were used in equal concentrations at a 1:1 ratio, after many trial experiments. DCP was selected as a free radical initiator due to its normal dissociation rate at 160 °C with minimum side products. After 1h of mixing, the solvents dichloromethane and cyclohexane were removed by rotary evaporation. The complete removal of the solvent mixture from the reaction mixture was confirmed by the constant weight. Then the reaction mixture was transferred to a test tube reactor and de-aerated for 30 min with sulphur-free nitrogen gas. After degassing, the temperature of the reactor was raised to 160 °C (at a heating rate of 10 °C/min) for 2.5 h without stirring. During the melt functionalization process, the same was dissolved in the molten HDPE and produced a homogeneous medium. After the melt functionalization process, the reactor was removed from the oil bath, cooled to room temperature and the samples were collected and cut into small pieces. These were put in toluene at 130 °C for 30 min for the purpose of isolation. 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. It is very difficult to isolate the non-cross linked HDPE from

the functionalized HDPE because of its solubility. Even after the functionalization process, the grafting occurred in a random way. 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 recorded and quantitative calculations were done with the non-cross linked, functionalized polymers.

Characterization

FTIR spectra were recorded on a 8400 S Shimadzu FTIR spectrometer in KBr pellets in the range from 400 to 4000 cm⁻¹. 7 mg of metal salt functionalized HDPE sample was grinded with 200 mg of KBr and made as a pellet under 750 tons of pressure. In order to avoid errors while recording the FTIR spectrum, corrected peak areas were considered. To cross check the corrected peak area values, the FTIR spectra were recorded for the same sample disc in different parts. After proper base line correction (to avoid error) with the aid of FTIR software, the same corrected peak area values were obtained. FTIR spectrum was recorded thrice for the same sample disc and the same corrected peak area values have been obtained. In such a way, the errors were nullified. Further the efficiency of FTIR software was cross checked manually by predicting the lower and upper limits and the corrected peak area was determined. In this case also we got the same corrected peak area value as reported previously. Three-point (4000, 2000 and 450 cm⁻¹) baseline correction was made to nullify the error in peak area measurement for accurate calculation. For the quantitative determination of % ester grafting, the following corrected areas of the peaks, which were assigned at 1730 (C=O) and 720 (C-H out of plane bending vibration) cm⁻¹ were determined and the relative intensity (RI) was calculated as mentioned below. For the RI measurement, the C-H bending mode appeared at 1450 cm⁻¹ can also be considered because of its sharpness and more dense nature. The present investigation followed the literature report [5, 6] strictly because of the availability of proportionality constant for the A₁₇₃₀/A₇₂₀.

$$RI \text{ of carbonyl ester } (RI_{[C=O/C-H]}) = A_{1730}/A_{720} \dots (1)$$

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

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

[20]. During the melt functionalization reaction, gel formation due to the cross-linking (C.L.) reaction is also possible. At higher degree of functionalization, the % C.L. was low. The cross-linked gel was insoluble in any of the solvents available at the laboratory. For the ease of dissolution purpose, we chose the soluble part of the functionalized HDPE sample alone. At the same time, melt functionalization occurred in the cross-linked gel too. In the present investigation, we considered the non-cross linked HDPE with ester functionalized samples only. The % C.L. was determined by the following formula:

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

DSC of the sample was recorded using the Universal V4.3A TA instrument under nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 300 °C. XRD was recorded using the Rigaku Rint 2000 (Japan) diffractometer at room temperature with CuKα1 radiation in the 2 theta value range of 20 to 60°. The voltage and current of X-ray tubes were 40 kV and 100 mA, respectively. Elemental analysis was carried out using Elementor GmbH Vario El instrument. Synthesized nano material topography and size were observed by HRTEM on a JEM-200 CX transmission electron microscope.

RESULTS AND DISCUSSION

For the sake of convenience, the results and discussion part is sub-divided in: 1) synthesis and characterization of Zn DMA and 2) melt surface grafting of Zn DMA onto HDPE backbone.

