

Functionalization and Cross-Linking of High-Density Polyethylene in the Presence of Dicumyl Peroxide—An FTIR Study

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ABSTRACT: High-density polyethylene was thermolysed with short-chain organic compounds (additives) with an ester functional group in the presence of free radical initiator such as dicumyl peroxide at 160°C. The experimental results inferred that an additive with a hydrogen donor containing a thiol group showed better efficiency toward functionalization and an additive with a methylene bridged group showed better efficiency toward cross-linking. The FTIR spectral results indicated that the area of the carbonyl peak at 1730 cm⁻¹ increased with the increase in percentage grafting of additives with simultaneous increase of cross-linking.

The ester grafting was further confirmed by saponification reaction. The possibility of acid functionalization via intramolecular hydrogen transfer was also checked through acid hydrolysis of the saponified products. A suitable reaction mechanism was proposed in order to explain the experimental and spectral data obtained. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 766-774, 2005

Key words: HDPE; peroxide; thermolysis; functionalisation; cross-linking; FTIR spectroscopy; mechanism

INTRODUCTION

Day by day the utilization of polyolefins, particularly polyethylene, is increased in the packaging sector and in the automobile industry. But its applications are restricted to some extent due to its lack of chemical functionality, poor dyeability, solubility in organic solvents at higher temperature, and high sensitivity toward photo or thermal oxidation degradation reactions. In order to outwit these problems, grafting with a functional group containing compounds in the presence of organic peroxides was investigated.¹ The atactic polypropylene (aPP) was functionalized with the hydroxyl group containing additive in the presence of dicumyl peroxide at 170°C.^{2,3} Epoxy functionalized polyolefin was reported by Akinori and research team.⁴ Acid and ester groups have been introduced into the polyolefin backbone in the presence of various organic peroxides.⁵⁻⁷ Grafting of maleic anhydride onto various polyethylene in the presence of peroxide was reported by Clark et al.⁸ Fatou and co-workers⁹ reported the functionalization of PE with diethyl malate at its melting temperature. Also they reported

that the crystallinity value was found to decrease while the degree of grafting increased. *t*-Butyl cumyl peroxide-initiated grafting of isocyanate onto polypropylene was reported with decreased PP melting point, onset temperature, and heat of fusion.¹⁰ Assoun and research team¹¹ studied the functionalization of PP through the thermal decomposition of acid functionalized peroxides. PP was functionalized in the melt phase by grafting with itaconate in the presence of Lupersol-101 as a free radical initiator.¹² Recently Navarre et al.¹³⁻¹⁶ published different ester functionalized HDPE with cross-linking. Anbarasan and co-workers^{17,18} communicated the results on functionalization and cross-linking of HDPE in the presence of acrylic peroxide and various organic peroxides. The aim of the present investigation is to report the functionalization of HDPE with simultaneous cross-linking in the presence of DCP as a free radical initiator with various organic ester functionalized compounds (additives) at 160°C under an inert atmosphere.

EXPERIMENTAL

DCP was purchased from Aldrich Chemicals (Lyon, France) and used without any further purification. HDPE was purchased from Across Chemicals. In order to remove the antioxidant present in the HDPE sample it was purified prior to thermolysis reaction.

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The purification procedure is as follows: 10 g of HDPE (Across, Ref. No. 17851) with molecular weight of 125,000 g/mol was dissolved in 400 ml of 1,2-dichlorobenzene (DCB) (Across, Ref. No. 11318) at 145°C. After the complete dissolution of HDPE in DCB, it was precipitated in 1 L of acetone (Xilab Chemicals), filtered, and washed during 24 h in a Soxhlet apparatus with dichloromethane (DCM) (Xilab Chemicals). The PE mass thus obtained was dried under a vacuum at 60°C until there was no change in mass. Additives used in the present investigation were ethyl-1-thiol propanoate (A_1), ethyl-1-phenyl acetate (A_2), ethyl-1-methoxy acetate (A_3), ethyl-1-methoxy acrylate (A_4), toluene acetate (A_5), and diethyl malonate (A_6) (purchased from Across Chemicals and used as such).

Thermolysis reaction of peroxide in the presence of HDPE/additive mixture

A total of 1 g of HDPE was taken in a 25-ml round-bottom flask and a definite quantity of peroxide solution (6 ml solvent mixture—dichloromethane (9 ml)/cyclohexane (1 ml)). The required amount of any one of the above-mentioned ester functionalized additives was added with the HDPE/peroxide mixture. The contents were mixed well for 2.5 h at room temperature. After thorough mixing, the solvents were removed with the help of Rota vapor under reduced pressure until a constant mass was obtained. Thus, the obtained polymer/peroxide mixture was placed in a mini reactor (Buchi glasuster BM 100). The reactor was closed and degassed by the injection of argon for 30 min. The reactor was heated in an oil bath at a temperature of 160°C for 2.5 h without any stirring.

