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PII: S0032-3861(97)00253-X

Polymer Vol. 39 No. 1, pp. 193–201, 1998
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0032-3861/97/$17.00+0.00

Modification of low density polyethylene (LDPE) by graft copolymerization with some acrylic monomers

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(Revised 6 March 1997)

Graft copolymerization of low density polyethylene (PE) with acrylic acid (AA), ethyl acrylate (EA) and butyl acrylate (BA) using dicumyl peroxide (DCP) as the initiator was studied using differential scanning calorimetry (DSC) under the dynamic (non-isothermal) condition and in the shear mixer of a Brabender plasticorder at 170°C (443°K). DSC studies allowed measurements of the heat of reaction and the kinetics and energetics of the overall reaction during graft copolymerization. For each monomer system, the reaction was first order with respect to monomer concentration and the observed activation energy (150–170 kJ mole^{-1}) followed the order AA > EA > BA. The grafting efficiency (%) was highest when using AA. The higher volatility of the EA monomer makes it less suitable for grafting on PE under a shearing action at 170°C (443°K). A low DCP dose (0.75 mmole per 100 g of PE) produced optimum conversion and grafting effects. Studies of melt rheology at 190°C (463°K) showed that 10–15% grafting of acrylic polymers on polyethylene resulted in a three- to five-fold increment in the melt viscosity of the polymer and substantial lowering in its melt flow index (MFI). Some cross-linking of PE during DCP-induced grafting unavoidably occured as a side reaction, particularly for grafting using the AA monomer and generally when using a high DCP dose (> 1.0 mmole per 100 g of PE) for all the monomers. The nature and extent of changes in the mechanical properties of PE on acrylic grafting depended on the chemical nature of the monomer used and on the extent of grafting achieved. © 1997 Published by Elsevier Science Ltd.

(Keywords: acrylic grafting on polyethylene; reactive processing of polyethylene; melt rheology of modified polyethylenes)

INTRODUCTION

Modifications of non-polar polymers such as polyolefins by graft copolymerization with selected polar monomers and vice versa have recently received considerable attention[1–6]. Properties such as adhesion, clarity, environmental stress cracking resistance, thermo-oxidative stability, ion-exchange capacity, etc., may be notably improved by such modifications[7–10]. Graft copolymers are also widely recognized as novel, potential additives to impart improved compatibilizing influence (interaction promoter) in binary or multi-component polymer blends[11–14], and they are finding growing use in reactive blending[15–17].

Peroxide-initiated free radical polymerization is probably the simplest, oldest and most widely used method for the synthesis of graft copolymers, and this technique is also adaptable to a variety of commercial applications[18,19].

Vinyl grafting of polyethylene (PE) and related polymers performs better on a large scale under shear-mixing conditions at or above the melting point of the (preformed) polymer, using selected peroxides as initiators of graft copolymerization[16,17]. Variable proportions of (i) ungrafted chains of the preformed polymer used and (ii) of the ungrafted vinyl polymer formed, along with the desired (iii) graft copolymer are commonly found to be present together in the gross products of most graft copolymerizations.

The present paper describes results relating to studies of graft copolymerization of acrylic acid and selected acrylic esters on low density polyethylene (LDPE) [henceforth to be simply referred to as polyethylene (PE)] under the influence of dicumyl perioxide (DCP) as the initiator of polymerization at 170°C (443°K) in a shear mixer.

EXPERIMENTAL

Materials

Polyethylene (PE grade NCPE 4445 from Neste Polyten, Sweden) with a density of 0.915 kg m^{-3} and a melt flow index (MFI) of 2.0, and dicumyl peroxide (DCP) (Perkadox BC, assay 99%, from Akzo Chemie, the Netherlands) were used without further purification. Laboratory reagent (LR)-grade inhibited monomers, namely acrylic acid (AA) ethyl acrylate (EA) and butyl acrylate (BA) were used as received from BDH, India.

METHODS

Graft copolymerization

Graft copolymerization as studied in a differential scanning calorimeter (DSC). A Mettler DSC 20 equipment (TA 3000 system) fitted with a TC10A microprocessor was used for this purpose. PE used for the study was converted into powder form by its precipitation with acetone from hot xylene solution at 130°C (403°K) with high-speed stirring in an ice bath. The precipitated powder was dried in a vacuum at 50°C (323°K). For studies of grafting by DSC, a requisite amount of an acrylic monomer (acrylic acid

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(AA), ethyl acrylate (EA) or butyl acrylate (BA)) was used to dissolve a known amount of DCP and the monomer–initiator solution was thoroughly mixed with the desired amount of PE powder in a morter. The PE powder or the PE–DCP–monomer mixture (6.0 ± 0.1 mg) prepared for grafting was encapsulated in a hermetically sealed pan of the DSC instrument and heated at a rate of 20°C min^{-1} up to 250°C (523°K) under a cover of flowing nitrogen gas at a flow rate of 80 ml min^{-1}. Use of the appropriate software provided plots of (a) heat flow (exothermal) *versus* temperature and (b) percentage conversion *versus* time; printouts bearing data on reaction enthalpy (ΔH), order of the reaction, and activation energy were also provided by the microprocessor.

Graft copolymerization as studied in the Brabender plasticorder. Fifty to 60 g of PE was mixed with the desired doses of the selected monomer (acrylic acid/ethyl acrylate/butyl acrylate) and the initiator (DCP) in a beaker and the mixture was fed into the cam-type mixing head (N5OH) of the Brabender plasticorder (PLE 330) set at a temperature of 170°C (443°K). The rotor speed was maintained at 50 rpm and the grafting reaction was continued for 20 min in the closed mixer under the prevalent thermomechanical condition. The torque change with time was monitored in each case. At the end of the specified time of reaction (20 min), the grafted products were taken out from the mixer for testing and analysis.

Characterization of products of graft copolymerization

It is well known and understood that a graft copolymerization process includes some unavoidable homopolymerization over and above the actual grafting process, and may even cause some degree of cross-linking in specific cases. The homopolymers formed are commonly removed or isolated by selective solvent extraction. It is also theoretically likely that a portion of the preformed polymer would escape grafting and remain unchanged after the graft copolymerization process.

