FREE RADICAL GRAFTING OF METHACRYLIC ACID AND STYRENE ON LOW DENSITY POLYETHELENE

By

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Abstract
Binary mixture of methacrylic acid and styrene monomers, in presence of benzoyl peroxide as an initiator, were grafted onto low density polyethylene. Characterization of the grafted polyethylene was accomplished using Fourier transform infrared spectroscope (FTIR), differential scanning calorimeter (DSC), and melt flow indexer (MFI). Presence of carbonyl peaks in the spectra of grafted polyethylene, low MFI value as compared to pure polyethylene, and higher endothermic peaks in thermogram of grafted polyethylene affirmed grafting of methacrylic acid and styrene onto polyethylene. It was observed that by increasing the amount of initiator, the melting point was increased.

Keywords: Polyethylene, Grafting, Rheology, DSC (Differential Scanning Calorimeter), FTIR (Fourier Transform Infrared Spectroscopy), HDPE (High Density Polyethylene), LDPE (Low Density Polyethylene), MFI (Melt Flow Index).

1. PAPER OBJECTIVE

LDPE is the version of PE plastic (Thermoplastic) having low density. It has less strength, hardness, and density than those of HDPE, but more malleability [1-2]. LDPE is lighter than water, and can be machined, molded, articulated together using thermal welding but it is difficult to glue using an adhesive. Its appearance is wax-like, lackluster and opaque. The use of UV-stabilizers (carbon black) ameliorates its weather resistance but bouts it black. Some of its types can be applied in connection with the food stuffs [3]. LDPE shows bounded resistance against oxidizing agents and halogenated hydrocarbons and therefore, is suited for short term use only. In addition it shows inadequate UV resistance [4-5].

The existing modification techniques of polyolefins emphasize grafting as an enthralling method to confer a number of functional groups on to the surface of polyolefins [6, 8-9]. To attain certain characteristics we modify the structure of the base polymer. A large number of methods are being used to modify a polymer e.g. grafting (Copolymerization), mixing (Composites). Extensive work has been done on grating of polyethylene to form a co-polymer [10-11]. These techniques include chemical, radiation, photochemical, plasma-induced and enzymatic grafting. Here in our experiment we have grafted two monomers (MMA, Styrene), in presence of BPO as initiator, on main chain of LDPE. Large work has been done on grafting of single monomer. But little work has been done on two monomers. So little bit information is available for the case of two monomer grafting. Number of researchers [13-15] have reported chemical grafting of exclusively one monomer on to polyethylene but minor work has been done on binary monomer mixture grafting especially by using a mixture of two monomers namely methacrylic acid and styrene.

2. EXPERIMENTAL

2.1 Materials

Basic materials used in these experiments were low density polyethylene (LDPE), meth acrylic acid (MAA), styrene, and benzyl peroxide (BPO). LDPE used here is a molded grade.

2.2 Synthesis of grafted polyethylene

Weighed amounts of LDPE, styrene, water, and meth acrylic acid were placed in a round bottom flask. The mixture temperature was increased up to 93 ^{o}C. As the desired temperature

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was attained, BPO was added to the mixture and thorough agitation was carried out. The mixture was kept at the reaction temperature for a period of 3-4 hours. After completion of reaction, product was washed with 0.1 N NaOH, dried, then washed with water, followed by washing with 0.1 N HCl, dried and then again washed with water. The sample is then finally dried in an oven and further analysis was carried out.

Then we prepare five more samples in a similar way but varying the concentration of initiator. In each of the subsequent samples we increase the amount of initiator by 0.25g while keeping all the other experimental parameters and quantities same. Composition of mixture is shown in Table 1.