Synthesis and characterization of Zn DMA

FTIR study

Figure 1 shows the FTIR spectrum of Zn DMA. The important functional groups present in Zn DMA are characterized below. The Zn DMA spectrum contains free hydroxyl stretching (3617 cm⁻¹), C-H symmetric stretching (2842 cm⁻¹), C-H anti-symmetric stretching (2926 cm⁻¹), C=O stretching (1738 cm⁻¹), C=C stretching (1646 cm⁻¹), C-H bending vibration (1562 cm⁻¹), C-O-C linkage (1141 cm⁻¹), C-H out of plane bending vibration (814 cm⁻¹) and Zn-O stretching (460 cm⁻¹). Appearance of these peaks confirmed the chemical functionalities of Zn DMA. The hydroxyl stretching is associated with the intercalated water molecules in Zn DMA [30] and the presence of the same can be further confirmed by DSC analysis.

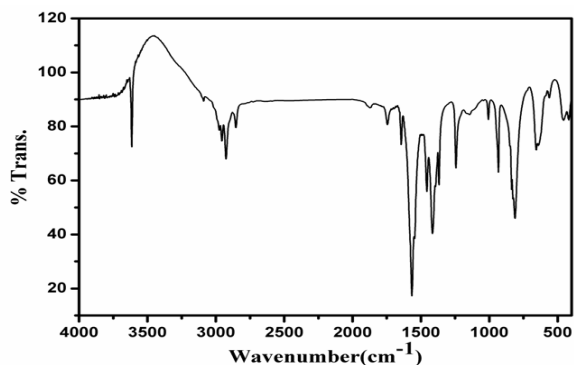


Fig. 1. FTIR spectrum of Zn DMA

DSC study

Figure 2 shows the DSC of Zn DMA. The DSC thermogram exhibits two endothermic peaks at 179.5 °C and 235.5 °C for the removal of intercalated water molecules and the melting temperature (T_m) of Zn DMA respectively. Recently, Anbarasan and co-workers [25] reported the DSC of Ca DMA with very high melting temperature. The present system also yielded a similar result.

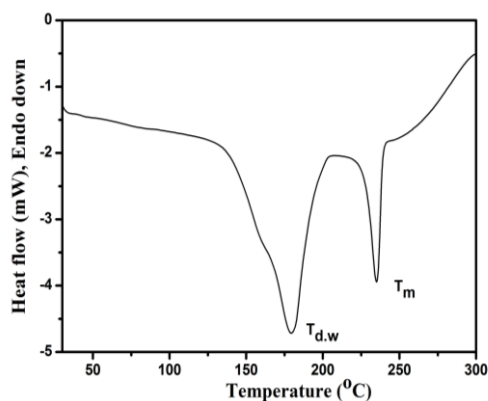


Fig. 2. DSC of Zn DMA

XRD analysis

Figure 3 represents the XRD of Zn DMA. The diffractogram shows many sharp crystalline peaks of Zn DMA. This confirmed that Zn DMA is a crystalline powder. Appearance of a peak at the 2 theta value of 22.80° confirmed the presence of d_{111} crystal plane. Other important crystal planes such as d_{100} (31.6°) and d_{101} (36.1°) were also available. Thus, the XRD confirmed the highly crystalline nature of Zn DMA.

Elemental analysis

Further, the structural composition of Zn DMA was confirmed by elemental analysis. Zn DMA produced the following data on elemental analysis: C-38.08%, H-3.51%, O-58.41% and supported the following structural formula: $C_8H_{10}O_4Zn \cdot 2H_2O$.

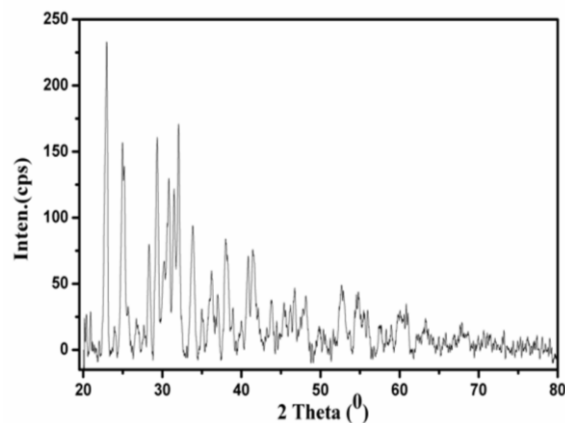


Fig. 3. XRD of Zn DMA

HRTEM report

Figure 4 shows the HRTEM images of Zn DMA. Figure 4a exhibits the distorted layered structural arrangement of different crystal planes of zinc ions. The layered structure of Zn^{2+} ion was broken by the salt formation with methacrylic acid. The length and breadth of the zinc ion in Zn DMA was found to be 10-12 nm and <0.10 nm, respectively. Figure 4b represents the nanosphere-like structure of Zn DMA with a diameter of <5 nm.