Percentage conversion, percentage grafting and grafting efficiency (%). A weighed quantity of the gross polymer product from the grafting experiment carried out in the plasticorder was taken and the unreacted monomer was removed under vacuum at 40–50°C (313–323°K). The respective acrylic homopolymers were separated by extraction of the gross product using suitable solvents. Ethyl alcohol was used to separate poly (acrylic acid) (PAA) homopolymer and tetrahydrofuran was used to separate poly(butyl acrylate) (PBA) homopolymer and poly(ethyl acrylate) (PEA) homopolymer from the corresponding gross products. Finally, the solvent used was removed from the residual (graft) copolymer by drying in a vacuum at 40–50°C (313–321°K) to a constant weight. Percentage conversion, percentage grafting and grafting efficiency (%) were calculated as follows:

$$\text{Conversion\%} = \frac{M_1 - M_0}{M} \times 100 \qquad (1)$$

$$\text{Grafting\%} = \frac{M_2 - M_0}{M_0} \times 100 \qquad (2)$$

$$\text{Grafting efficiency (\%)} = \frac{M_2 - M_0}{M_1 - M_0} \times 100 \qquad (3)$$

where M_0 and M denote mass (in grams) of PE and the monomer initially taken, M_1 and M_2 denote, respectively, mass (in grams) of gross product formed and residual graft copolymer after extraction of homopolymer from the gross product.

Infrared (IR) analysis. Ungrafted PE and grafted PE (residue after exraction of acrylic homopolymer from the gross product of graft copolymerization) samples were characterized by examination of their infrared spectra employing thin films in each case in a Shimadzu infrared spectrophotometer (IR 420).

Tensile properties. Tensile properties of PE, and some grafted PE samples (PEgAA and PEgBA) were measured in a Zwick universal testing machine (model 1445) using a dumbell specimen according to ASTM D415-80 at 298 ± 2°K with a cross-head speed of 0.5 m min^{-1}. The data presented are the average of five tests in each case.

Rheological characterization.

(i) *Melt viscosity.* Melt viscosities of ungrafted PE, DCP treated PE and selected grafted PE fractions (obtained after removal of the acrylic homopolymers by solvent extraction) were measured using a low rate of shear (0.2 s^{-1}) at 190°C (463°K) in a Rheotron plate and cone viscometer from Brabender.

(ii) *Melt flow index (MFI).* The MFI of PE and selected grafted PE samples were measured as per ASTM D1238 at 190°C (463°K) and under a 2.16 kg load in a melt flow index apparatus from Davenport, UK (model 737-034).

Degree of cross-linking and gel content (%). The gel content (%) of DCP-treated and grafted polyethylenes were assessed from the insoluble fraction by the extraction of respective samples with boiling xylene for 12 h as per ASTM D2765-68 (method A). A higher gel content is an indication of a higher degree of cross-linking.

RESULTS AND DISCUSSION

Overall graft copolymerization as studied by DSC

Enthalpy change. Typical DSC traces for overall graft capolymerization using DCP and the three different acrylic monomers (AA, EA, BA) separately in comparable doses are shown in *Figure 1*. For AA the reaction exotherm started to show up from a lower temperature and it also showed a lower peak temperature, 150°C (423°K). The exotherm peak for grafting using EA and BA appeared at nearly 175°C (448°K).

For each grafting reaction, the DCP concentration, [DCP], was varied over the range of 0.375–1.75 mmole per 100 g of PE, whilst the momomer concentration, [monomer], was varied over a range of 50–250 mmole per 100 g of PE. A low [monomer] was used to avoid the runaway reaction. The overall change of enthalpy or heat of reaction (ΔH) for different monomer systems with a change in the doses of DCP and monomer are shown in *Figure 2*. In each case the heat of reaction (ΔH, J g^{-1}) for the overall graft copolymerization increased with an increase in the monomer dose for a given dose of DCP and PE. The increase in ΔH initially followed a linear relationship up to a certain dose level of monomer (150–200 mmole per 100 g of PE) which depended on the type and nature of the monomer used. The exothermic nature as given by the ΔH

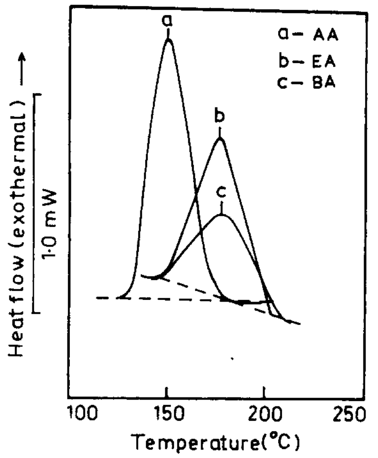


Figure 1 Typical DSC traces (exotherms) for overall graft copolymerization of PE (100 g) covering grafting and homopolymerization reactions. Monomer used: (a) AA, (b) EA, and (c) BA, each 150 mmole in the presence of DCP (0.75 mmole)