Table 1. Composition of mixture

Materials	**S* 1**	**S* 2**	**S* 3**	**S* 4**	**S* 5**
Methacrylic acid (ml)	12.75	12.75	12.75	12.75	12.75
Styrene (ml)	1.66	1.66	1.66	1.66	1.66
BPO (g)	0.75	1.0	1.25	1.50	1.75
Water (ml)	150	150	150	150	150
LDPE (g)	50	50	50	50	50

* S = Sample #

2.3 FTIR spectroscopy

The FTIR spectrums were recorded on JASCO FT/IR-4100 infrared spectrometer. Potassium bromide was used as an inert background material to get the spectra of both pure and grafted samples of polyethylene. The analysis was done in the wave number region of 400 to 4000 cm^1.

2.4 Differential scanning calorimetry

DSC curves were obtained at heating rate of 10 ^oC min^{-1} in Shimadzu DSC 60-An apparatus. Both pure and grafted samples were analyzed against aluminum as reference material. The temperature range for experiment was selected to be 180-190 ^oC.

2.5 Rheological testing

MFI of the grafted and pure samples was determined by using MFI apparatus (KARG Industrietechnik) in accordance with the ASTM D 1238-04 under load ranges of 1000 to 5000 grams for grafted sample awhile that of pure sample was determined under load ranges 500 to 3000 grams, with die diameter of 2.095 mm and at 190 ^oC temperature.

3. RESULTS AND DISCUSSIONS

3.1 Thermal Analysis

Following histograms (given below) of pure LDPE and grafted samples show that an elevation in melting point occurs and melting point jumps from 130 ^oC to 131.85 ^oC and with further increase in initiator concentration it moves to 133.2 ^oC and becomes constant. This increase in melting point can be attributed to the presence of polar groups generated after grafting. Another important point is that this change in melting point, however, is relatively low and can be ascribed to low level of grafting. On a molecular level, the grafted chains are relatively difficult to move, rotate, and oscillate as compared to ungrafted ones; thus elevating the melting point of the material.

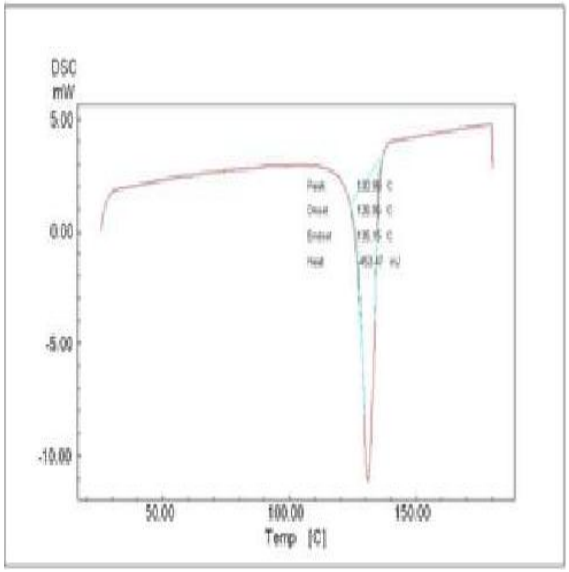

Figure 1. Thermogram of pure LDPE

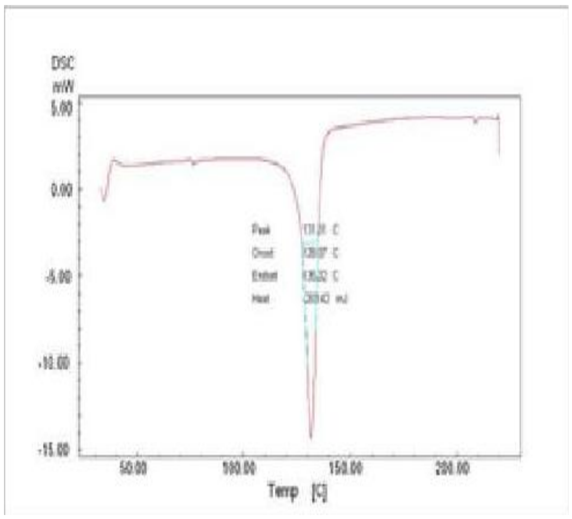

Figure 2. Thermogram of Grafted Copolymer having initiator concentration of 0.75 gm