Isolation and determination of amount of cross-linked HDPE

Rectangular-shape bags made of steel (porosity, 100 mesh from Société Gantois, France) were prepared with a size of 5 × 2.5 cm and weighed (W_1 g). After the thermolysis reaction, the thermolysed polymer sample containing both cross-linked and non-cross-linked parts was removed from the reactor and cut into small pieces. These pieces were divided into three equal parts and taken in three steel bags and weighed (W_2 g). The weighed steel bags containing polymer pieces were placed in 125 ml of DCB for 16 h at 145°C with stirring. During this extraction period all soluble polymers in the medium and those that came out of the steel bags were dissolved. The polymer sample remaining in the steel bags is the cross-linked polymer. Now the steel bags were removed from the reaction medium and extracted with 150 ml DCM for 2 h. After extraction with DCM the steel bags were dried at 60°C

under a vacuum till constant mass (W_3 g) was obtained.

The polymer dissolved (non-cross-linked) in the medium was precipitated by the addition of 400 ml of DCM, filtered, dried (at 60°C under a vacuum), and weighed to constant weight (W_4 g). The % cross-linking (% CL) was calculated from the formula

$$\% \text{ cross linking} = \frac{W_3 - W_1}{W_2 - W_1} \times 100.$$

The weight of the cross-linked polymer was further confirmed by weighing the amount of soluble polymer. In the present study only the soluble polymer after thermolysis reaction was considered for further characterization studies.

Saponification

After thermolysis reaction 1 g of (soluble part) modified HDPE was taken in a round-bottom flask and dissolved in 125 ml of toluene at 110°C. After the complete dissolution of polymer, 25 ml of 0.05 mol L⁻¹ aqueous solution of KOH was added and stirred for 2 h. After 2 h of saponification, the content was cooled down and filtered. The precipitate was washed with 30 ml of water and 20 ml of ethanol/water (50:50) mixture and finally with acetone. It was dried overnight under a vacuum at 60°C. The FTIR spectrum was recorded for the saponified polymer sample.

Acid hydrolysis

In order to determine the acid functionalization, the saponified product was subjected to acid hydrolysis. A total of 0.50 g of the saponified product was taken in a round-bottom flask filled with 125 ml of toluene and heated to 110°C. After the complete dissolution of the polymer in toluene the temperature was reduced to 90°C. Then 25 ml of 0.10 mol L⁻¹ HCl was added and acidolysis was continued for next 2 h. After acidification, the content was cooled and filtered. The precipitate was washed with water, water/ethanol mixture, and finally acetone as in saponification. The dried mass was subjected to FTIR spectroscopy.

FTIR spectroscopy

FTIR spectra of HDPE samples in the form of film before and after peroxide treatment were recorded using a Perkin-Elmer Paragon 1000 instrument. For FTIR film preparation only the soluble part of the modified HDPE was considered. After the spectrum was recorded, baseline corrections were made carefully and the area of the peaks was determined using FTIR software. For the quantitative determination of

percentage grafting, the area of the peak at 1730 and 720 cm^{-1} was determined and relative intensity was calculated as

$$\text{Relative intensity (RI)} = A_{1730}/A_{720}$$

$$\% \text{ Ester grafting} = \frac{\text{RI}_{\text{ester}} \times W}{C \times 1.52} \times 100,$$

where W is the weight of non-cross-linked polymer, C is the concentration of peroxide, and 1.52 is the calibration coefficient taken from our earlier publication,¹⁴ and

$$\% \text{ Acid grafting} = \frac{\text{RI}_{\text{acid}} \times W}{C \times 1.40} \times 100,$$

where 1.40 is the calibration coefficient taken from our earlier publication.¹⁴

RESULTS AND DISCUSSION

Thermolysis of HDPE in the presence of organic peroxides lead to various reactions like functionalization (ester, acid, and ketone), increase in crystallinity, β -scission, double bond formation, and cross-linking. Normally β -scission is favorable in the case of PP. In the case of PE cross-linking reaction is a dominant reaction. In the present investigation we concentrated only on the % CL and % functionalization (% Fn).

The % CL and % Fn of various additives were checked and compared. Based on the structure five different category of additives were used: additives with hydrogen donor group (A_1), methylene bridged group (A_6), neutral bulky electron rich group (A_2 , A_5), electron withdrawing group (A_3), and finally a dou-

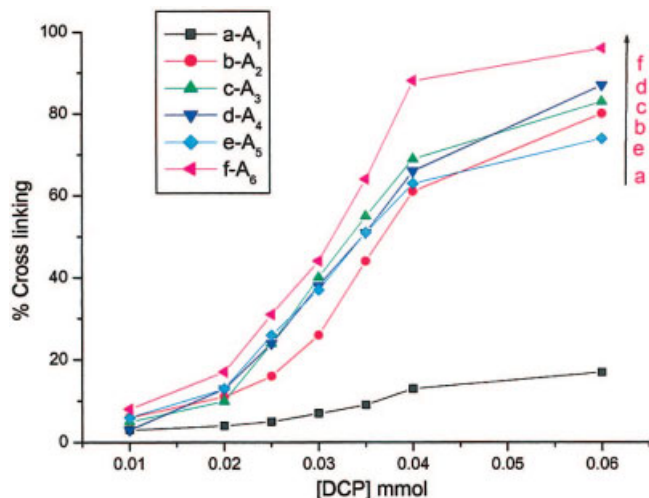


Figure 1 [DCP] vs. % CL. (a) A_1 , (b) A_2 , (c) A_3 , (d) A_4 , (e) A_5 , (f) A_6 . Temperature = 160°C; time = 2.5 h.