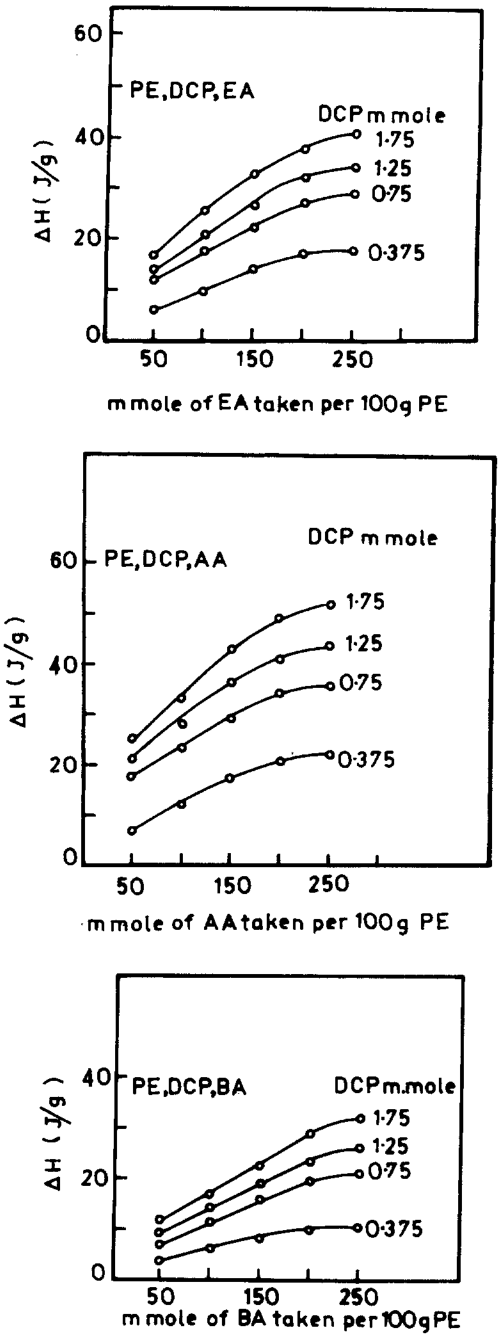


Figure 2 Plots of overall enthalpy change (ΔH, J g^{-1}) *versus* [monomer] at different DCP doses for graft copolymerization of PE covering grafting and homopolymerizations. Monomer used (a) [AA], (b) [EA] and (c) [BA]

value observed followed a levelling-off trend beyond this initial linear zone, apparently as a consequence of a dilution effect or a starving situation with respect to radical supply. For a particular dose of DCP and monomer for a given amount of PE, the enthalpy change or the reaction exotherm (ΔH, J g^{-1}) followed the order AA > EA > BA, see *Table 1* and *Figure 2*. It is also clear from *Figure 2* that for a given monomer dose level, ΔH is higher for a higher level of DCP. Again, the slope of the AH *versus* [monomerl plots increased with an increase in [DCP].

Kinetics of overall graft copolymerization (including grafting and homopolymerization) as studied by DSC. The onset of the exothermic change due to polymerization of the monomer taken as shown in the DSC thermogram occurs 15–20°C earlier if the monomer–DCP mixture is heated dynamically in the absence of PE than when heated in the presence of PE at a specified heating rate. The heat evolved can be used for the kinetic analysis of the overall graft copolymerization, covering the grafting and homopolymerization reactions. The total area (A) under the reaction exotherm in the DSC thermogram gives a measure of the total heat (ΔH) evolved during the overall polymerization, i.e. $\Delta H = A$, and the heat of overall polymerization per mole is given by A/n_0, where n_0 is the initial number of monomer molecules.

Again, heat evolved or the enthalpy change (dH) over a small time interval (dt) of polymerization is known[20] to be proportional to the number of monomer molecules (dn) that have reacted during that time interval, so that one may write

$$\mathrm{d}H \,\alpha\, -\mathrm{d}n \tag{4}$$

or

$$\mathrm{d}H = -\left(\frac{A}{n_0}\right)\mathrm{d}n \tag{5}$$

or

$$\mathrm{d}H = -\left(\frac{A}{n_0/V}\right)\mathrm{d}[M] \tag{6}$$

where V is the total volume of the reaction system and d[M] is the concentration of monomer that has reacted during the time interval dt. The constant of proportionality A/n_0 is the heat of reaction per mole of monomer used.

We may further write from equation (5)

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = \left(\frac{n_0}{A}\right)\frac{\mathrm{d}H}{\mathrm{d}t} \tag{7}$$

Following on from equation (6) we may then write

$$-\frac{\mathrm{d}[M]}{\mathrm{d}t} = \left(\frac{n_0}{AV}\right)\frac{\mathrm{d}H}{\mathrm{d}t} \tag{8}$$

For the overall graft copolymerization including acrylic homopolymerization and grafting of acrylic chains on PE as studied here at a fixed dose of initiator and assuming first-order kinetics, the overall rate of monomer

Table 1 Overall graft copolymerization of acrylic monomers on polyethylene (PE) as studied by DSC: thermochemical and kinetic analysis using 0.75 mmole DCP per 100 g of PE as the initiator

Monomer (mmole per 100 g of PE)	Heat of reaction (ΔH) (J g^{-1})	Reactionorder (n)(mean)	Energy of activation (kJ mole^{-1})	ln k_0 (S^{-1})
Acrylic acid				
50	18.0	1.01 ± 0.02	170 ± 10	40 ± 5
100	23.0		170 ± 10	40 ± 5
150	28.5		170 ± 10	40 ± 5
200	33.5		170 ± 10	40 ± 5
250	35.0		170 ± 10	40 ± 5
Ethyl acrylate				
50	12.0	1.02 ± 0.02	160 ± 10	35 ± 5
100	18.0		160 ± 10	35 ± 5
150	23.0		160 ± 10	35 ± 5
200	27.0		160 ± 10	35 ± 5
250	29.0		160 ± 10	35 ± 5
Butyl acrylate				
50	7.0	1.02 ± 0.03	150 ± 10	35 ± 5
100	11.5		150 ± 10	35 ± 5
150	16.0		150 ± 10	35 ± 53
200	19.5		150 ± 10	35 ± 5
250	21.0		150 ± 10	35 ± 5

consumption be written as:

$$-\frac{d[M]}{dt}=k[M]=\left(\frac{n_0}{AV}\right)\frac{dH}{dt} \tag{9}$$

or

$$\frac{dH}{dt}=k[M]\left(\frac{AV}{n_0}\right) \tag{10}$$

Here, (AV/n_0) signifies the heat of reaction per unit monomer concentration and $[M]$ is the monomer concentration. The number of moles of monomer (n) present at any instant is equal to the initial number of moles (n_0) minus the overall number of moles that have reacted $[n_0(a/A)]$, i.e.

$$n=n_0-n_0\left(\frac{a}{A}\right) \tag{11}$$

where 'a' is the partial (shaded) area of the overall DSC exotherm indicating the overall enthalpy change or heat evolved at time t, as shown schematically in *Figure 3*. Similarly the monomer concentration $[M]$ at any instant of time can be expressed as

$$[M]=\frac{n_0}{V}-\frac{n_0}{V}\left(\frac{a}{A}\right)=\frac{n_0}{V}\left(\frac{A-a}{A}\right) \tag{12}$$