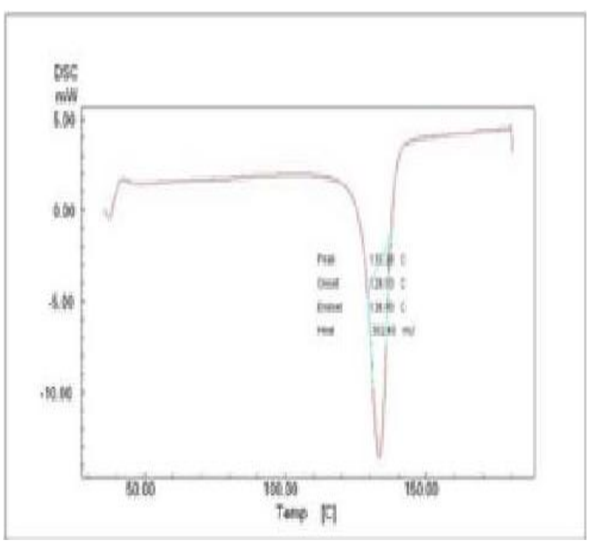

Figure 3. Thermogram of Grafted Copolymer of LDPE at 1.00 gm of initiator concentration

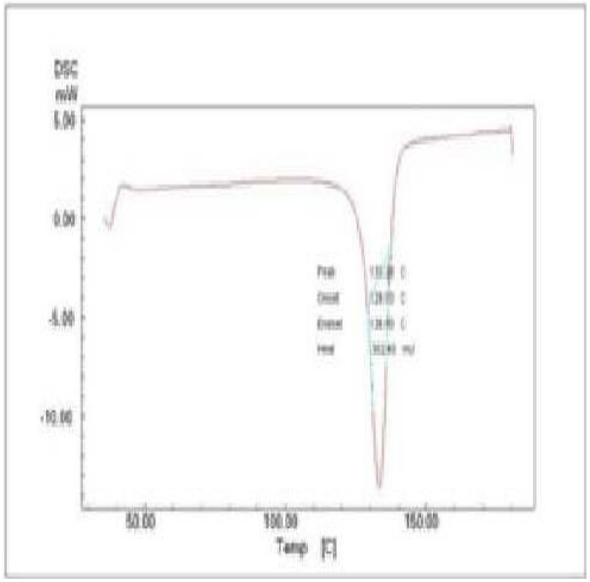

Figure 4. Thermogram of Grafted Copolymer of LDPE at 1.25 gm of initiator concentration

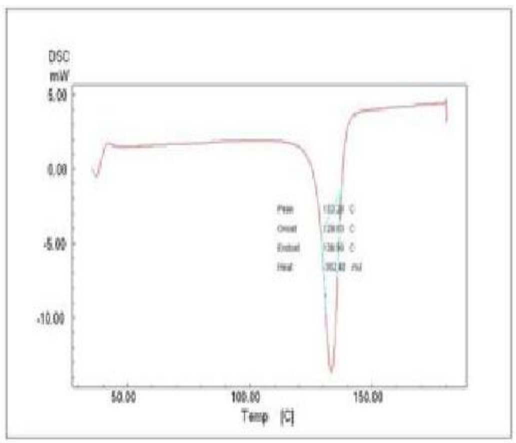

Figure 5. Thermogram of Grafted Copolymer of LDPE at 1.50 gm of initiator concentration