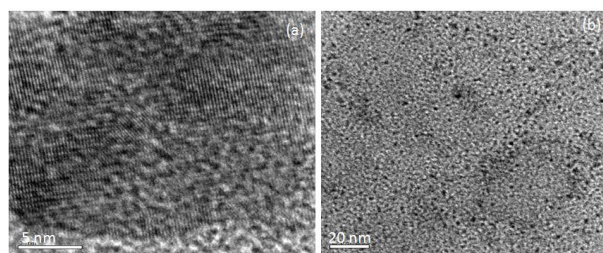


Fig. 4. HRTEM of Zn DMA

Melt functionalization of HDPE with Zn DMA

Effect of (% w/w of Zn DMA) on the RI values of carbonyl group and % C.L

The synthesized Zn DMA was melt functionalized with HDPE in the presence of equal concentration of DCP, a free radical initiator, under nitrogen atmosphere at 160 °C. The % w/w of Zn DMA was varied from 1 to 5%. Figure 5a shows the FTIR spectrum of pristine HDPE. The important peaks are characterized below: A broad peak around 2900 cm^{-1} is due to the C-H anti-symmetric stretching vibration. A small hump at 2646 cm^{-1} corresponds to the C-H symmetric stretching vibration. The C-H bending vibration appears at 1469 cm^{-1} . A sharp peak at 721 cm^{-1} is ascribed to the C-H out of plane bending vibration. Figure 5 b-f shows the FTIR spectra of HDPE after melt functionalization with 1 to 5 w/w % of Zn DMA. The system exhibits some new peaks. They are explained below: The OH stretching due to the intercalated water molecules is observed around 3500 cm^{-1} . The metal salt carbonyl group is

observed at 1721 cm^{-1} . The -OH bending vibration (due to the intercalated water molecules in the basal spacing of Zn DMA) is observed at 1646 cm^{-1} . A broad peak at 1586 cm^{-1} accounts for the presence of C=C double bond. This indicates that among the two double bonds, one C=C is freely available and the remaining one is involved in the melt functionalization reaction. The ester C-O-C linkage is observed at 1048 cm^{-1} . A peak at 609 cm^{-1} indicates the presence of Zn-O stretching. Appearance of these new peaks confirmed the chemical grafting of Zn DMA onto HDPE backbone.

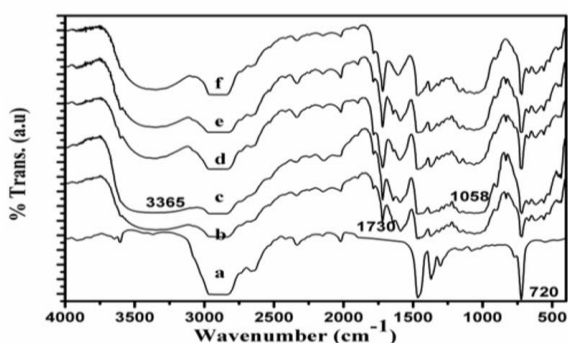


Fig. 5. FTIR spectra of HDPE functionalized with Zn DMA at a) 0% w/w, b) 1% w/w, c) 2% w/w, d) 3% w/w, e) 4% w/w, f) 5% w/w

While increasing the % w/w of Zn DMA and keeping the other experimental conditions constant, the FTIR-RI of carbonyl group linearly increased. The increase in carbonyl peak intensity is due to the Zn DMA grafting through active C=C double bond. In order to find the order of the functionalization reaction, the log-log plot was drawn between % w/w of DCP and $RI_{[C=O/CH]}$ (Figure 6a). The plot shows a linear increase in RI with the increasing % w/w of DCP. The reaction order was determined as 1.17 from the slope of the plot. This inferred that the melt functionalization reaction followed the 1.25 order of reaction with respect to % w/w of DCP, i.e., 1.25 mol of Zn DMA is required to functionalize one mol of HDPE. The rate of functionalization reaction (R_f) can be written as follows: $R_f \propto (\% \text{weight of Zn DMA})^{1.17}$. In this system, one can expect melt graft copolymerization reaction due to the presence of two double bonds in Zn DMA. Due to the absence of abnormal increase in $RI_{[C=O/CH]}$, no graft copolymerization reaction took place here. Moreover, the spectra indicated the availability of a free double bond. This means that one double bond of Zn DMA was involved in the melt functionalization reaction whereas the other one remained free. This is in accordance with the literature report [21]. The % grafting values are given in Table 1.