Substituting this value of $[M]$ in equation (10), we may write

$$\frac{dH}{dt}=k\left(\frac{n_0}{V}\right)\left(\frac{A-a}{A}\right)\left(\frac{AV}{n_0}\right)=k(A-a)$$

or

$$k=\left(\frac{dH}{dt}\right)/(A-a) \tag{13}$$

The rate constant k may be expressed in the Arrhenius form as

$$k=k_0\exp^{(-E/RT)} \tag{14}$$

where k_0 is the pre-exponential factor and E is the energy of activation for the overall polymerization process. Equation (13) was used for the kinetic analysis of the overall polymerization reaction including homopolymerization and grafting. Conversion of the selected monomer to polymer during the overall graft copolymerization at different isothermal conditions was directly obtained as a percentage conversion *versus* time plot with the help of the built-in software utilizing thermal response and data from dynamic (non-isothermal) DSC studies, and the relevant plots are shown in *Figure 4*. Data on enthalpy change (ΔH), ln k_0 and activation energy (E) as processed by the microprocessor and obtained in the print-out are shown in *Table 1*. First-order kinetics or the monomer order of unity as commonly revealed for the overall graft copolymerizations of AA, EA and BA on PE including homopolymerization in each case are a testimony to the kinetic approach envisaged and expressed by equations (10), (13) and (14).

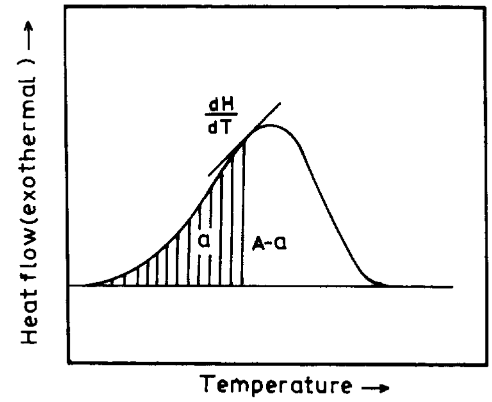


Figure 3 A schematic DSC thermogram showing a plot of heat evolved *versus* temperature for graft copolymerization (covering grafting and homopolymerization)

Graft copolymerization reactions as studied in a Brabender plasticorder

Graft copolymers expectedly admixed with some homopolymers were further prepared at 170°C (443°K) by reactive processing of PE with low doses of DCP and a selected acrylic monomer in the mixer of the Brabender plasticorder. Dynamic reaction condition at a temperature much above the melting point of PE was selected for continuous renewal of the monomer–polymer interphase by the shear action and to ensure improved grafting effects (percentage grafting and grafting efficiency).

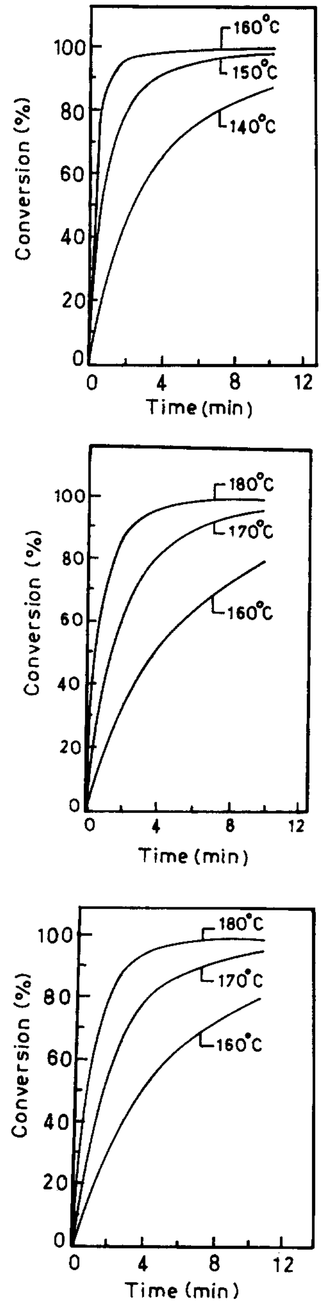


Figure 4 Percentage conversion *versus* time plots for DCP (0.75 mmole)-induced graft copolymerization of PE (100 g) and an acrylic monomer: (a) AA, (b) EA, and (c) BA, each 150 mmole (covering grafting and homopolymerization) as obtained from the print-out during studies of the process by DSC

Torque rheometry. The torque–time behaviours of the PE–monomer–DCP system and of the PE–DCP system bearing no monomer were studied under identical reaction conditions. The torque–time curve for only polyethylene was characterized by an initial sharp peak (due to material loading) followed by a zone of decreasing torque that finally reached a nearly steady value. Some observed torque–time traces are presented in *Figure 5*. A torque rise trend after attainment of the minimum steady torque was not observed for the control PE or PE treated with a low dose of DCP (≤ 0.75 mmole per 100 g of PE), thus indicating that when using no DCP or a low DCP dose, cross-linking of PE under the shear action at 170°C (443°K) was nil or negligible. For use of a higher DCP dose (≥ 1.25 mmole per 100 g of PE), however, a small torque rise (due to peroxide-induced cross-linking of PE) after attainment of the minimum was noticeable. In the presence of a monomer, however, shearing of PE even with a low DCP dose (0.75 mmole per 100 g of PE) under the given set of conditions caused the torque to follow an increasing trend (with a final plateau effect) after the initial attainment of a minimum, as shown in *Figure 5*.

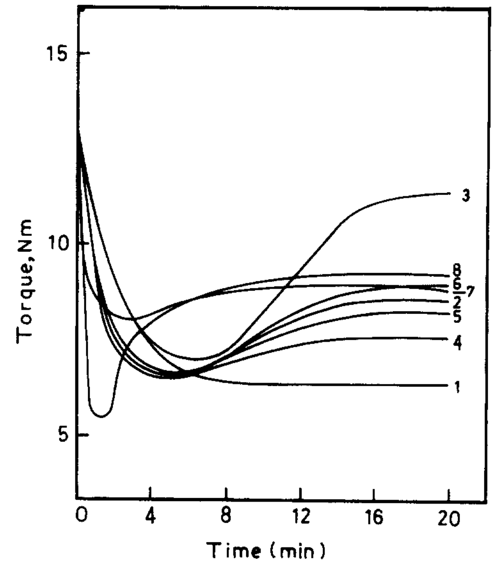


Figure 5 Torque *versus* time plots for reactive melt processing of PE using DCP in the absence or presence of a given dose of an acrylic monomer as studied at 170°C (443°K) in the Brabender plasticorder. In each case PE = 100 g. Data given for each curve are given for each curve are: curve number, DCP dose in mmole and dose level of monomer in mmole with identity of monomer in parenthesis. (1) 0.75, 0.00; (2) 1.25, 0.00; (3) 1.75, 0.00; (4) 0.75, 50 (BA); (5) 0.75, 100 (BA); (6) 0.75, 150 (BA); (7) 0.75, 100 (EA); (8) 0.75, 100 (AA)