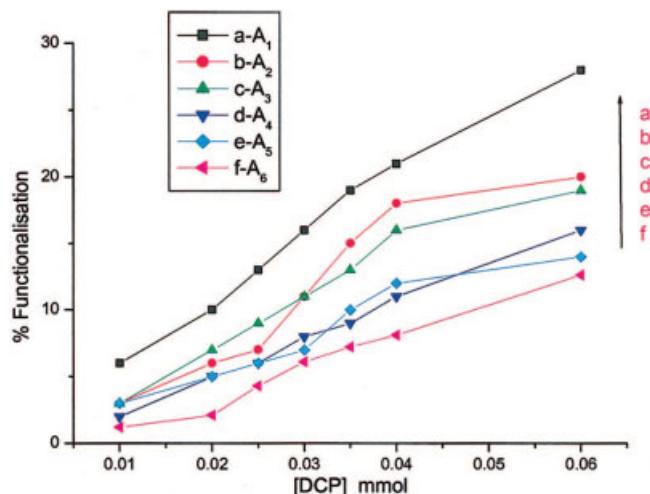


Figure 2 [DCP] vs. % Fn. (a) A_1 , (b) A_2 , (c) A_3 , (d) A_4 , (e) A_5 , (f) A_6 . Temperature = 160°C; time = 2.5 h.

ble-bond-containing group (A_4). Their efficiency toward cross-linking and functionalization was determined and compared. The reproducibility of the results were cross-checked by repeating the experiment under the same experimental conditions. The results showed within $\pm 5\%$ error.

Both ester and acid grafting calculations were tried in the present article through acid base titration. Unfortunately it failed due to the precipitation of polymer sample at lower temperature so that only FTIR-based results are reported here.

For the sake of convenience the Results and Discussion are divided into six systems. The concentration of DCP and additives was equally used and hence the % CL and % Fn were studied in terms of [DCP].

System -I, HDPE + DCP + A_1

When the concentration of A_1 and DCP was increased equally the % CL and Fn also increased simultaneously. This is indicated in Figs. 1A and 2A, respectively. The plot of concentration of DCP vs. % CL as shown in Fig. 1A gave a straight line. The plot of concentration of DCP vs. % Fn also gave a straight line as mentioned in Fig. 2A. The increase in CL is due to the formation of large number of PE macro radicals, which leads to mutual termination reaction. The increase in % Fn is due to the coupling of A_1 radical with PE macro radical.

The FTIR spectrum of A_1 grafted HDPE in the presence of DCP is shown in Fig. 3A. The area of carbonyl peak was determined from 1669 to 1800 cm^{-1} . The area of C-H deformation peak was also determined from 662 to 760 cm^{-1} and their ratio was determined. This ratio corresponds to the total quantities of carbonyl group formed due to ketone, acid, and ester