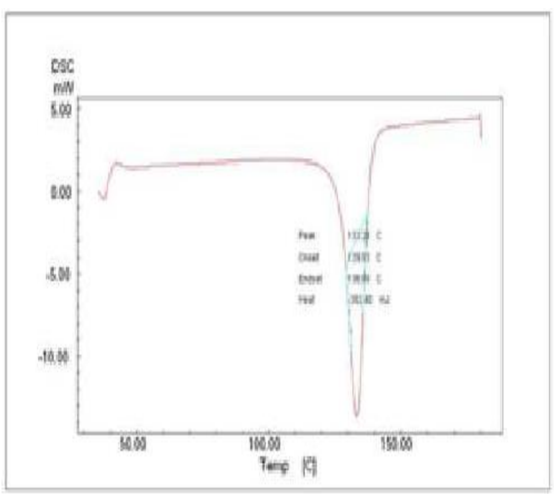

Figure 6. Thermogram of Grafted Copolymer of LDPE at 1.75 gm of initiator concentration

3.1.1 Percent Crystallanity

Melting endotherms were observed during the heating cycle in the DSC scan for pure and grafted HDPE in the temperature range of 0 ^{o}C to 150 ^{o}C.

Melting endotherms were maneuvered in to determine the values of onset and peak temperatures along with their observed heat of fusion dH_f^{obs} values for both the virgin and grafted samples (Table 2). The percentage crystallinity of the sample is calculated by use of following relationship:

$$\chi = \frac{dH_f^{obs}}{dH_f^{o}} \times 100$$

A value of enthalpy of fusion, dH_f^{o}, equal to 245 J/g for 100 % crystalline LDPE was used in above equation for calculating the percentage Crystallanity of both grades. Minute changes in melting temperature T_m of HDPE were observed on addition of grafting agents. Heat of fusion and % Crystallanity of HDPE decreased with grafting.

The Crystallanity has been decreased on account of the fact that with increase in grafting the crystal structure of pure sample gets distributed and results in the final lowering of decomposition temperature of grafted sample. After grafting of LDPE, the dispersed domains are produced that may act as a diluents resulting in decrement of dH_f^{obs} values and the percent Crystallanity.

Table 2: Percent Crystallanity from heat of fusion values corresponding to onset temperature and peak temperature for virgin and grafted LDPE

Sample	χ (%)
Pure LDPE	54.56
Grafted LDPE 0.75 gm BPO	52.23
Grafted LDPE 1.00 gm BPO	52.12
Grafted LDPE 1.25 gm BPO	51.56
Grafted LDPE 1.50 gm BPO	51.13
Grafted LDPE 1.75 gm BPO	50.83

3.2 Rheological Properties:

Rheological measurements are very important for quality control of raw materials, optimization of manufacturing processes and forecasting the performance of a material. Melt flow index (MFI) is a good indicator of flow properties of the material under consideration.

Figure 7 shows MFI of both grafted and ungrafted polyethylene grades at different loads. It is evident from the Figure 7 that MFI of ungrafted polyethylene is more than grafted polyethylene at different loads. This decrease in MFI after grafting is associated with the greater degree of branching of grafted polyethylene as compared to ungrafted polyethylene. Presence of branches diminishes the flow properties in polyethylene up to much extent. This decrease in MFI is also an indication of efficient grafting of MAA and styrene on polyethylene.

Higher viscosity of grafted LDPE than virgin LDPE is attributed to the presence of branches in grafted polyethylene which offer more hindrance to align themselves in the flow direction on applying stress as compared to the more flexible straight chains in ungrafted low density polyethylene. Grafted chains make some sort of physical entanglements among themselves which stand firm against applied stress, thus increasing melt viscosity. This decrease in viscosity with increasing strain rate reveals rheopectic behavior.