The increment in torque level was sharper when using a higher dose level of monomer used for grafting, see *Figure 5* (demonstrating the use of BA as the monomer). When using a DCP dose ≥ 0.75 mmole per 100 g of PE, the torque rise beyond the initial attainment of a minimum was usually higher when using a monomer in the system than in the absence of a monomer. The reactive processing of PE in the presence of DCP and a monomer in the plasticorder led to the formation of additional polymers; a good part of the polymer formed was grafted to PE, causing a prominent increase in its molecular weight and thus contributing to a net enhancement in the melt viscosity of the material being processed and hence to a rise in the torque value as recorded in the plasticorder. Partial and very limited cross-linking of PE may occur simultaneously to grafting, leading to microgel formation, and this might also contribute to the observed torque rise.

The nature and degree of variations of torque with time during the reactive processing leading to significant grafting of PE were characteristically dependent on the nature of monomer and dose levels of the monomer and DCP used for grafting. Torque-rise due to polymerization is higher when using acrylic acid compared to use of an acrylic ester as the monomer for grafting.

Characterization of grafted polyethylene

IR-analysis. The grafted polyethylenes were characterized using IR spectroscopy. The IR spectra of PE and acrylic-grafted PE products made free from associated homopolymers are shown in *Figure 6*. The characteristic absorption band for >C=0 stretching appeared at 1720 cm^{-1} for the acrylic acid grafted PE (PEgAA) and at

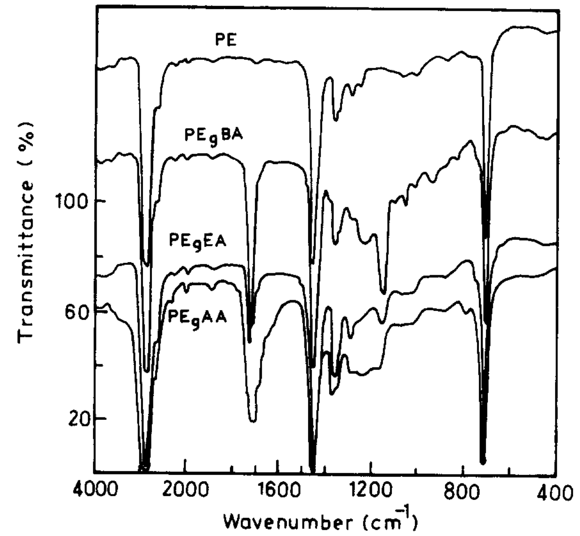


Figure 6 Infrared spectra of ungrafted PE and of graft copolymers of PE, namely PEgAA, PEgEA and PEgBA that were made free from associated homopolymers by appropriate solvent extraction

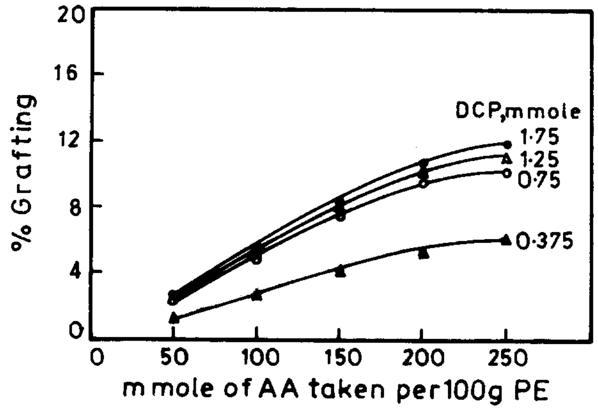


Figure 7 A plot of percentage grafting of PAA *versus* mmole of AA per 100 g of PE

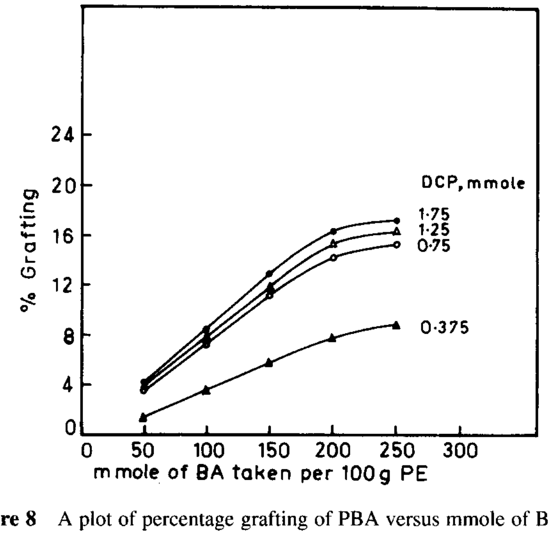


Figure 8 A plot of percentage grafting of PBA versus mmole of BA per 100 g of PE

1735 cm^{-1} for the acrylate grated PE (PEgEA and PEgBA). Two more distinct characteristic bands due to stretching of the C–O–C linkages of the ester groups of the grafted on acrylate chain segments appeared at 1160 and 1240 cm^{-1} in the spectra of PEgEA and PEgBA, respectively.

Grafting parameters and conversion. Plots of percentage grafting against monomer dose levels are shown in *Figures 7* and *8*. Different curves for a given monomer are for different dose levels of DCP. Grafting effects were usually more prominent when using AA and BA compared to using EA as the monomer; relatively low boiling point and higher volatility of EA made it much less suitable for use as a monomer for grafting on PE under the given shearing action at a high temperature, 170°C (443°K). A maximum of only 2% grafting was obtained at 170°C (443°K) in case of EA using 0.75 mmole DCP and 250 mmole EA for 100 g PE in the plasticorder. In-depth studies were therefore limited to the reactive processing of PE using only AA and BA as monomers and the grafted products obtained from them. Data relating to percentage conversion, percentage grafting and grafting efficiency (%) for AA and BA systems at different DCP doses are shown in *Tables 2* and *3*. Grafting efficiency is apparently on the high side when using AA in preference to BA as the monomer. Conversion usually followed an increasing trend when using a higher DCP dose in each case. A DCP dose of 0.75 mmole per 100 g of PE produced optimum conversion and grafting effects; a higher DCP dose produced only marginal gains in said parameters. Percentage grafting usually followed an increasing trend[2,3,6] with an increase in monomer and DCP dose levels (see *Tables 2* and *3*). Percentage grafting obtained in the present studies at 170°C in a closed shear mixer is higher in comparison than that of the previously reported level[6] of grafting of a methacrylate monomer via an extrusion grafting process at 200°C.