Table 1. Effect of % w/w of Zn DMA on % functionalization and % C.L.

% w/w Loading	HDPE-ZnDMA	
	% Functionalization	% Crosslinking
1	61.6	8.4
2	67.3	13.2
3	71.2	19.6
4	75.7	25.9
5	77.8	31.3

The % C.L. values on varying the % w/w of Zn DMA are indicated in Table 1. The % C.L. values varied from 8 to 31%. When compared with the mercapto ester grafting [7], the present system yielded higher % C.L. values due to the poor radical forming nature of Zn DMA. Moreover, it contains two double bonds and leads to cross-linking reaction. In order to find the order of % C.L. reaction, the plot of $\log(\% \text{weight of Zn DMA})$ vs $\log(\% \text{C.L.})$ (Figure 6b) was drawn and the slope was determined as 1.60. This confirmed the 1.50 order of C.L. reaction. The rate of C.L. ($R_{C.L.}$) can be written as follows: $R_{C.L.} \propto (\% \text{weight of Zn DMA})^{1.60}$. This infers that 1.60 mol of Zn DMA is required to cross-link one mol of HDPE backbone.

The % grafting values of the present system are low when compared with the mercapto ester grafting onto HDPE backbone [7]. This is due to the slow free radical formation nature of Zn DMA. The low % grafting of Zn DMA is due to the higher melting temperature and crystalline behaviour. Even though Zn DMA has a higher T_m , it was dissolved in the molten HDPE medium and was involved in the melt functionalization reaction with higher % C.L. values.

HRTEM report of HDPE-g-Zn DMA

Figure 7 shows the HRTEM image of Zn DMA grafted HDPE backbone. The Zn salt is uniformly distributed on the HDPE backbone with a size of less than 20 nm. This confirmed the chemical grafting of Zn salt onto HDPE backbone in the presence of a free radical initiator. Some agglomerated portion is also noticed.

Melt grafting mechanism

Anbarasan *et al.* [5, 7] explained the mechanism of free radical grafting of thioester onto HDPE backbone. A similar type of mechanism was applied to the present system too. However, the presence of two double bonds at the ends leads to different possible reactions. Melt functionalization reaction proceeds *via* free radical reaction. Free

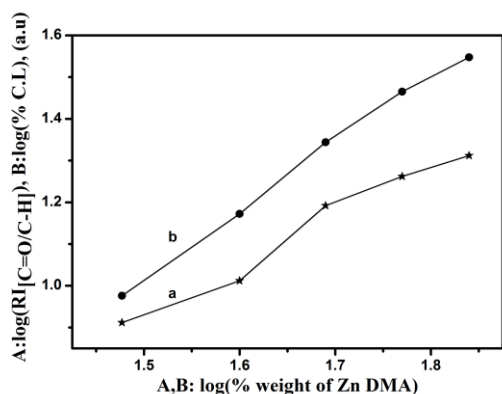


Fig. 6. Effect of (% w/w of Zn DMA) on a) $RI_{[C=O/C-H]}$ and b) % C.L of HDPE

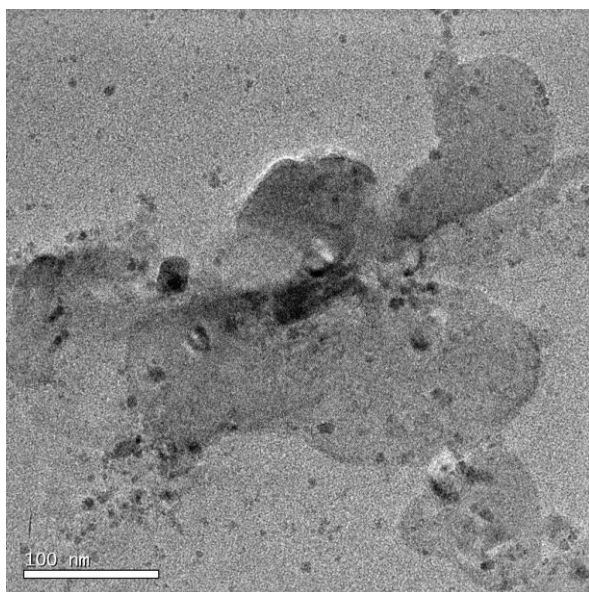
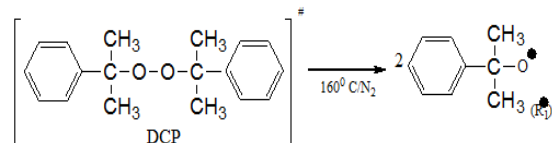
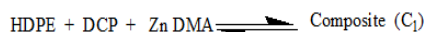