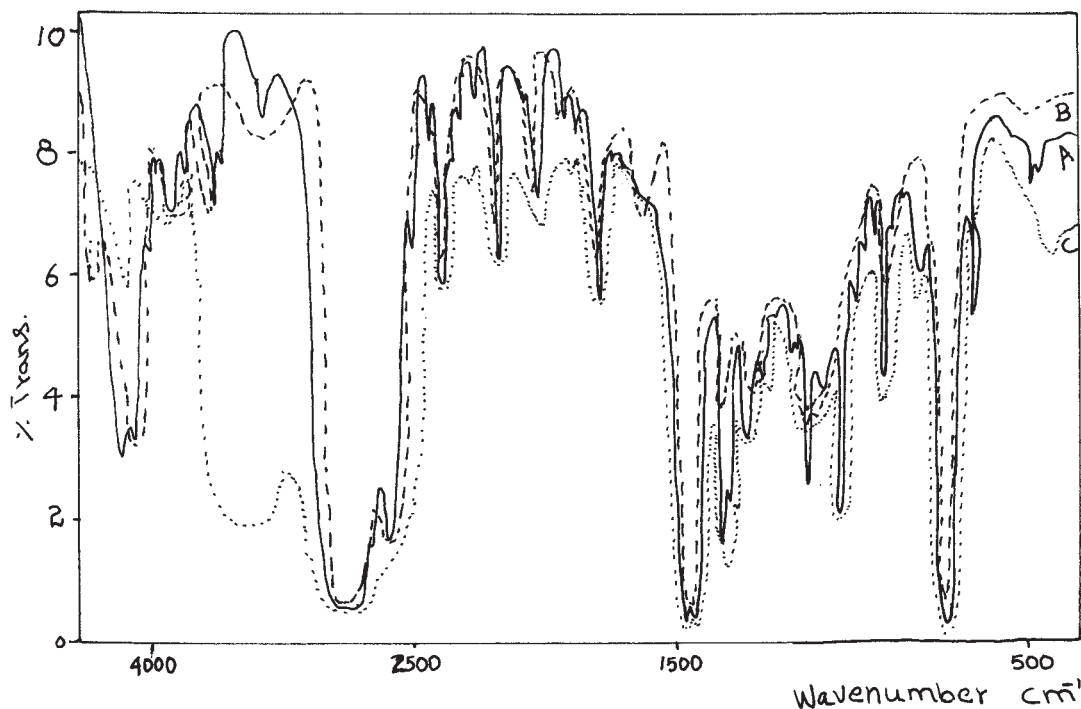


Figure 3 FTIR spectrum of HDPE-g- A_1 . A: Before saponification; B: after saponification; C: after acid hydrolysis.

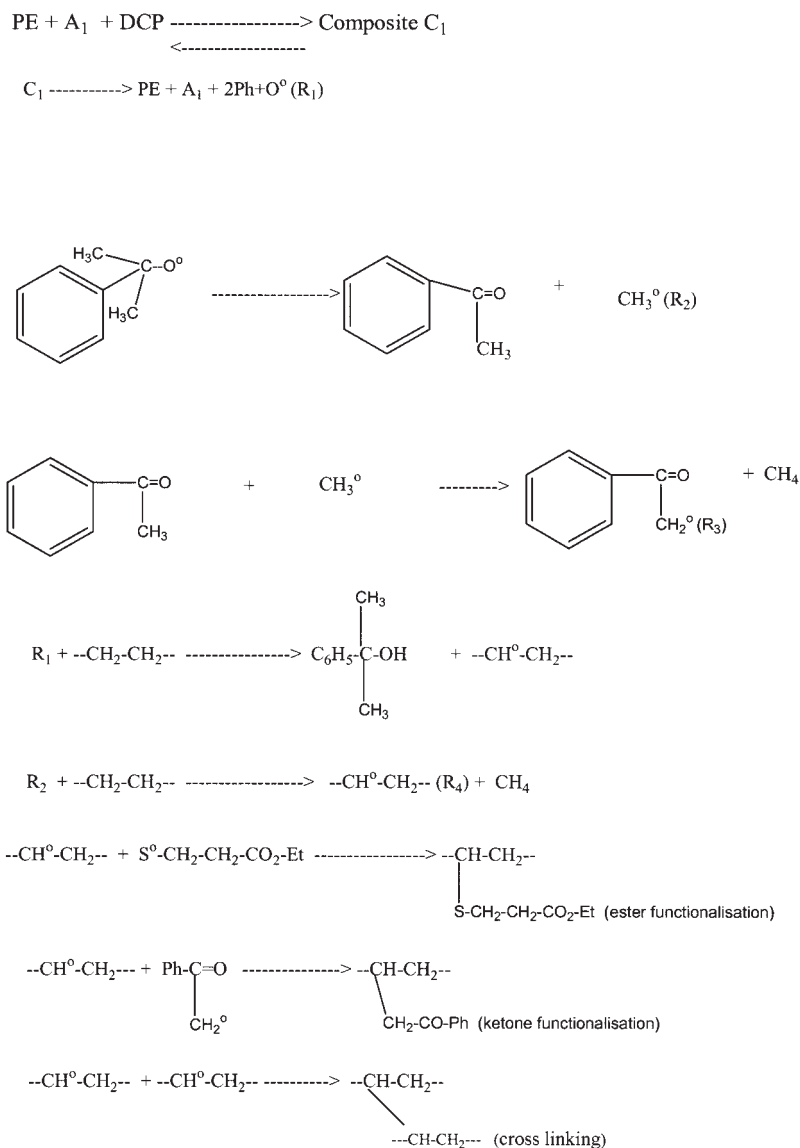
functionalization (T_1). The amount of aldehyde functionalization during thermolysis reaction was neglected. In order to determine the amount of ester functionalization, the A_1 grafted HDPE was subjected to base hydrolysis as mentioned under Experimental. Due to base hydrolysis a new peak at 1650 cm^{-1} appeared (Fig. 3B) in the FTIR spectrum due to the $\text{COO}^- \text{K}^+$ ion. The area of the peak between 1669 and 1800 cm^{-1} was again measured (T_2). $T_1 - T_2$ gives the percentage amount of ester grafting. At the end, the saponified sample was subjected to acid hydrolysis. Due to acid hydrolysis the peak at 1650 cm^{-1} disappeared and a new peak corresponding to OH stretch at 3200 cm^{-1} appeared (Fig. 3C). The area of the carbonyl peak from 1669 to 1800 cm^{-1} was determined (T_3). $T_3 - T_2$ gives the amount of acid grafted alone. In System I, 72% ester and 6% acid grafting were calculated at 0.06 mmol of [DCP]. The remaining ester and acid may be grafted in the insoluble part of the thermolysed HDPE. These results are in good accordance with that of Fodor et al.¹⁹ and Fattah and co-workers.²⁰ In the FTIR spectrum, other than the carbonyl peak another important peak at 1350 cm^{-1} was signed due to the C-S bond. This confirms the chemical grafting of A_1 onto the HDPE backbone. In order to explain the experimental and spectral data obtained, a plausible reaction pathway is proposed in Scheme 1.