Tensile properties. The tensile properties of PE and some of the grafted PE samples are shown in *Table 4*. On grafting of poly(acrylic acid) (PAA) on PE, the elastic modulus, yield stress and tensile strength[4] of the polymer were found to slowly follow increasing trends, even though the elongation at break (%) decreased gradually with increase in the percentage grafting value.

However, on grafting of poly(butyl acrylate) (PBA) on PE, the elastic modulus, yield stress, tensile strength and elongation at break (%) of the product followed decreasing trends with an increase in percentage grafting, as shown in *Table 4*. PAA grafting on PE apparently imparted a stiffening effect, while PBA grafting infused a plasticizing effect on the polymers.

Gel content and melt rheology. Varied degrees of cross-linking of PE are likely to occur as side reactions during the graft copolymerization. A torque-rise with time indicated in the plasticorder (*Figure 5*) as the graft copolymerization progressed may be explained partly on the basis of grafting and partly due to limited cross-linking. The gel content (hot xylene insoluble part) of the product shown in *Tables 2* and *3* may be roughly taken as an index of degree of cross-linking on a micro level. Cross-linking assumed more prominence in the AA system, more so for the use of a higher DCP dose and higher monomer dose[3,6].

Melt viscosity and melt flow index (MFI). Melt rheology of PE at 190°C (463°K) changed measurably subsequent to its melt processing under shear action at 170°C (443°K) for 20 min in the presence of DCP. Shear (melt) viscosity of PE corresponding to the application of low rate of shear (0.2 s^{-1}) at 190°C (463°K) in the plate and cone viscometer was found to be 8.1 × 10^3 PaS, and it grew to a value of 11.1 × 10^3 PaS after the PE was melt processed with a low

Table 2 Conversion and grafting effects in DCP-induced graft copolymerization of acrylic acid on PE at 170°C (443°K) for 20 min and gel content of the grafted products. PE used for grafting = 100 g

	DCP (mmole)																							
	0.375						0.75						1.25						1.75					
Acrylic acid (mmole)	0	50	100	150	200	250	0	50	100	150	200	250	0	50	100	150	200	250	0	50	100	150	200	250
Percentage conversion	—	39.0	42.0	44.0	43.5	39.2	—	72.0	73.0	75.0	72.0	61.8	—	79.0	80.0	81.4	78.4	68.0	—	84.0	85.5	85.0	82.0	72.8
Percentage grafting	—	1.29	2.74	4.25	5.62	6.20	—	2.45	4.9	7.56	9.6	10.2	—	2.67	5.33	8.10	10.37	11.16	—	2.81	5.69	8.50	10.80	11.89
Grafting efficiency (%)	—	92.3	90.5	89.4	89.6	87.7	—	94.4	93.1	92.8	92.2	91.4	—	93.6	92.5	92.1	91.8	91.1	—	92.8	92.4	92.5	91.4	90.6
Gel content (%)	0.0	3.7	5.6	7.0	9.1	10.0	0.0	7.2	10.0	13.4	15.2	17.1	0.0	15.2	18.4	21.5	24.0	25.6	18.0	23.0	24.2	26.0	28.1	30.5

Table 3 Conversion and grafting effects in DCP-induced graft copolymerization of butyl acrylate on PE at 170°C (443°K) for 20 min and gel content of the grafted products. PE used for grafting = 100 g

	DCP (mmole)																			
	0.375					0.75					1.25					1.75				
Butyl acrylate (mmole)	50	100	150	200	250	50	100	150	200	250	50	100	150	200	250	50	100	150	200	250
Percentage conversion	31.0	37.0	40.7	39.0	36.8	70.0	71.0	72.0	70.0	60.4	78.0	78.5	79.3	77.0	66.8	85.0	85.8	86.3	82.0	72.0
Percentage grafting	1.53	3.71	6.15	7.81	8.97	3.70	7.37	11.30	14.30	15.40	3.97	7.97	12.17	15.63	16.53	4.22	8.56	13.07	16.40	17.30
Grafting efficiency (%)	77.40	78.37	78.70	78.20	76.0	82.8	80.98	81.50	80.0	79.40	79.4	79.0	79.8	79.2	77.2	77.6	77.8	77.9	78.0	75.0
Gel content (%)	0	0	0	0	0	0	0	0	0	0	3.5	5.2	6.3	7.1	8.0	19.3	20.7	21.5	22.3	23.5

Table 4 Tensile properties of PE and some selected grafted PE products. PEgAA and PEgBA: DCP dose used during graft copolymerization = 0.75 mmole per 100 g of PE

Polymer	Grafting (%)	Elastic modulus (MPa)	Yield stress (MPA)	Tensile strength (MPa)	Elongation at break (%)
PE	0.00	6.2	13.8	14.5	585
PEgAA	2.45	6.3	14.2	15.0	450
	4.90	6.4	14.3	15.3	441
	7.56	6.6	14.4	15.8	432
	9.60	6.8	14.5	16.2	418
	10.20	6.9	14.6	16.5	400
PEgBA	3.70	4.2	12.4	13.8	570
	7.37	4.2	11.3	13.5	562
	11.30	4.1	10.6	13.2	553
	14.30	4.0	9.8	12.7	538
	15.40	3.9	9.5	12.5	533

dose of DCP (0.75 mmole per 100 g of PE). Limited microgel formation due to peroxide-induced cross-linking of PE may explain this observation. Similarly, the melt flow index (MFI) of PE dropped from a value of 2.0 (initial) to 1.2 on shearing with a low dose of DCP (0.75 mmole per 100 g of PE) under the given set of conditions. However, formation of microgels due to mild cross-linking for use of the above-mentioned low DCP dose (0.75 mmole per 100 g of PE) did not lead to any measurable gel content, but use of a relatively high DCP dose (1.75 mmole per 100 g of PE) led to a partly cross-linked product[3,6] having a melt viscosity at 190°C. This was too high to be studied in the Rheotron plate and cone viscometer, and it gave a moderate (18%) gel content value (*Table 2*).