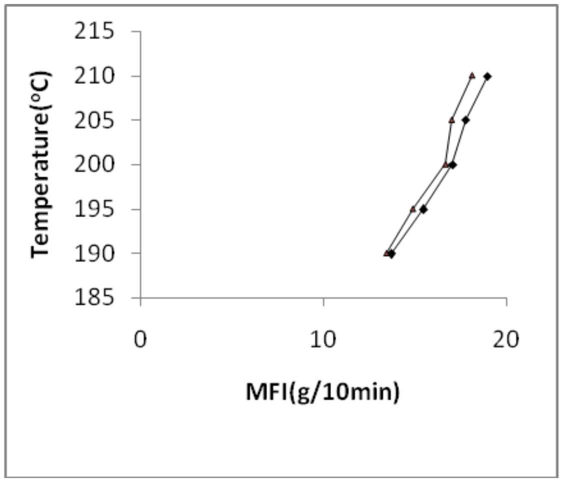

Figure 7. Effect of temperature on Melt flow Index

Note: *Upper curve (grafted sample); lower curve (pure LDPE)*

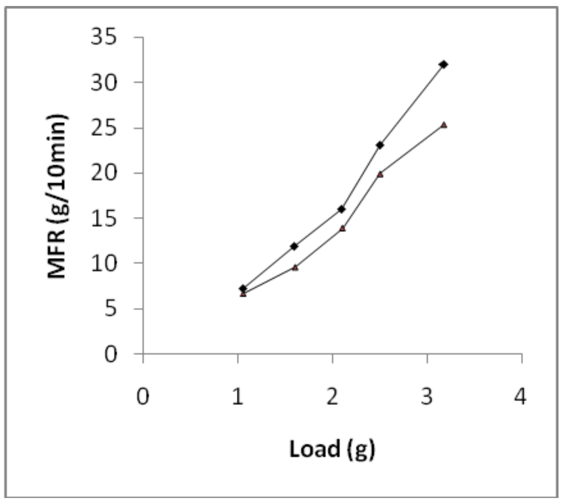

Figure 8. Effect of Load on Melt flow Index

Note: *Upper curve (grafted sample); lower curve (pure LDPE)*

3.3 Structural Analysis

From FTIR results, it is obvious that by the grafting of LDPE with styrene and methyl methacrylate, frequency changes which reveals the change of functional group of aromatics and hydrocarbons (C-H).