When we compare the reactivity of R_1 , R_2 , and R_3 , R_2 is more aggressive than R_1 and R_3 . This can further be supported by showing higher % Fn and lower %

CL. When we come to the % Fn, the ketone functionalization is due to acetophenone radicals (R_3) and the ester Fn is due to thioester radicals (R_5). In the case of ketone functionalization, side chain ketone functionalization is the most feasible route. Because thermolysis reaction was carried out under inert atmosphere, consequently attack by molecular oxygen on the HDPE backbone is neglected. Coupling of macro radicals (R_4) led to cross-linking. From the above chemical reactions we can say that the formation of HDPE macro radicals (R_4) may be due to R_1 and the thioester radical is due to R_2 . If the case is reversed, % CL will be higher than % Fn due to the aggressiveness of the methyl radical (R_2).

System II, HDPE + DCP + A_2

The concentration of A_2 varied between 0.01 and 0.06 mmol. It is interesting to note that both % CL and % Fn increased with an increase in $[A_2]$ as shown in Fig. 1B and 2B, respectively. During functionalization the PE macro radicals were coupled with the methine radical of A_2 . Figure 1B shows three portions: the first portion was a slow increase in % CL; the second was a rapid increase; and the final was again a slow increase in % CL. But Fig. 2B shows a straight line. When compared with A_1 , System II showed higher % CL but lower % Fn. Higher % CL with lower % Fn indicated the poor formation of A_2 radical; i.e., A_2 showed little chemical inertness toward the thermolysis reaction. The functionalization was confirmed through FTIR spectro-



Scheme 1

copy (Fig. 4). The area of the carbonyl peak at 1730 cm^{-1} before and after saponification was measured. According to that the ester and acid grafting were found to be 15 and 3%, respectively.

System III, HDPE + DCP + A_3

The % CL and % Fn were determined for this system by varying the concentration of DCP between 0.01 and 0.06 mmol with equal concentration of A_3 . Figures 1C and 2C explain the nature of % CL and % Fn. As described above, the ester and acid grafting were calculated as 17 and 4% from Fig. 5. When compared with A_1 , it exhibited higher % CL but with A_2 it showed lower % CL. This may be due to the effect of methoxy group present in A_3 to stabilize the formation

of A_3 radical. Hence it provides a way for the mutual coupling of PE macro radicals.

System IV, HDPE + DCP + A_4

Ethyl crotonate was subjected to thermolysis reaction with HDPE in the presence of DCP for various concentrations. As usual the % CL and % Fn increased with increase in $[A_4]$. This can be seen in Figs. 1D and 2D. From Fig. 6 the ester and acid grafting were calculated as 9 and 5%, respectively. The % Fn of A_4 was lower when compared with A_1 . This may be due to the steric hindrance caused by the bulky methyl and ester group so that under normal reaction conditions crotonate will not undergo the polymerization reaction. In this system one could expect the graft copolymeriza-