Trends of change in the melt flow index (MFI) and relative (melt) viscosity (η/η_0) of PE (where η is the melt viscosity of grafted PE and η_0 is the melt viscosity of initial PE) on acrylic grafting using AA or BA as monomer and 0.75 mmole of the DCP initiator for 100 g of PE during graft copolymerization at 170°C (443°K) are shown in *Figures 9* and *10*. Here, the grafted PE was made free from the respective acrylic homopolymer by solvent extraction. For the AA system, the melt viscosity [*Figure 9a*] initially showed significant enhancement for a low level (2–3%) of poly(acrylic acid) (PAA) grafting; thereafter, the melt viscosity followed a levelling-off trend with a further increase in percentage grafting of PAA. The change in melt viscosity [*Figure 10a*] of PE on poly (butyl acrylate) (PBA) grafting follows a similar pattern, the difference being that the polyacrylate-grafted PE (PEgBA) showed the levelling-off trend in melt viscosity after attaining a much higher grafting level (10–12%).

The trends of change in MFI for grafting PAA or PBA on PE are more or less similar; over low degrees of grafting, the MFI value dropped somewhat sharply[2,6] and as percentage grafting increased further, the drop in MFI followed a levelling-off trend as shown in *Figure 9b* and *Figure 10b*.

Mechanism of grafting and associated side reactions

When molten PE is sheared with an appropriate mixture of a peroxide (DCP) and an acrylic monomer above the decomposition temperature of the peroxide, the sequence of reactions that would occur is as follows:

(a) Decomposition of the peroxide to primary radicals

$$\underset{\text{(peroxide)}}{R-O-O-R} \rightarrow \underset{\text{(primary radical)}}{2RO^{\cdot}} \qquad (15)$$

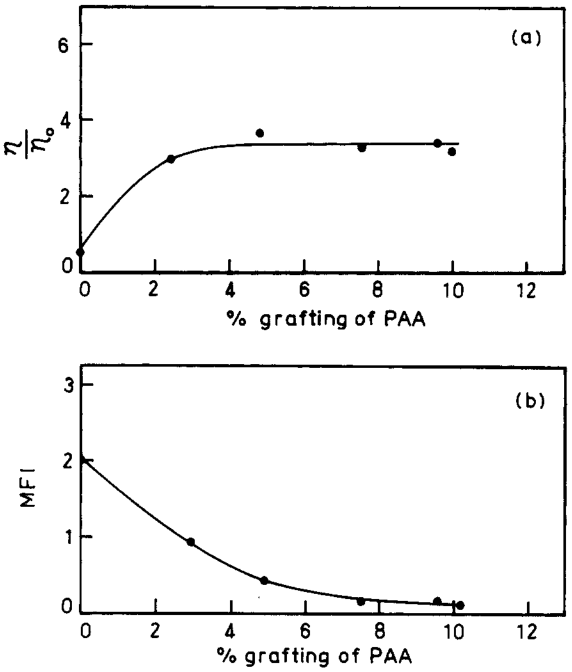


Figure 9 Plots showing variation of (a) relative melt viscosity, η/η_0, and (b) melt flow index, MFI with variation of percentage grafting of PAA on PE: DCP dose used for grafting = 0.75 mmole per 100 g of PE

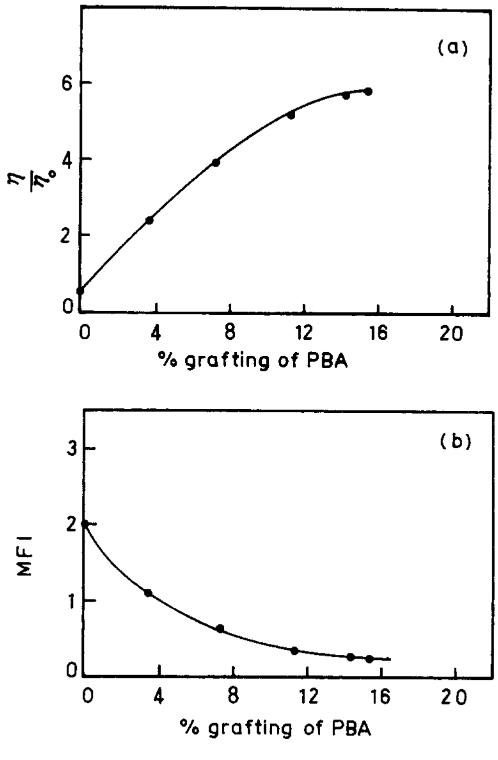


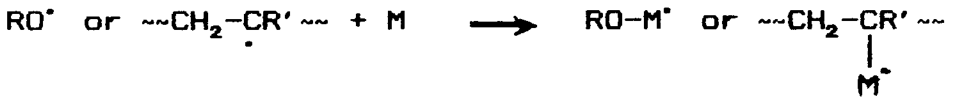
Figure 10 Plots showing variation of (a) relative melt viscosity, η/η_0, and (b) melt flow index, MFI with variation of percentage grafting of PBA on PE: DCP dose used for grafting = 0.75 mmole per 100 g of PE

(b) Radical transfer reactions involving the primary radical and PE used

$$2RO^{\cdot} + \underset{\text{(PE)}}{-CH_2-CH_2-CH_2-CHR'-}$$

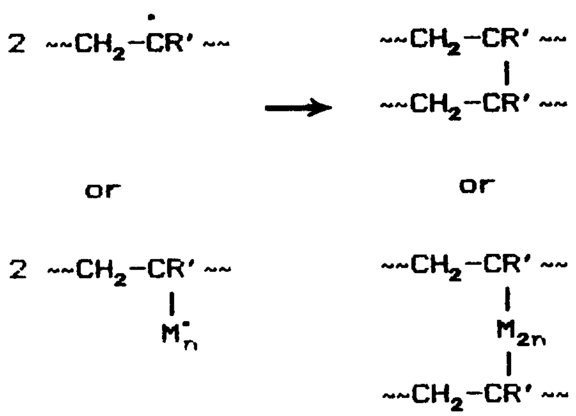
$$\rightarrow \underset{\text{(PE macroradical)}}{-\dot{C}H-CH_2-CH_2-\dot{C}R'-} + 2ROH \qquad (16)$$