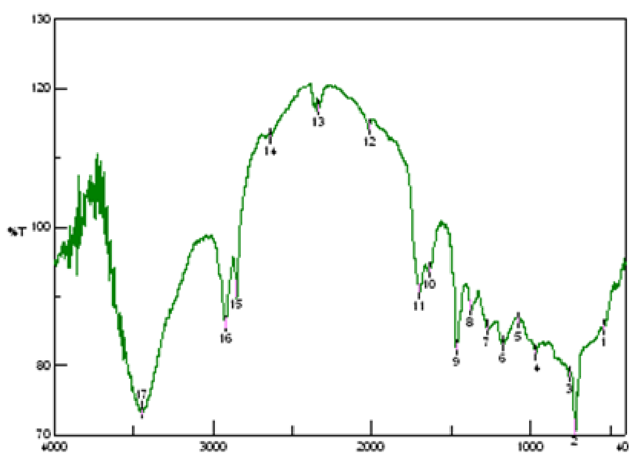

Figure 9. FTIR Spectrum of Pure LDPE

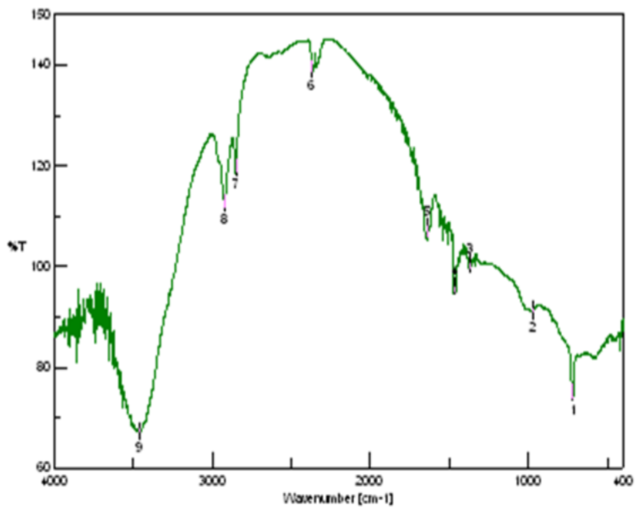

Figure 10. FTIR Spectrum of Grafted LDPE having 0.75 gm initiator concentration

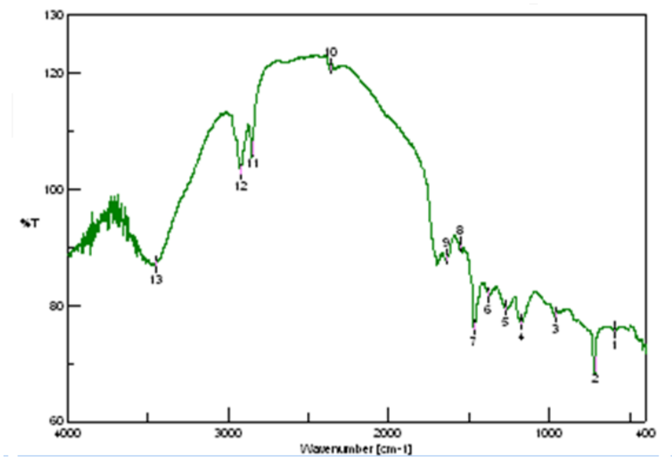

Figure11. FTIR Spectrum of Grafted LDPE having 1.00 gm initiator concentration

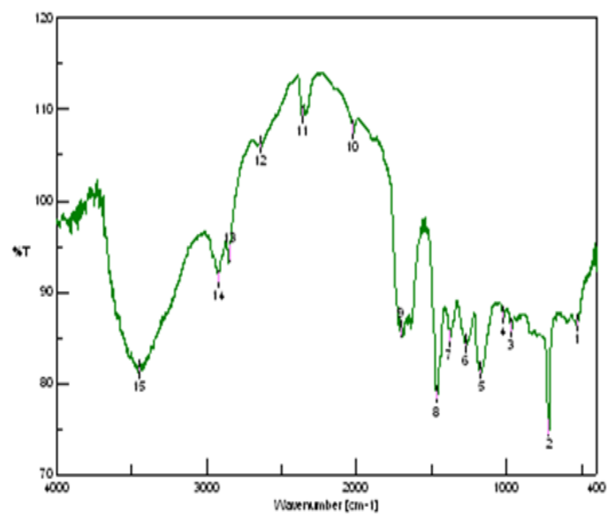

Figure 12. FTIR Spectrum of Grafted LDPE having 1.25 gm initiator concentration

3.3.1 Degree of Grafting

Degree of grafting is defined as the extent to which the original polymeric sample has been grafted. The degree of grafting of methacrylic acid-grafted-LDPE sample is found by simply measuring the change in weight of the grafted sample after complete drying. Percent degree of grafting can be calculated from the following relationship:

$$\hat{g} = \frac{E_s}{E_g - E_s} \times 100$$

Where $\hat{g}$ is the percent degree of grafting of LDPE, E_s is the equivalent weight of styrene and E_g is the equivalent weight of grafted LDPE. Values of percent degree of grafting for different samples are given below as shown in Table 3.

Table 3: Percent degree of grafting of LDPE grafted with different amounts of initator

Serial #	BPO (gram)	$\hat{g}$ (%)
1	0.75	27.21
2	1.00	27.35
3	1.25	27.74
4	1.50	28.03
5	1.75	28.78

4. CONCLUSION

1. The above discussion reveals that a reasonable amount of grafting achieved using Styrene and MMA using BPO (as an initiator) and Rheological properties have been changed due to grafting process which is indicated by lower value of MFI of grafted polyethylene as compare to virgin LDPE.

2. For same strain rate, higher stress is required for grafted polyethylene as compared to virgin polyethylene due to resistance in flow offered by branched chains.

3. Viscosity also increases by introduction of branches.

4. From DSC analysis, it is concluded that melting point of LDPE increases after grafting.

5. As we increase the concentration of initiator so little effect on properties observed, but grafted material becomes more brittle than pure LDPE.

5. ACKNOWLEDGEMENT

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