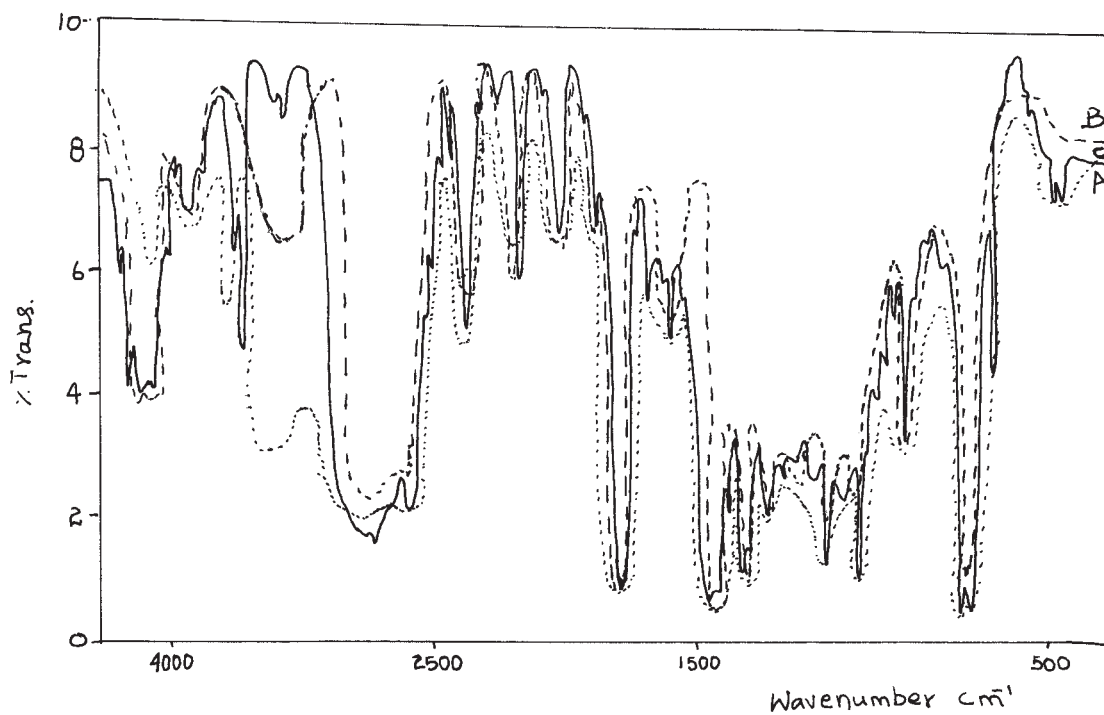


Figure 4 FTIR spectrum of HDPE-g-A₂. A: Before saponification; B: after saponification; C: after acid hydrolysis.

tion of crotonate (because it contains one double bond in its backbone) onto HDPE due to the free radical and thermal initiation. But this was not true

as evidenced by the % Fn, i.e., it gave very poor functionalization. The functionalization mechanism is as follows.

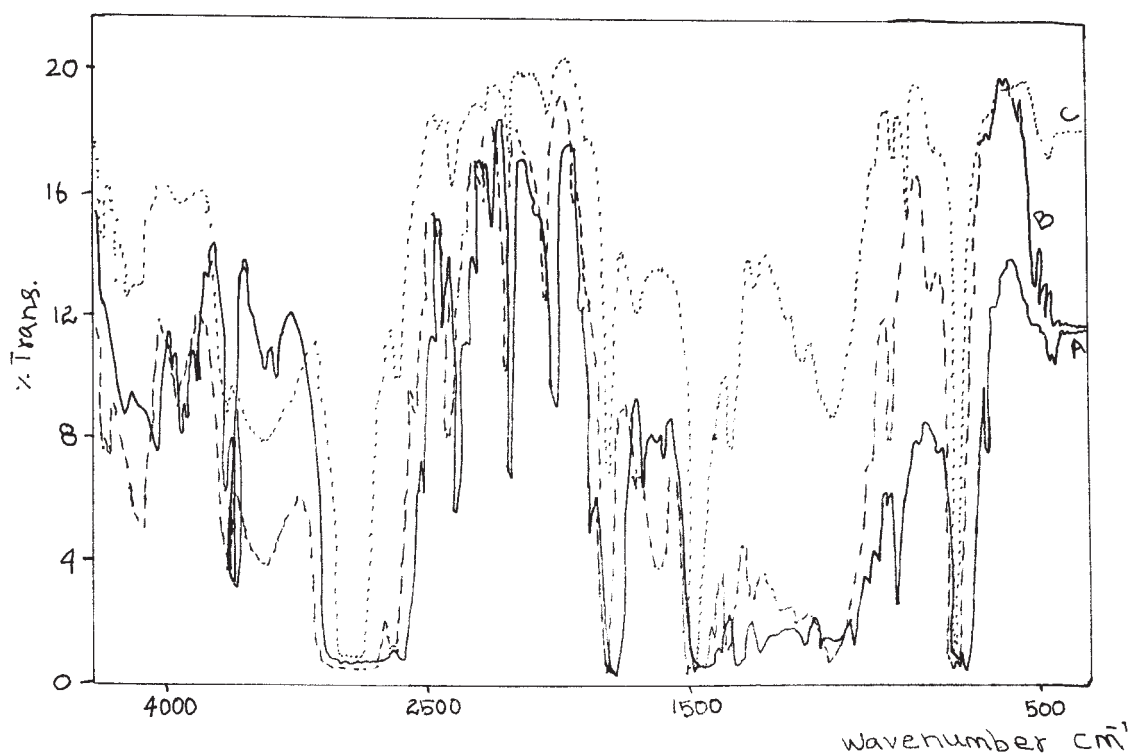


Figure 5 FTIR spectrum of HDPE-g-A₃. A: Before saponification; B: after saponification; C: after acid hydrolysis.