Fig. 7. HRTEM image of HDPE-g-Zn DMA

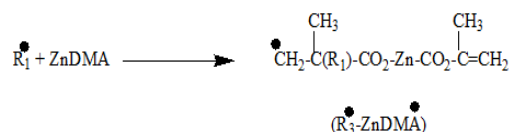
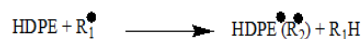
radical reactions proceed in three steps, namely, initiation, propagation and termination (Scheme 1).

DCP, a free radical initiator, produced two cumyloxy radicals on heating to 160 °C at a normal dissociation rate. Formation of free radicals is the initiation step of the melt functionalization reaction. In the first step, DCP undergoes dissociation to form two cumyloxy radicals. These radicals can interact either with HDPE or with Zn DMA. Following interaction with HDPE, HDPE macro radicals will be formed. Following interaction with Zn DMA, a Zn DMA radical will be formed. The coupling of a HDPE macro radical and a Zn DMA radical leads to the formation of metal salt functionalized HDPE. This means that the formed free radicals interacted with HDPE and produced HDPE macro radicals for functionalization and C.L. reactions. In the present investigation we used a 1:1:1 ratio of HDPE, Zn DMA and DCP. Coupling of HDPE macro radicals led to C.L. reactions.

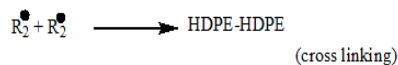
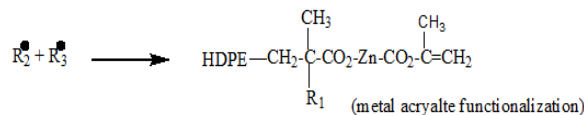
Initiation



Propagation



Termination



Scheme-1 Melt functionalization of HDPE with Zn DMA

CONCLUSIONS

The FTIR spectrum and DSC report confirmed the presence of intercalated water molecules in Zn DMA. A peak at 609 cm^{-1} in the FTIR spectrum confirmed the chemical grafting of Zn DMA onto HDPE backbone. Further, a melting temperature (T_m) of 235.5 °C was observed on the DSC thermogram of Zn DMA. HRTEM revealed the nanosize of Zn ions in Zn DMA with broken layered structure and showed the sphere-like structure of Zn DMA. XRD revealed the crystalline structure of Zn DMA with d_{111} plane. The melt functionalization of Zn DMA onto HDPE followed the 1.25 order of reaction for functionalization and 1.5 order of reaction for crosslinking. The lowest % functionalization of Zn DMA was due to higher melting temperature and more crystalline structure. According to the adopted reaction mechanism, the melt functionalization reaction proceeded through a free radical process.

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СИНТЕЗА, ОХАРАКТЕРИЗИРАНЕ И ФУНКЦИОНАЛИЗИРАНЕ В СТОПИЛКА НА ПОЛИЕТИЛЕН ВИСОКА ПЛЪТНОСТ С ЦИНКОВА СОЛ

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(Резюме)

Синтезиран е цинков диметакрилат (Zn DMA) и е охарактеризиран чрез аналитични методи, например инфрачервена спектроскопия с Фурие-трансформация (FTIR), рентгенова дифракция (XRD), диференциална сканираща калориметрия (DSC) и трансмисионна електронна микроскопия с висока разделителна способност (HRTEM). Синтезираният Zn DMA е подложен на функционализиране в стопилка с полиетилен висока плътност (HDPE) при 160°C в среда на азот. За реакцията на функционализиране е използван Като инициатор ди-кумил пероксид (DCP) в отношение 1:1 спрямо цинковата сол. FTIR-спектроскопията и HRTEM-методът потвърждават количествено химическото присаждане на Zn DMA върху макромолекулния скелет на полиетилена. Методът на относителния интензитет (FTIR-RI) е използван за откриването на реакцията на функционализиране в стопилка. Предложен е правдоподобен механизъм на реакцията.