(c) Addition of monomer (M) to primary radical or the PE macroradical



$$RO^{\bullet} \text{ or } \sim\sim CH_2-\underset{\bullet}{C}R'\sim\sim + M \longrightarrow RO-M^{\bullet} \text{ or } \sim\sim CH_2-\underset{\displaystyle M^{\bullet}}{\underset{|}{C}}R'\sim\sim \quad (17)$$

(d) Cross-linking by mutual termination of the grafted-on propagating chains or PE macroradicals



$$\begin{array}{ccc} 2\ \sim\sim CH_2-\overset{\bullet}{C}R'\sim\sim & \longrightarrow & \begin{array}{c}\sim\sim CH_2-CR'\sim\sim\\ |\\ \sim\sim CH_2-CR'\sim\sim\end{array} \\ \text{or} & & \text{or} \\ 2\ \sim\sim CH_2-\underset{\displaystyle M_n^{\bullet}}{\underset{|}{C}}R'\sim\sim & & \begin{array}{c}\sim\sim CH_2-CR'\sim\sim\\ |\\ M_{2n}\\ |\\ \sim\sim CH_2-CR'\sim\sim\end{array}\end{array} \quad (18)$$

CONCLUSION

The graft copolymerization of PE with low doses of acrylic monomers (AA, EA, BA) at 170°C (443°K) under the influence of a peroxide (DCP) initiator in the shear mixer of a Brabender plasticorder resulted in grafted products showing a much higher melt viscosity and a prominently low melt flow index compared to the parent PE. Overall, monomer consumption during the grafting process commonly followed first-order kinetics as revealed by studies of the process using differential scanning calorimetry (DSC).

Some homopolymerization of the monomers used and some degree of peroxide-induced cross-linking of PE as revealed by the data on grafting efficiency and gel content also took place as side reactions[6]. Generally, cross-linking could be kept to a very low level or practically eliminated if the dose of the initiator (DCP) was kept relatively low. Poly(acrylic acid) grafting (up to 10%) rendered PE somewhat stronger and stiffer (tensile strength[4] and modulus becoming higher), while up to 15% grafting of poly (butyl acrylate) rendered PE mechanically weaker (tensile strength and modulus becoming lower); in each case the elongation at break (%) followed a decreasing trend with increasing percentage grafting. Enhanced polar interactions with a good scope for hydrogen bonding between the grafted-on acid units and prominent scope for chain branching and ultimate cross-linking (due to high monomer/polymer transfer constants and gel effect) during polymerization of acrylic acid[21,22] may explain the relatively high gel content and high modulus or strength characteristics for PEgAA.

REFERENCES

1. Sen, A.K., Mukherjee, B., Bhattacharyya, A.S., De, P.P. and Bhowmick, A.K., *Journal of Applied Polymer Science*, 1992, **44**, 1153.
2. Song, Z. and Baker, W.E., *Polymer*, 1992, **33**, 3266.
3. Ganzeveld, K.J. and Janssen, L.P.B.M., *Polymer Engineering Science*, 1992, **32**, 467.
4. Brown, S. B., in *Reactive Extrusion Principles and Practice*, ed. M. Xanthos. Hanser, Munich, 1992, p. 75.
5. Kim, H.G., Lee, J.H., Lee, H.B. and John, M.S., *Journal of Colloid Interface*, 1993, **157**, 82.
6. Oliphant, K.E., Russel, K.E. and Baker, W.E., *Polymer*, 1995, **36**, 1597.
7. Ide, F. and Sasaki, I., US Patent No. 4 003 874. Mitsubishi Rayon, 1977.
8. Nagara, M. and Wakamatsu, M.H.T., *Japan Kokai Tokkyo Koho*, 1992, **4**, 108.
9. Sen, A.K., Mukherjee, B., Bhattacharyya, A.S., De, P.P. and Bhowmick, A.K., *Polymer Degradation and Stability*, 1992, **36**, 281.
10. Ximenes, M., Irismar, N., Serr, O.A. and Barros, G.G., *Polymer Bulletin*, 1992, **28**, 61.
11. Lohse, D.J., Dutta, S. and Kresge, E.N., *Macromolecules*, 1991, **24**, 561.
12. Bonner, J. G. and Hope, P. S., in *Polymer Blends and Alloys*, ed. M. J. Folkes, P. S. Hope. Blackie, Glasgow, 1993, p. 46.
13. Kumar, G., Neelakantan, N.R. and Subramanium, S., *Journal of Applied Polymer Science*, 1994, **52**, 483.
14. Dutta, S. and Baird, D.G., *Polymer*, 1995, **36**, 505.
15. Liu, N.C., Baker, W.E. and Russel, K.E., *Journal of Applied Polymer Science*, 1990, **41**, 2285.
16. Xanthos, M. and Dagli, S.S., *Polymer Engineering Science*, 1991, **31**, 929.
17. Liu, N.C. and Baker, W.E., *Polymer*, 1994, **35**, 988.
18. Swarbrick, P., Green, W. J. and Maillefer, C., US Patent, No. 4 117 195. BICC and Establishment Maillefer, 1978.
19. Cartasegna, S., *Rubber Chemistry and Technology*, 1986, **59**, 722.
20. Borchardt, H.J. and Daniels, F., *Journal of the American Chemical Society*, 1957, **79**, 41.
21. Nemee, J. W. and Bauer, W. Jr, in *Encyclopedia of Polymer Science and Engineering*, Vol. 1, ed. H. F. Mark, N .M. Bikales, C. G. Overberger and G. Menges. Wiley, New York, 1985, p. 221.
22. Berger, K. C. and Brandrup, C., in *Polymer Handbook*, 3rd edn, ed. J. Brandrup and E. H. Emmergut, Wiley Interscience, New York, 1989, Ch. II, p. 81.