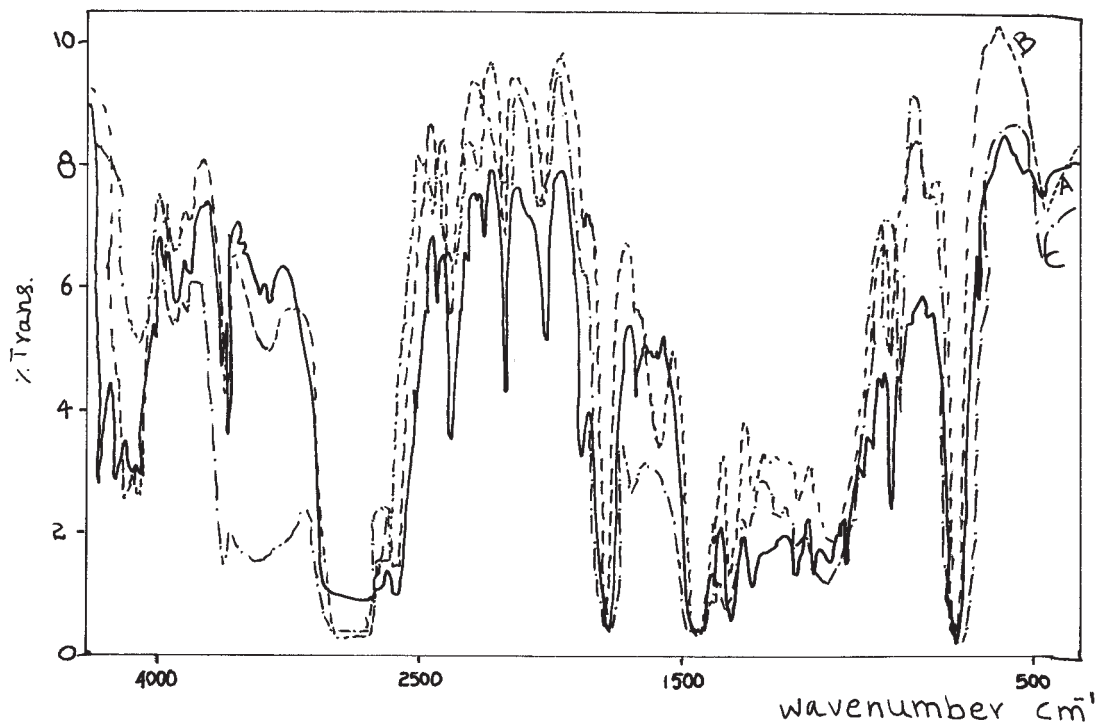


Figure 6 FTIR spectrum of HDPE-g- A_4 . A: Before saponification; B: after saponification; C: after acid hydrolysis.

System V, HDPE + DCP + A_5

Figures 1E and 2E explain the % CL and % Fn efficiency of A_5 on HDPE in the presence of DCP. It infers

that the % CL and % Fn increased with increase of $[A_5]$. Figure 7 was used to calculate the ester and acid functionalization. One can calculate 8% ester and 5% acid grafting from Fig. 7. When compared with previ-

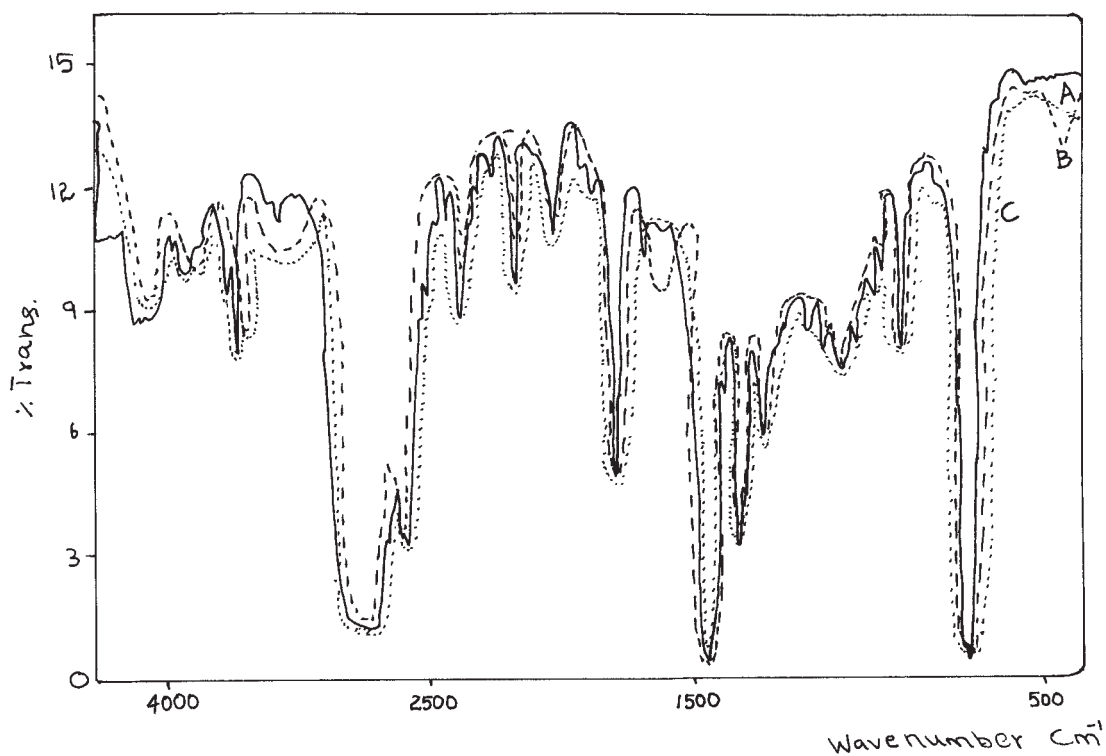


Figure 7 FTIR spectrum of HDPE-g- A_5 . A: Before saponification; B: after saponification; C: after acid hydrolysis.

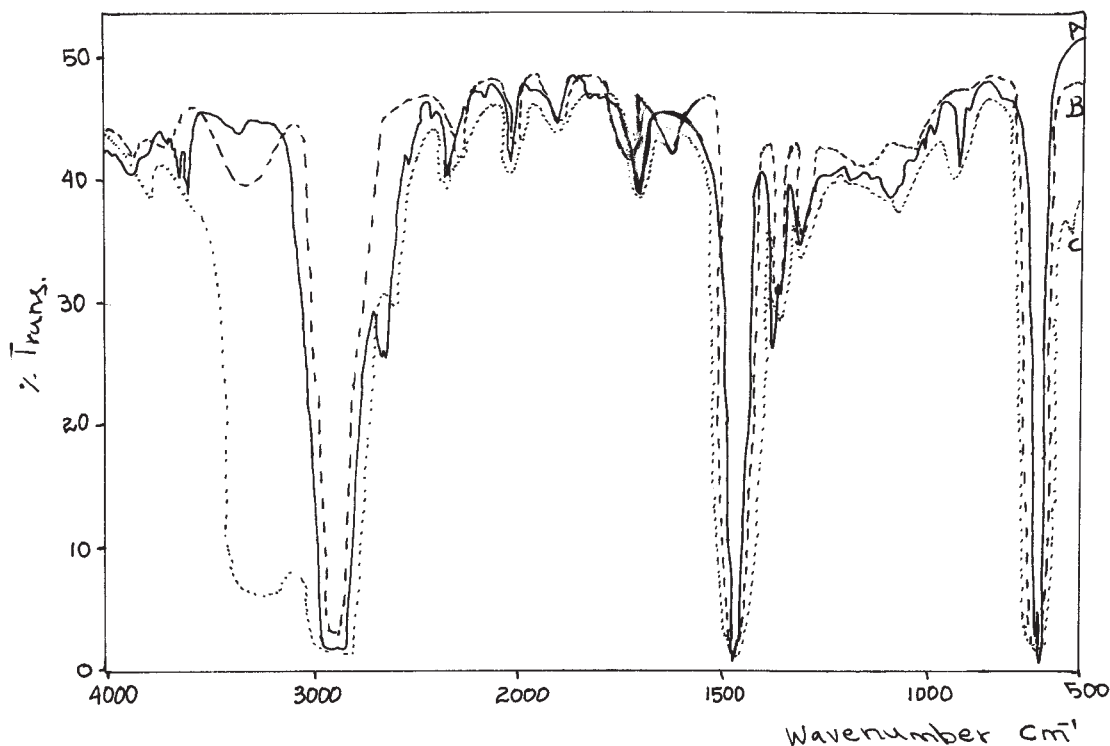


Figure 8 FTIR spectrum of HDPE-g- A_6 . A: Before saponification; B: after saponification; C: after acid hydrolysis.

ous systems A_5 showed moderate % CL. The methine radical formed in A_5 is surrounded by bulky groups and hence the activity of A_5 radical toward coupling with PE macro radicals is restricted.

System VI, HDPE + DCP + A_6

Among the additives used here for functionalization, A_6 showed very poor efficiency. But it gave very high % CL. We can see this tendency in Figs. 1F and 2F, respectively. From Fig. 8, 5% ester and 2% acid of A_6 were grafted onto HDPE in the presence of DCP. A_6 showed better efficiency toward % CL than the previous systems. In System VI a methine radical was formed and its chemical activity was restricted by the adjacent ester groups. Hence the A_6 radical could not effectively couple with the PE macro radical. Due to this reason A_6 led to high % CL of HDPE.

For the sake of comparison, instead of thiol ester (A_1), thiol acid (A_7) was used with random concentration and its efficiency toward % CL and % Fn was checked and compared with A_1 . A_7 gave a 70% CL at 0.06 mmol of [DCP] but A_1 gave only 17% at the same concentration. A_7 showed a total functionalization of only 3%. The saponification and acid hydrolysis results exhibited negative results. This accounted for the higher % CL with very poor % Fn. This is because of the condensation reactions of the pendant acid group. Further research work is going on in order to provide

a proper explanation for this behavior of thiol acid (A_7).

CONCLUSIONS

From the above experimental results the important points are presented here in conclusion.

- (1) Thiol ester (hydrogen donor additive) showed higher % Fn (due to the formation of terminal thiol radical) whereas diethylmalonate (methylene bridged additive) showed higher % CL (due to the formation of suppressed methine radical).
- (2) The area of the carbonyl peak increased with increase in % grafting of additives.
- (3) In the case of crotonic ester very poor % grafting was noticed without graft copolymerization due to steric repulsion.
- (4) During the thermolysis reaction the thiol acid additive was subjected to the side condensation reaction.
- (5) By thermolysis reaction HDPE was successfully functionalized with simultaneous cross-linking.

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